Progress in the Analysis of Complex Atmospheric Particles

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Abstract

This manuscript presents an overview on recent advances in field and laboratory studies of atmospheric particles formed in processes of environmental air-surfaces interactions. The overarching goal of these studies is to advance predictive understanding of atmospheric particle composition, particle chemistry during aging, and their environmental impacts. The diversity between chemical constituents and lateral heterogeneity within individual particles adds to the chemical complexity of particles and their surfaces. Once emitted, particles undergo transformation via atmospheric aging processes that further modify their complex composition. We highlight a range of modern analytical approaches that enable multi-modal chemical characterization of particles with both molecular and lateral specificity. When combined, they provide a comprehensive arsenal of tools for understanding the nature of particles at air-surface interactions and their reactivity and transformations with atmospheric aging. We discuss applications of these novel approaches in recent studies and highlight additional research areas to explore environmental effects of air-surface interactions.

1. Introduction

Atmospheric aerosols are complex multi-phase chemical systems composed of a myriad of components from both natural (sea spray, dust storms, pollen, biological particle discharge, biogenic emissions of organic particles, etc.) and anthropogenic (combustion related emissions from industry and transportation) sources. They can be either directly emitted (primary aerosols) or formed by gas-to-particle conversion processes (secondary aerosols). In many locations, primary and secondary aerosol components are mixed within individual particles (internal mixing) and between separate particles (external mixing). These result from components exchanging between different aerosol phases during atmospheric aging and transport.(1) Aerosols impact profoundly a number of environmental issues such as radiative forcing of the Earth's climate,(2) air quality(3), visibility,(4) public health and toxicology,(5) biogeochemical cycles,(6) and nutrient transport in natural ecosystems.(7) Despite their acknowledged importance, our understanding of complex multiphase chemistry of atmospheric aerosols remains insufficient to quantitatively predict their role in the atmospheric environment. The inherent complexity of aerosols requires developments and novel applications in analytical chemistry to characterize particle composition, morphology, phase and internal structures, their transformations through multi-phase chemistry of atmospheric aging, and the associated consequences on cloud-nucleating propensity and optical properties.

The field of aerosol analytical chemistry has been substantially advanced over the last two decades, as summarized in comprehensive review manuscripts(8-16) and book chapters(17; 18) that feature developments of state-of-the-art instruments and methodologies for online and offline aerosol characterization. Advantages of online mass spectrometry and optical spectroscopy techniques are the ability to probe aerosolized materials with high temporal resolution enabling in-situ studies of particle size and composition, and following transformations as they occur in real-world field studies, test facilities, and environmental chambers. Offline techniques applied to particle samples, and their unique advances fall within chemical imaging of individual particles and molecular-level speciation of complex organic constituents in bulk particle samples. Offline techniques also offer the practical advantage of the option for correlative multi-modal characterization of particles samples.

This paper highlights recent advances in aerosol chemistry revealed by offline methods used to study air-surface interactions and processing where environmental particles containing surface components are ejected into the atmosphere. Currently, the mechanisms and atmospheric impacts of such processes lie at the forefront of aerosol research.

2. Multimodal Chemical Characterization of Particles

Data on chemical composition, size, morphology, internal mixing, and phase states of particles obtained by offline analysis methods are crucial for understanding aerosol formation and reaction mechanisms, their atmospheric evolution, and their impacts and source apportionment. However, acquiring comprehensive information on the chemical composition of atmospheric particles is challenging because no single analytical chemistry technique can provide all the information required. For example, electron and X-ray microscopies elucidate morphology and internal structure at the nanometer scale.(19-21) However, in the case of electron microscopy, chemical information is limited to elemental composition of particles, while the nature of elemental chemical bonding can be inferred from X-ray microscopy. Mass spectrometry techniques, assisted with novel ambient pressure ionization/substrate sampling sources, enable detailed molecular-level characterization of individual constituents of organic particles (at the expense of spatial resolution).(8; 11; 16) As a result, comprehensive characterization of atmospheric particles typically requires combining analytical methods to yield complementary information ranging from microscopic properties of individual particles to advanced chemical characterization of the complex molecules they are composed of. A variety of microscopy, microprobe, spectroscopy and mass spectrometry techniques are commonly applied to characterize the size, morphology, phase and composition of particles collected in field campaigns and laboratory studies.(8; 10; 11; 16; 21; 22) Typically, information from one analytical technique guides further measurements and laboratory studies. Below we describe how qualitative and quantitative information obtained from these studies is essential for evaluating optical properties of particles, understanding their aging, reactivity, hygroscopicity and cloud-forming propensity.

