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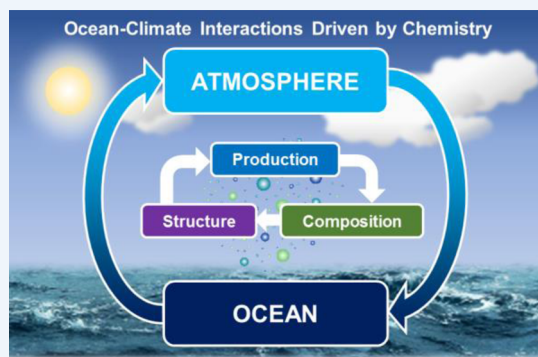
Sea Spray Aerosol: The Chemical Link between the Oceans, Atmosphere, and Climate

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ABSTRACT: The oceans, atmosphere, and clouds are all interconnected through the release and deposition of chemical species, which provide critical feedback in controlling the composition of our atmosphere and climate. To better understand the couplings between the ocean and atmosphere, it is critical to improve our understanding of the processes that control sea spray aerosol (SSA) composition and which ones play the dominant role in regulating atmospheric chemistry and climate.



OCEAN AND ATMOSPHERE: INTERCONNECTED THROUGH CHEMISTRY

The oceans, atmosphere, and clouds are all interconnected through the release and deposition of chemical species. Through such ocean–atmosphere exchange processes, it has been proposed that the ocean can act as a planetary thermostat (see Figure 1). To better understand the biogeochemical connections between the ocean and atmosphere, it is critical to improve our understanding of the processes that control sea spray aerosol (SSA) composition and determine which play roles in regulating atmospheric chemistry and climate. SSA represents the largest global aerosol source and plays a major, largely undetermined role in affecting our atmosphere. Furthermore, the addition of SSA to our atmosphere has been a suggested geoengineering approach for increasing the albedo of marine clouds to offset the warming of our planet induced by greenhouse gases.¹

While scientists have learned an extensive amount about the composition of SSA, understanding the properties and reactivity of this complex chemical system still represents an enormous challenge. Recent studies have made significant strides in establishing techniques to accurately produce SSA in a laboratory setting to develop a deeper understanding of the molecular composition of freshly produced SSA.^{2–6} Reproducing real world processes in the laboratory has allowed for controlled experimental studies that directly probe links between seawater and SSA chemistry. Simulations and parametrizations of the factors controlling SSA composition can put us in position to predict how ocean and atmospheric reaction processes influence climate.

The chemical composition of SSA controls its interactions with reactive trace gases and the surrounding environment. Processes that occur on the surface of SSA particles depend on complex chemical interactions that largely remain misunderstood. Over the years, numerous studies have shown that SSA is more than just sodium chloride and instead comprised of inorganic salts as well as biologically produced organic species. Further, many key chemical properties (e.g., surface activity, solubility, interfacial molecular structure) have been observed to play a large role in defining the transfer of chemical matter from the ocean to SSA. Adding to this complex process is the continuously changing chemical composition of the ocean, which is largely controlled by biological processes. The role of heterotrophic bacteria has been shown to be a major driver of SSA chemistry, controlling the types and relative amount of organic material transferred from seawater into the atmosphere in the form of SSA.^{7,8} Combined, these factors create a population of nascent SSA particles observed to be diverse in molecular composition, mixing state, morphology, and reactivity. Secondary heterogeneous reactions and aging processes can further transform the chemical composition and related properties of nascent SSA. In addition, biologically produced volatile organic compounds, which can diffuse into the atmosphere as gas phase species, have the potential to act as aerosol precursors and affect the growth and composition of SSA. Overall, it has yet to be determined whether seawater chemistry or secondary processes are more important in