2.1. Chemical Imaging Techniques.

Applications of microscopy, micro-spectroscopy, and imaging mass spectrometry techniques (i.e., CCSEM/EDX, ESEM, FIB/SEM, HRTEM/EELS, STXM/NEXAFS, TOF-SIMS, nano-SIMS, micro-FTIR and micro-Raman spectroscopy) have focused on aspects of multi-phase atmospheric chemistry and physics using chemical imaging (elemental and molecular group mapping) of field and laboratory particle samples. Recent literature (2012-2015) includes a broad range of topics such as: particle type assessments in field and test facility studies based on their composition and mixing states,(23-34) particle transformations due to atmospheric aging processes in field(23; 26; 35-38) and simulated laboratory experiments,(39-43) in-situ observations of phase transitions(44-47) and liquid-liquid phase separation(48-51) in hydrated particles, depth-profiling(52) and cross-sectioning(53-55) examination of particle internal composition, assessment of particles ice nucleation propensity(56-61) and optical properties(62-64) inferred from chemical imaging observations, and understanding the kinetics

and mechanisms of atmospheric aging processes based on the isotope ratio measurements(65; 66) on individual particles.

SEM and TEM coupled to EDX microanalysis are commonly used for analysis of particle morphology, size, elemental composition, and internal structures with nanometer (SEM) and sub-nanometer (TEM) lateral resolution.(19; 21) Operation of SEM in computer-controlled mode (CCSEM) permits routine analysis of hundreds-to-thousands of particles deposited on substrates, and provides statistically significant data on particle-type populations. TEM is used for more narrowly focused studies on particle internal composition and mixing state. EELS coupled to TEM enables assessment of chemical bonding for selected elements within individual particles. Crystalline structures of crustal particles can be determined through analysis of the selected-area electron diffraction. Although conventional SEM and TEM require vacuum environments, chambers and sample holders have been developed that allow exposure of particles to a few Torr of residual gas during imaging, i.e. environmental operation (ESEM and ETEM, respectively). Using water vapor, ESEM and ETEM allow real time imaging of hygroscopic transformations over the entire range of relative humidity (RH from 1 to 100%). Finally, novel dual beam FIB/SEM instruments have been applied for cross-sectioning and chemical imaging of particle interiors.

Synchrotron-based soft X-ray microscopes (STXM/NEXAFS) enable chemical imaging of particles with advanced speciation of carbon bonding and chemical characterization of different forms of organic material.(20) STXM has lower lateral resolution (>20 nm) than SEM and TEM, but its higher chemical specificity has made it an instrument of choice for analysis of organic and mixed organic/inorganic particles. Chemical bonding and oxidation states of other common elements in atmospheric particles (e.g. N, O, S, Fe, etc.) can be also investigated, depending on the specific STXM instrument. Selected features of NEXAFS spectra, indicative of specific element functionalities are used to construct particle component maps, grouping and assessment of particle-types and their mixing states.(67) Similar to ESEM and ETEM, recently developed environmental sample holders(68; 69) enabled studies of particle hygroscopic transformations(51; 70) providing chemical imaging specificity of liquid-liquid phase separation.(48)

SIMS instruments operate in vacuum and interrogate solid samples using a primary ion beam and collecting secondary ions ejected from the sample.(71) Using a TOF mass analyzer, a signature mass spectrum with lateral resolution of a few nanometers is obtained. If a low primary ion dose is used, analysis is limited to the outermost layers of particles.(72) Whereas a higher current primary ion beam allows depth profiling of chemical stratification within particles.(73; 74) Nano-SIMS instruments detect simultaneously a limited number of selected ions (up to seven), but with the higher mass resolution necessary for quantitative analysis of isotopic fractionation of elements contained in particles. This isotopic analysis can provide fundamental insights into sources and the atmospheric history of particles.(66; 75)

Raman and FTIR spectrometers are complimentary methods because vibrational modes that are not allowed in the IR may be Raman active.(76) When interfaced with optical microscopes, they allow chemical imaging of micrometer size particles(77; 78) and in-situ monitoring of spectral bands correlated with physicochemical transformations of particles.(58-60; 74) Using specially designed sample holders and flow reactor assemblies, measurements of water uptake by particles, their subsequent phase transformations and ice nucleation of ice can be quantified.

Due to their chemical complexity, many studies employ multi-modal combinations of the chemical imaging techniques to unravel the complex multiphase particle chemistry.

2.2. Atmospheric Transformations of Particles

Understanding aerosol effects on the environment and climate requires an adequate description of particle physicochemical properties at their emission source and predictive understanding of their consequent atmospheric transformations (that are yet insufficiently understood for many types of aerosols). Processes of multiphase reaction chemistry, segregation of different components within individual particles, uptake of gaseous species, coagulation, modifications of particle morphology, etc. – all have profound impacts on particle hygroscopic and optical properties, viscosity and mixing state, reactivity and propensity to serve as CCN and IN.

Chemical imaging approaches are used to elucidate transformations of specific particle types collected in field and laboratory studies. Mechanisms are usually inferred from field observations, which in turn guide follow-up laboratory studies designed to test a hypothesis. Figure 1 compares STXM maps of relatively fresh and aged marine particles collected onboard research aircraft in central California. Particle regions enriched in organic acids are shown in green, and inorganic (mostly NaCl) components are shown in blue.(26) The maps indicate morphology and internal composition changes due to in-particle reactions between organic acids and NaCl components, as confirmed by laboratory studies.(39; 40) Complementary multimodal STXM, CCSEM/EDX and micro-FTIR techniques showed that particles containing sea salt and weak organic acids undergo irreversible transformations through multi-phase chemistry driven by acid-displacement reactions and subsequent degassing of volatile products HCl or HNO_3 products. These chemical reactions are accelerated by particle dehydration cycling and result in changes in particle viscosity, hygroscopicity, phase transitions and separations, and thereby modify particle environmental impacts and lifecycle.(44; 79; 80)

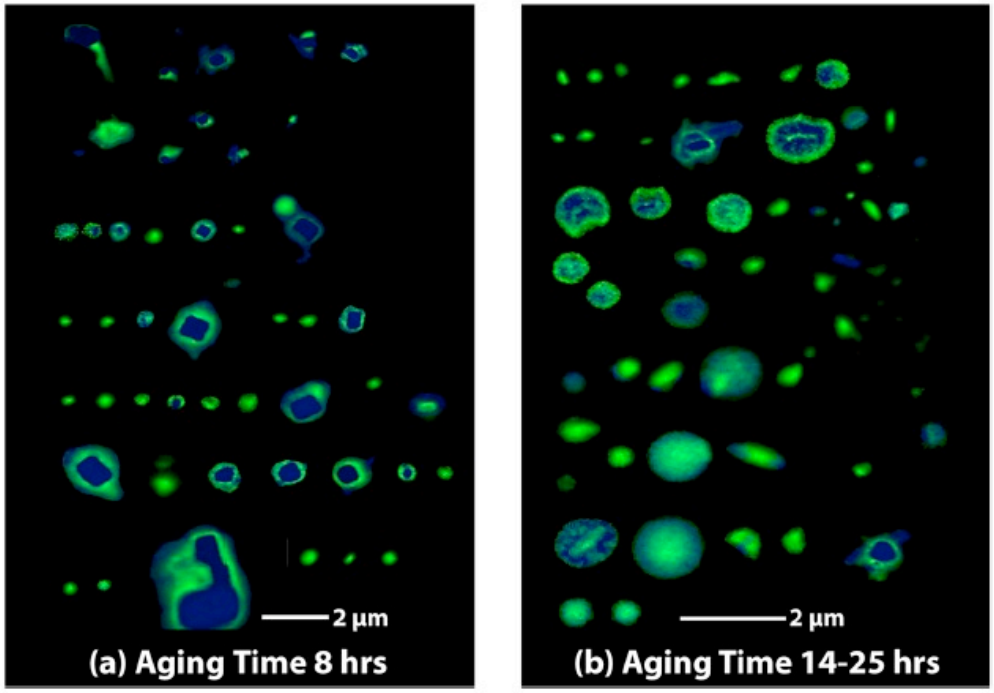

Figure 1. STXM maps of particles of a marine origin with different transport (and hence, aging) times from the CARES 2010 field study.(81) Areas dominated by organic carbon are green, and inorganic components are blue. (Reproduced with permission from reference (26). Copyright 2012 Wiley-Blackwell).

The complementary combination of STXM/NEXAFS and CCSEM/EDX chemical imaging data sets has also provided a quantitative assessment of mixing states of carbonaceous particles aged in the photochemical environment of urban plume.(23; 24) STXM provided experimental visualization of how soot and organic carbon constituents were mixed within individual particles and CCSEM provided corresponding information on the inorganic content. Combined, this unique study provided a quantitative assessment of the particle-type classes,(23) and individual particle characteristics such as the particle-specific diversity, bulk population diversity, and mixing state index determined for particles with different atmospheric aging history.(24) It showed that the mixing states of urban particles in the Sacramento, CA region were driven by local emissions of black carbon-containing particles that were coated by products from gas phase secondary chemistry and/or coagulated with sea spray, sulfate, and organic particles originating from refineries in the San Francisco Bay region. These unique results provided the first quantitative description of particle mixing state changes during transport parameterized for use in atmospheric modeling simulations. This allows additional model refinement based on the results of the multi-modal chemical imaging of particles.