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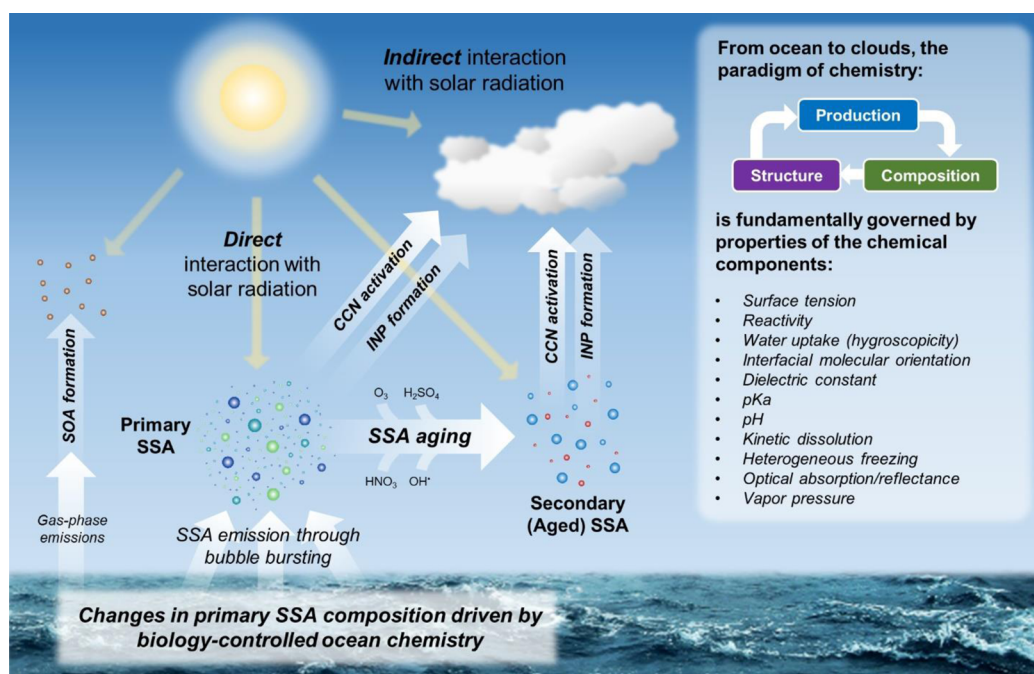


Figure 1. From ocean to clouds, dynamic biological processes control seawater composition, which in turn controls primary SSA composition. Fundamental chemical properties of primary SSA govern its ability to interact with solar radiation directly and indirectly (through the formation of cloud condensation nuclei (CCN) and ice nucleating particles (INP)) and undergo secondary chemical transformations.

controlling SSA composition and properties that ultimately affect climate.

For decades, there has been a gap between field observations and laboratory studies of complex tropospheric aerosols. Top down measurements of the complex chemistry of real-world SSA can guide bottom-up experimental studies using more simplistic model systems (Figure 2). Such efforts have been

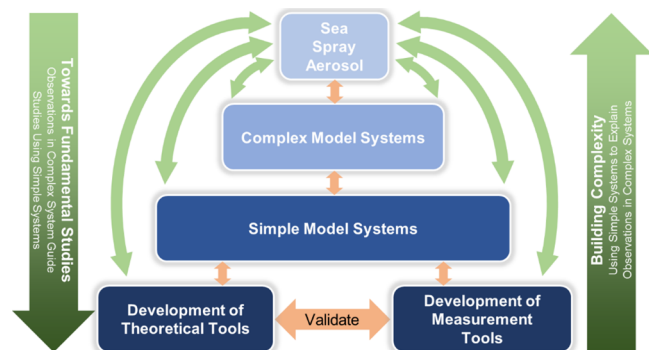


Figure 2. Observations while studying the complex chemistry of real-world SSA can be used to drive more fundamental bottom-up approaches to understand the molecular-level mechanisms that define SSA chemistry in the open ocean. The development and integration of both experimental and theoretical tools are key steps in such an endeavor.

used to elucidate fundamental chemical and physical mechanisms of SSA formation, heterogeneous reactions at particle interfaces, and linking SSA chemistry with climate-relevant properties.

Many of the studies highlighted in this Commentary were achieved through the development of new methods, the integration of experimental and theoretical approaches, and key interdisciplinary efforts between chemists, oceanographers,

and marine biologists. In particular, through Center-enabled research,⁹ recent developments of novel laboratory-based coupled ocean–atmosphere approaches have provided the basis for understanding fundamental chemical processes that control the interplay between the oceans, atmosphere, and climate. More specifically, we summarize recent discoveries in how the molecular composition of nascent SSA is affected by seawater chemistry. We then move on to highlight unexpected discoveries concerning interfacial chemistry (i.e., gas phase uptake, interaction with water vapor, and ice nucleation) of complex SSA and the observed deviation from predicted behavior based on previous studies of simple model systems used in laboratory studies. Finally, research priorities that will help advance our understanding of factors controlling SSA chemistry, and the related impact on clouds and climate are presented.