Increasingly, chemical imaging methods are used for dynamic in-situ laboratory studies that simulate the atmospheric particle life cycles using specially designed micro-reactors. Elucidating

the effects of particle composition and their transformations on processes governing cloud microphysics, such as hygroscopic growth, phase transitions, and nucleation of cloud droplets and ice crystals is of particular interest. ESEM and ETEM studies have advanced our understanding of the hygroscopic behavior of individual particles composed of inorganic salts and their mixtures.(19) Microscopic observations with high (nano-meter) lateral resolution allow direct detection and visualization of multistep phase transitions and separations - processes that are not easily probed by other techniques. However, electron microscopies do not allow simultaneous chemical analysis while particles undergo hygroscopic transformations. Instead, Electron microprobe techniques are done under high vacuum (dry conditions of particles) and also typically cannot distinguish between organic constituents in particles. Complementary STXM/NEXAFS observations provide chemical bonding specificity, albeit at lower lateral resolution than ESEM and ETEM.(48; 82) One recent example of dynamic chemical imaging was performed on particles containing ammonium sulfate and organic carbon components. STXM maps showed that even in fully deliquesced particles organic and inorganic liquid components were notably separated with the organic components enriched in the outer layer.(48) During dehydration experiment, STXM/NEXAFS was used to determine the contributions of each component in the liquid phases and to monitor dynamics of liquid-liquid phase separations. It has been observed that both liquid phases contained inorganic and organic components, while their fractionation between the phases gradually increased at lower RH. Other study showed that multiple solid and liquid phases appear along with changes in the microstructures of filed collected particles during relative humidity cycling.(51) A recent multi-modal study included STXM/NEXAFS characterization of field collected particles for quantifying C, N, and O, followed by in situ chemical imaging of water uptake by particles, which in turn was followed by SEM/EDX microanalysis of dry particles. From analysis of NEXAFS spectra recorded for individual particles during hydration the mass of water absorbed by each individual particle was quantified. Combining the STXM/NEXAFS and SEM/EDX data sets allowed determination of mass-based hygroscopicity parameters for field collected atmospheric particles.(82)

Additional characterization of particle organic material can be achieved using micro-Raman spectroscopy. This method integrates Raman scattering spectrometry with an optical microscope to allow spectra acquisition from microscopic samples. Micro-Raman analysis is performed at substantially lower lateral resolution (>100 nm) than electron and X-ray methods, but provides complementary chemical information. Figure 2 shows the micro-Raman data set acquired over a ~15 μm multi-component sea salt particle at increasing values of RH.(60) Dynamic transformation is assessed based on the changes in Raman spectra indicative of water uptake and dissolution of sulfates in the outer particle layers. These are exhibited by the increase of hydrate (3400 cm^{-1}) and aqueous sulfate (981 cm^{-1}) peaks. Binary chemical imaging maps that outline locations of dissolved sulfate within interior of the particle were constructed

from the peak intensities. To simulate conditions of low-temperature anvil cirrus formation, sea salt particles were imaged in a set of systematic deliquescence and ice nucleation experiments. The observations indicated that fresh and aged sea-salt particles can induce ice crystal formation through both deposition and immersion nucleation modes.(60)

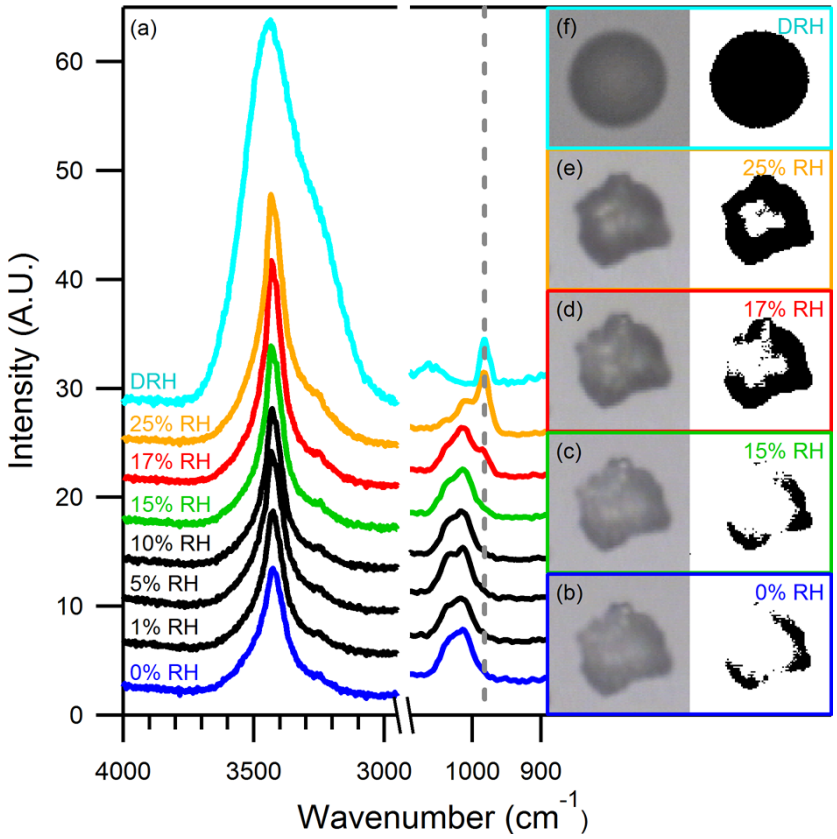

Figure 2. Raman spectra (a) and optical images (b–e) of an approximately 15 µm mixed sea salt particle captured during water uptake/ice nucleation experiments. Dynamic changes in particle composition corresponding to water uptake and dissolution of sulfate components at the outer particle layers are evidenced by differences in the spectra and the binary maps (right panels). For comparison, a fully deliquesced sea salt particle is shown in (f). (Reproduced with permission from reference (60). Copyright 2014 American Chemical Society).