■ PRODUCING REPRESENTATIVE SSA

Explaining field study observations of atmospheric processes requires the accurate reproduction of nascent SSA that has the identical composition to that produced over the open ocean. Transferring the full complexity of the real-world ocean–atmosphere system into the laboratory is quite challenging and requires the replication of physical, biological, and chemical processes. In the ambient ocean environment, SSA production occurs through two general pathways.^{6,10,11} The first involves rupturing of the bubble film, producing “film drops”, followed by bubble cavity collapse yielding “jet drops”.¹² The number and size of film and jet drops are inherently determined by the size distribution of bubbles that are entrained in seawater as well as the chemical composition of the sea surface microlayer (SSML) and bulk seawater.^{10,11,13} Several laboratory-based approaches have been developed to produce SSA. These include pushing air through sintered materials, pressurized atomizers, impinging a plunging waterfall or jet onto the

seawater surface, and producing waves within a large wave channel.^{2,5,6,14} Detailed studies of SSA production methods have shown that both breaking waves and plunging waterfall techniques replicate ambient SSA subpopulations of particles with the proper size and physical and chemical properties.^{2,5} Other variables, such as temperature,¹⁵ surfactant chemistry,^{13,16} and white cap foam formation⁵ are also critical factors in producing real world SSA populations. The development of these innovative laboratory-based methods has opened the doors for exploring the composition, reactivity, and properties of a globally abundant tropospheric aerosol, fresh SSA, under controlled conditions.

■ UNDERSTANDING THE INFLUENCE OF INTERFACIAL INTERACTIONS AND OCEAN BIOLOGY ON SSA COMPOSITION

Nascent SSA particle formation occurs across an air–liquid interface. Thus, the chemical composition of SSA particles depends on the chemical components present at the surface of the ocean when bubbles rupture. Many studies approximate the composition of nascent SSA as only sea salt (i.e., NaCl and lesser concentrations of other alkali and alkali earth metals). However, using both online and offline single-particle techniques, it has been shown that nascent SSA contains distinct particle populations with concentrations of organic and inorganic compounds that differ between individual particles as well as from seawater.^{2,5,8} The organic to inorganic ratio within individual SSA particles has been shown to vary as a function of particle size, containing up to 80% organic carbon by mass.¹⁷ While the majority of supermicrometer SSA particles contain mostly sea salt (i.e., Na⁺, K⁺, Mg²⁺, Ca²⁺, and Cl⁻), SSA particles become more enriched with organic species relative to inorganic species as particle diameter decreases down to submicrometer sizes. This trend has been shown in the average bulk aerosol composition as well as at the single particle level. Single particle analysis has revealed that with decreasing particle diameter, an increasing fraction of submicrometer particles are homogeneous mixtures of OC and inorganic ions.⁸ Given that the relative concentrations of organic matter (OM) to inorganic salts in the ocean is extremely low (60–90 μM OM compared >0.46 M Na⁺),^{12,18} the high relative fraction of OM in SSA shows that the transfer of organic species from the ocean to SSA proceeds through selective processes. Studies have observed a significant portion of the organic fraction in submicrometer SSA as water-insoluble.¹⁹ Ion–organic interactions have been shown to drive changes in the molecular composition at the liquid–air interface.²⁰ These investigations suggest that the solubility, interaction with ions, and subsequent surface tension properties of marine organic matter play a large role in defining their selective enrichment in SSA. The supermicrometer particle organic fraction consists primarily of “oxygen-rich” species (e.g., polysaccharides and proteins), while submicrometer SSA particles are dominated by more “aliphatic-rich” species (e.g., lipids and alkanes).^{4,21} Additionally, smaller particles enriched with organic species have been linked to selective enrichment of Ca²⁺ relative to other alkali and alkali earth metals.^{5,22,23} Probing individual SSA particles through functional group analysis has further revealed large particle-to-particle variability within the SSA population.^{8,24} Such particle-to-particle diversity can critically influence the cloud forming potential of SSA; however it is currently not accounted for in any atmospheric or climate model.

Previous studies hypothesized seawater chlorophyll-a levels, a common metric for phytoplankton abundance, should be related to the relative organic content of freshly produced SSA. However, there has been disagreement in the community as some studies have observed a strong relationship, while others have not.^{12,25} It has been suggested that much of the discrepancy can be explained by taking both heterotrophic bacteria and phytoplankton concentrations into consideration.⁴ Heterotrophic bacteria play a major role in the ocean by transforming labile organic matter emitted by phytoplankton²⁶ into degradation products that become more efficiently transferred from the ocean into SSA. Recent laboratory-based approaches have provided evidence that bacterial and viral processing are key drivers of changes in fresh SSA composition during microbial blooms.^{2,3,8} “Microbial loop” processes lead to distinct phases in the turnover of dissolved organic carbon in seawater,³ ultimately leading to changes in both the mixing state of SSA particles and the composition of bulk SSA.⁴ Such changes in SSA composition include a relative increase in the abundance of distinct, insoluble organic particles types^{5,8} as well as their organic volume fractions.²⁷ The ability to accurately reproduce the physical processes and biology that ultimately control the surface composition of SSA was a critical step in linking the ocean to climate that has now led to studies probing climate-relevant interactions of SSA particles with reactive gases and water uptake as well as the ability to nucleate ice.

■ CHEMISTRY-DRIVEN INTERACTIONS BETWEEN SSA, TRACE ATMOSPHERIC GASES, AND WATER

Heterogeneous chemical reactions can alter the chemistry and resultant climate properties of aerosol particles. Moreover, such reactions can serve as critical nutrient sources to ocean biology through the atmospheric deposition of aerosol particles to the ocean. The ability of a given gas to react with particles is acutely controlled by chemical composition, especially at the particle surface. However, the specific drivers of chemical changes are not always clear. Investigations into the role of ions in SSA indicate cations such as Mg²⁺ and Ca²⁺ can enhance organic species at the interface, which has implications for surface packing of organic molecules and subsequent interfacial reactivity (see Figure 3a).²⁸ For example, in lab studies, well-ordered or thick organic films have been shown to impair the uptake of N₂O₅ (an atmospheric trace gas of importance due to its impact on the ozone and NO_x cycles), while more loosely packed organics have less of an effect.^{29,30} Interestingly, studies seeking to replicate microbial blooms in a controlled manner (using informed representative organic species for each stage of the bloom) showed that N₂O₅ uptake on SSA did not differ significantly from simplistic laboratory-generated NaCl particles (see Figure 3b).³¹ This implies either (1) the complex nature of the organic species result in loose surface packing^{20,32} or (2) the organic species are well mixed or present in low enough concentrations so as not to impact uptake. Both have significant implications for understanding how chemical changes dictate aerosol climate properties (i.e., heterogeneous reactivity, hygroscopicity, and interaction with solar radiation). A particularly exciting aspect of this study is that the uptake coefficient for N₂O₅ observed in these lab studies matched the near consistent values obtained from N₂O₅ uptake to ambient seawater samples from both the Atlantic and Pacific as proxies for aerosol interfaces, thus advancing our fundamental understanding of atmospheric processes in marine environments. However, not all reactive gases will behave similarly.