2.3. Molecular-level Characterization

Understanding molecular compositions and transformations of complex mixtures of OA components is arguably the most significant challenge in atmospheric aerosol research. Because of its ability to provide molecular-level information, HRMS assisted with ambient pressure surface ionization is uniquely suited for chemical characterization of aerosol samples collected on substrates.(11) For instance, a novel nano-DESI/HRMS approach enables rapid and

sensitive (<10 ng) analysis of laboratory and field collected aerosol samples.(83) Nano-DESI enables fast and efficient collection, soft ionization, and analyte transfer that together significantly improve detection limits (compared to other ambient ionization methods). Nano-DESI does not require special sample preparation or pretreatment.(83) Elemental compositions of individual constituents of OA are determined based on high mass resolution and high mass accuracy of the acquired spectra.(16) Their possible molecular structures can be inferred from analysis of fragmentation patterns obtained in MS^n experiments.(84; 85) This technique has provided molecular and structural characterization of molecules in field collected OA, including those containing nitrogen,(85-87) sulfur,(85; 88) and various metals.(89) Nano-DESI has also been used in laboratory studies of the molecular transformations of OA relevant to the formation of atmospheric brown carbon.(22)

Figure 3 shows a schematic drawing of the nano-DESI technique and the HRMS spectra of ambient OA collected during the 2010 CalNex campaign at Bakersfield, CA.(86) For comparison, characteristic HRMS spectra collected at the daytime and the nighttime are shown.
The high fraction of CHO compounds, characteristic for fresh OA produced by photochemistry and ozonolysis, dominate the daytime spectrum. The increased fractions of nitrogen-containing $CHON_{1-2}$ compounds are evident in the nighttime spectrum. By comparing plausible reactant-product pairs within molecular species identified in the mass spectra, changes in the OA chemical composition between day and night were assessed. Over 50% of the $CHON_{1-2}$ species had CHO precursor product pairs consistent with imidization reactions and formation of species with –C=N–C=C– chemical bonds (Schiff bases). These reactions involve ammonia and carbonyl groups on the precursor species, and they suggest a potential role of the Schiff bases in forming nitrogen-containing OA.(86) Formation of these low-volatility and potentially light absorbing compounds may play an important role in OA atmospheric transformations that remain poorly understood.

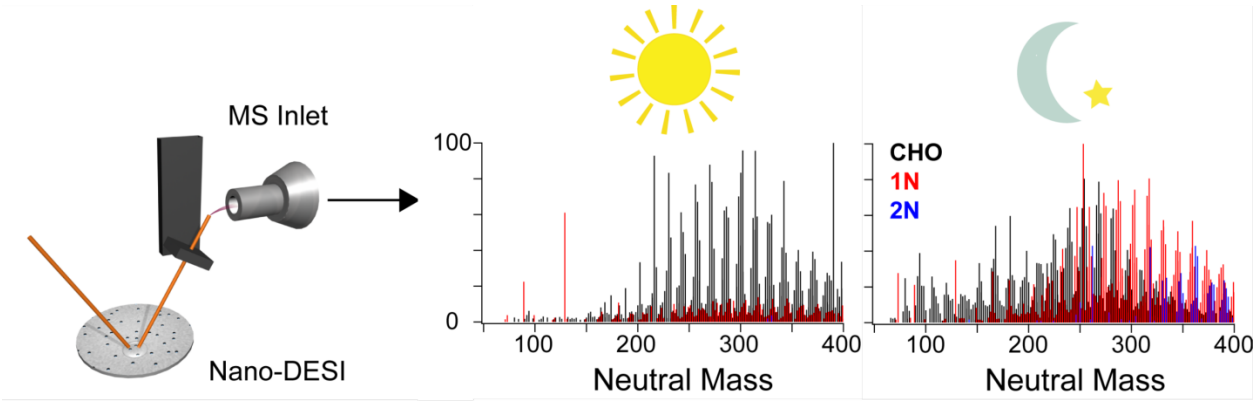

Figure 3. Left panel: Schematic of the nano-DESI analysis of organic aerosol. In nano-DESI, the analyte deposited on a substrate is probed by an online liquid extraction followed by soft nanoelectrospray ionization. Right plots: Representative nano-DESI mass spectra of samples from Bakersfield, CA collected duirng day and night, respectively. The colors correspond to the number of N atoms in the chemical formula with black = 0 N, red = 1 N, blue = 2 N. (Reproduced with permission from reference (86). Copyright 2013 Elsevier, Ltd.).