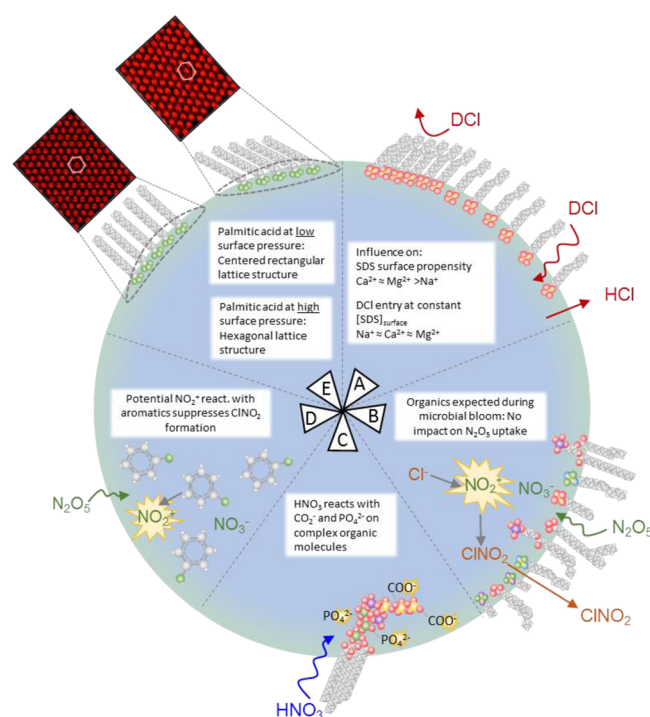


Figure 3. Representation of various results obtained either directly from complex studies or from simple systems informed by observations of complex systems. As a whole, this illustrates the intricacies involved in SSA chemistry at the molecular level. Organic surface concentration and packing resulting from ionic interactions, and the subsequent impact on gas phase uptake is illustrated in segment A.²⁸ Segment B shows results that N_2O_5 uptake is not suppressed in the presence of complex organics produced over the course of a microbial bloom.³¹ Segment C illustrates a previously unrecognized reaction pathway for HNO_3 with functional groups present in bioorganic molecules produced during microbial blooms.³⁴ Segment D shows a previously unrealized competition between aromatic organics and Cl^{-} for NO_2^{+} resulting from N_2O_5 uptake to a surface.³⁵ Segment E shows patterning of organics under various surface pressures, potentially facilitating templating of ice on an aerosol surface. Segment E was reproduced with permission from ref 36. Copyright 2015 American Chemical Society.

Heterogeneous uptake investigations on complex aerosol generated during periods of heightened microbial activity found that HNO_3 (important sink for nitrogen oxides in the NO_x cycle) exhibited a range of reactivity, correlating with specific organic species,³³ thus illustrating that the diversity in chemical composition of an externally mixed SSA population can lead to particle-to-particle variability in HNO_3 reactivity. Strikingly, internal redistribution of ions and interfacial organic enrichment was also observed within individual SSA particles following reaction with HNO_3 , an unexpected result based on studies using simple model systems.³³ In a further study, HNO_3 reaction with SSA, typically assumed to proceed as a purely inorganic reaction of $HNO_{3(g)}$ with $NaCl_{(aq)}$ leading to $NaNO_{3(aq)}$ and $HCl_{(g,aq)}$, actually showed increased uptake in the presence of organic biomolecules containing phosphate and carboxylate functionality. It is hypothesized that the increased uptake is due to direct HNO_3 reaction with the functional groups on these biomolecules (Figure 3c).³⁴ Thus, this study on realistic SSA organic and inorganic mixtures revealed a previously unrecognized reaction pathway in the atmosphere for nitration of aerosol particles and represents a paradigm shift

away from the traditional focus of strictly inorganic salt reactions with reactive gases.³⁴ Similarly, another shift in the understanding of heterogeneous chemistry arose from work utilizing seawater surfaces as representations of air–sea and air–particle interfaces for N_2O_5 reactive uptake. It was discovered that upon N_2O_5 reaction with aromatic species at the surface of seawater, such as those found in proteins, the gas phase product yield of $ClNO_2$ (produced via $N_2O_{5(g)} \rightarrow N_2O_{5(aq)} + NaCl_{(aq)} \rightarrow ClNO_{2(g,aq)} + NaNO_{3(aq)}$)²⁹ was suppressed to values far lower than anticipated. This finding was attributed to the previously unrecognized atmospheric reaction path, where organic nitrification reactions between NO_2^{+} and aromatic rings in humic substances or proteins suppress the production of $ClNO_2$ (Figure 3d).³⁵

Previous studies in marine environments have shown a change in cloud properties in regions of phytoplankton blooms. It has been hypothesized that the critical factors that drive such changes are the relative organic content and composition of SSA particles as well as their size distributions and number concentrations. Based on recent studies showing that submicrometer SSA particles are enriched with fatty acids and other aliphatic-rich organic species,^{4,22} such enrichment would be expected to result in depressed particle hygroscopicity.³⁶ Surprisingly, concentrations of cloud condensation nuclei (CCN) throughout induced microbial blooms (which lead to enrichment of aliphatic-rich species in submicrometer SSA) have been observed to change by less than 3%.³⁷ Artificial blooms doped with proxy compounds for marine organic matter have yielded similar results.³⁶ The discord between the cloud forming ability and SSA composition was suggested to be driven by the influence of particle surface tension in defining cloud droplet activation. However, the role of surface tension in defining cloud droplet activation is currently under scrutiny,³⁸ and thus future laboratory studies are needed. Contrasting observations between laboratory studies and ambient measurements that compare changes in the organic volume fraction of SSA particles to their CCN activity also suggest marine clouds may be impacted by differences in SSA flux, particle size distributions, or secondary reaction processes. More studies are needed to determine which factors play a dominant role in controlling the chemistry of SSA particles that form cloud droplets.