3. Exchange of Chemical Constituents at Air-Surface Interfaces

Although atmospheric aerosol chemistry and physics processes are complex, the fundamental scientific understanding of aerosols has advanced tremendously over the last two decades. These advances were based on combinations of field, laboratory, and modeling studies. For example, just in the past year numerous comprehensive review manuscripts summarized existing knowledge on aerosol sources, composition, transformations and impact.(5; 22; 90-94) These reviews also highlighted scientific challenges and future directions in aerosol research. Recent studies indicate an insufficient understanding of atmospheric processes involving aerosols that are either directly ejected from environmental surfaces(95; 96) or indirectly controlled by the composition and physicochemical transformations of the corresponding surfaces.(97) In this particular scientific area, novel methodologies for particle chemical imaging and molecular-level characterization are essential for providing new transformational insights and discoveries. The synopsis of this section is not intended as an inclusive review of environmental processes at air-surface interfaces. Rather, we embrace selected topics where offline analysis methods are best suited to provide key advances to examine unrecognized processes of particle ejection and transformation.

3.1. Wind Blown Dust

Wind-blown mineral dust is one of the major sources of primary atmospheric particles that affect atmospheric environment and climate through light absorption and scattering, and acting as either CCN or IN.(98) Atmospheric aging of dust particles, through multiphase chemistry during their transport and cloud processing, results in their internal mixing with condensed-

phase organic constituents that modify particle composition and physical properties. Over the last decades, research efforts focused separately on either mineral dust or OA atmospheric chemistry. These studies provided fundamental knowledge on the atmospheric impact of either dust(98) or OA.(99) However, very few studies examined the effects of condensed organic constituents reacting *with* mineral dust. For example, Fe(III)-rich components of mineral dust can induce a variety of photo-chemical reactions with organic compounds in the presence of sunlight where Fe(III) can act as either a reactant or as a catalyst.(92; 100) These reactions determine the physical properties of mixed "OA/Fe(III)" particles, such as phase state and viscosity, interactions with water, gas-particle partitioning, reactivity, etc. On regional and global scales, reactions of long range transported Fe containing particles are of significant interest because they impact biological productivity of phytoplankton in the oceans and consequently the biogeochemical cycling of sulfur.(101)

As discussed in section 2.2., in marine particles, organic acid components of OA can react with inorganic components through multi-phase aqueous chemistry where the reaction equilibrium is shifted to the products by rapid irreversible degassing of volatile products.(26; 39; 40) These reactions are common for a broad class of water-soluble organic acids present in both biogenic and anthropogenic OA. Analogous reactions and formation of organic salts are reported for particles containing calcite components of mineral dust.(80; 102) Considering this reactivity for Fe(III)-containing dust components, the organic salts produced would preferentially form on particle outer layers. For instance, the (oxyhydr)oxide surface of hematite can be eroded by carboxylic acids (R-COOH) driven by evaporation of water (a reaction product). The hematite degradation processes may be further enhanced in the presence of UV-Vis radiation because of the unique chelating and photo-catalytic activity of Fe(III). Specifically, chelated [Fe(III) - R-COOH] complexes absorb light in the UV-Vis range and decompose into Fe(II) and $^{\bullet}$R-COOH pairs.(103) $^{\bullet}$R-COOH radicals can subsequently decompose into smaller oxygenated organic compounds, CO_2 and peroxides. The radicals may participate in oligomerization processes, while CO_2 and high volatility oxygenated organics can partition into the gas phase. Peroxides can drive Fenton chemistry, Fe(II) to Fe(III) re-oxidation, creating a photo-catalytic cycle in which organic acid components are continuously converted into reactive products, followed by their decomposition and oligomerization reactions. Modeling these photo-catalytic processes suggests they may drive aqueous phase aging of atmospheric organics in the presence of Fe(III), a topic requiring further study.(104)

Consistent with the above discussion, multi-phase photochemistry of mixed OA/dust particles may also contribute to new particle formation and growth in dust plumes mixed with anthropogenic pollution. Figure 4 illustrates Asian dust transformation in a context of photo-induced, dust surface-mediated reactions inducing new particle formation as reported in recent field measurements.(97) Complementary to known heterogeneous atmospheric chemistry of dust, the photo-catalytic processes in mixed OA/dust particles may have an additional impact

on the environment. Specifically, gas-phase partitioning of volatile oxygenated organics produced through photochemistry in mixed OA/Fe(III) particles may be an unrecognized source of nucleating vapors contributing to new particle formation and growth.

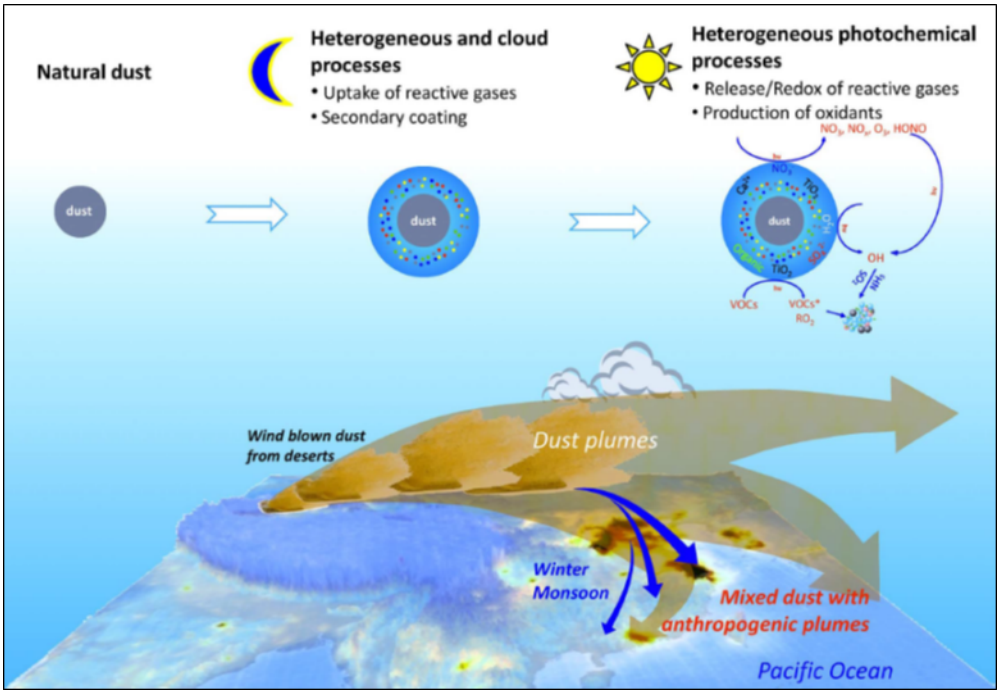

Figure 4. Schematic Transformations of Asian dust during its atmospheric transport: 1) Fine mineral dust is aerosolized by winds in the remote Gobi desert area, 2) dust particles acquire secondary coatings when transported over industrial regions with anthropogenic pollution, 3) aged dust particles are transported into the Pacific region and experience multi-phase photochemistry that releases reactive gases relevant to new particle formation and growth. (Reproduced with permission from reference (97) Copyright 2014 Nature Publishing Group).

As a result of the OA/Fe(III) multi-phase chemistry discussed above, multiple changes in particle properties are expected. First, the optical properties of these systems would be altered depending upon different scenarios of atmospheric aging and specific OA composition (e.g. biogenic - less aromatic versus anthropogenic - higher aromatic precursors; chelated Fe(III)-organic complexes are strong chromophores). Second, changes in particle viscosity are expected because of the gas-phase partitioning of CO_2 and volatile organic products on one side, and resulting oligomerization processes on the other side. These factors strongly affect particles' CCN and IN ability. The degree to which these combined processes alter OA composition, particle optical properties, and their CCN and IN ability remain an open question. These questions can be addressed through complementary applications of off-line techniques that probe particle samples collected in field and laboratory studies.

3.2. Air-Surface Interfaces of Biological Particles

Windblown biological particles play a vital role in the Earth's system through various processes at the atmosphere-biosphere interface. During the past decade, biological particles received extensive attention not only because of public health impacts, but also due to their role in climate, atmospheric chemistry and physics.(105-108) Biological particles influence cloud microphysical processes by serving as CCN and IN, thereby affecting the hydrological cycle and Earth's climate. Biological particles are emitted by living organisms directly to the atmosphere and consist of various cellular particles such as pollen, fungal spores, bacteria, viruses, fragments of plants and animals, debris of dead organisms. Atmospheric biological particles can be found in a broad size range, diameters vary from nanometer (e.g., viruses, macromolecules) up to few hundred micrometers (pollens, plant debris).(5; 90) Estimated mass emissions into the atmosphere range from 10-10^3 Tg yr^{-1}(109) and they are believed to be the dominant source of organic aerosol in the tropics.(110)

Fungal spores are major contributors to biological particles and their emission estimates range between 8 to 186 Tg yr^{-1}.(105; 106; 110) Global model simulations estimated that fungal spores contribute 23% of total primary emissions of organic aerosol in the atmosphere.(110) Plants, vegetation, soils, litter and decaying organic matter are the major sources of fungal spores emitted by active discharge or winds.(105; 110) Several studies suggest that biological particle emissions are linked to atmospheric conditions such as rainfall, relative humidity, winds and thunderstorms, that influence daily variations in the number fluxes.(111-113) Furthermore, these atmospheric conditions trigger emission and deposition of biological particles, thus impacting the microbiome of ecosystems at the Earth surface.(5) Summer rain in boreal and semi-arid forests led to an increase both in biological particle and total particle concentrations.(114) One hypothesis is that fungal spores and other biological particles are lofted from splashing of rain droplets encountering soil and leaf surfaces.(114)