Another critical result to emerge from studying complex aerosols in an isolated environment concerns the ability of SSA to act as ice nucleating particles (INPs). Ice nucleation measurements exhibited an elevation in INPs of up to 50 times that of prebloom levels during the peaks of multiple microbial blooms, which was attributed to changes in SSA chemical composition.³⁹ This study confirmed that INPs are in fact produced in SSA, suggesting significant implications for precipitation and radiative forcing in remote marine regions.³⁹ Additionally, molecular dynamics simulations of ocean relevant fatty acids have shown that organic ordering can occur at the air–water interface in forms potentially favoring ice formation (Figure 3e).⁴⁰ Future studies will explore how surface interactions between organic and inorganic species lead to structural properties at the interface that favor ice nucleation.

An increasing number of studies illustrate that the full complexity of interactions between chemical species must be included when probing the interplay between SSA chemistry, reactivity, water uptake, and ice nucleating propensity. As such, it is important to investigate the fundamental mechanisms driving SSA chemistry using bottom-up approaches with

integrated methodologies. Thus, simple systems informed by results from complex systems have been utilized to establish model chemical systems that can be leveraged to provide parametrizations of SSA chemistry that improve the understanding of real world complexity in the future. These include using standard scales derived from reference chemical systems against which to compare gas entry through organic surface active species,²⁸ organic species detected in complex SSA to inform molecular-scale simulations to produce thermodynamic models that can use surface tension values to predict the morphology of liquid–liquid phase separated organic-containing aerosol,⁴¹ and model SSA compounds to better predict CCN activation of distinct SSA particle types.³⁶

SUMMARY AND FUTURE PROSPECTS

In order to make connections between findings in laboratory and field studies, unique approaches have been developed to bring the real-world complexity of sea spray aerosol into the laboratory to allow direct investigation of microscopic and molecular processes. From these studies, it has been discovered that nascent SSA contains a highly diverse population of particles with respect to chemical composition that is directly influenced by dynamic physical and biological processes occurring in the ocean. While some properties of nascent SSA, including IN ability and particle morphology, have displayed strong changes in response to microbial-induced alterations to SSA chemical composition, others such as CCN propensity and heterogeneous reactions with certain trace gases remain surprisingly unaffected. Furthermore, results for the uptake of gas-phase molecules and water by complex nascent SSA has been shown to differ from those obtained using simple model systems. This suggests that the interfacial chemistry of nascent SSA involves a synergistic array of multiple processes and interactions.

Moving forward, much remains to be learned about the complex interplay between the oceans, atmosphere, and climate. Given the critical role of SSA in this scheme, we put forth several grand challenges that are critical steps in understanding SSA impacts on atmospheric chemistry and climate:

- Developing a better understanding of the role of physicochemical properties of organic species and the intermolecular and ion–molecule interactions in determining the composition of freshly emitted SSA.
- Linking changes in ocean chemistry with changes in SSA flux and particle size distributions.
- Probing the evolution of SSA composition due to secondary reactions, including photochemistry, oxidation, and heterogeneous processing, and comparing the influence of these processes to that of ocean biology in defining SSA–climate interactions.
- Investigating fundamental physicochemical mechanisms and interactions that define interfacial SSA chemistry and how each controls heterogeneous reactivity, cloud droplet activation, and ice nucleation.
- Understanding how emissions of biogenic volatile organic compounds (BVOCs) produced in seawater can serve as aerosol precursors that affect the growth, composition, and climate properties of SSA.

Many current knowledge gaps will continue to be addressed by integrating top-down and bottom-up experimental approaches. Furthermore, it is crucial to use theoretical and

computational approaches to provide a strong underpinning of the proposed mechanisms that are derived from experimental observations. A major goal is to integrate theory and experiment to improve our overall understanding of SSA chemistry at a level that climate models can use to accurately predict the influence of the ocean via chemistry on climate and the environment.

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Notes

The authors declare no competing financial interest.

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