Due to their similarities with other carbonaceous particles, measuring and detecting biological particles by in-situ aerosol characterization methods is challenging. This results in ambiguous data on their atmospheric concentrations and chemical composition(115), which produces large uncertainties in estimates of their global budget.(105) Off-line micro-spectroscopy techniques, i.e. electron microscopy, micro-Raman and micro-FTIR spectroscopy, light microscopy and biochemical staining, and autofluorescence based techniques, are exceptionally well suited for detecting and quantifying morphological characteristics and chemical fingerprints of biological particles.(34; 111; 116)

Coarse pollen grains attract water below water saturation, can act as CCN and further regulate precipitation by acting as coalescence embryos.(117) However, pollen grains tend to

rupture when exposed to high humidity (or hydrate in rainwater), and release cytoplasmic debris and starch grains in the size range from few nanometers to several micrometers.(118; 119) Fragmented pollen particles may increase the number and mass loading of atmospheric organic particles, and release pollen associated allergens as respirable particles.(119) From the perspective of climate, these fragmented particles can act as cloud condensation nuclei(120) and ice nuclei.(121) From the health perspective, they may have an adverse impact on air quality.

Fungal spores are smaller (1-6 μm in diameter) than pollen grains (5-150 μm), and have a higher concentration (number: ~10^4 m^{-3}; mass: 1 μg m^{-3}) in the continental boundary layer.(122) In tropical areas, such as the Amazon basin, fungal spores are a major fraction of supermicron aerosol particles.(105) Recent studies show that, similar to pollens, fungal spores can rupture when exposed to high relative humidity and subsequent drying. Figure 5 shows selected SEM images of ruptured fungal spores after humidification and drying. Because new particle formation events and subsequent growth of ultrafine particles are seldom observed in the Amazon basin, their formation mechanisms remain enigmatic.(123) However, during the wet season, bursting events of ultrafine particles in the diameter range of 10-40 nm are frequent.(123) Expulsion of the nanoparticles and submicron particles from fungal spores under moist conditions in the Amazon basin (relative humidity >70%) and/or outflow from deep convective clouds (in-cloud processing of fungal spores) could be common in other tropical areas and may provide insight into new particle formation. Chemical imaging and microscopy characterization of substrate deposited particles and monitoring their transformations using environmental cells are among the most promising methods to study spore fragmentation phenomena and their climatic impacts.

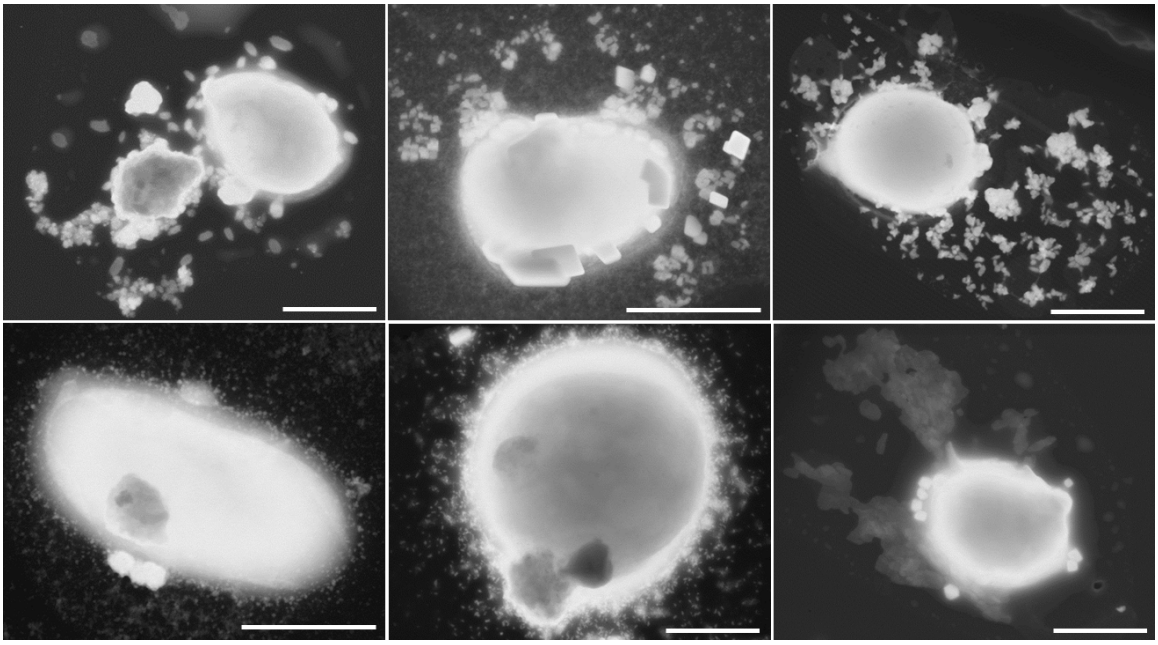

Figure 5. SEM images of fragmented fungal spores and expulsion of subfungal spore particles. The examples shown in the images are fungal spores collected in the Amazonia. Images revealed that size of the expelled fungal spores vary substantially, ranging from a few to hundreds nanometers. Scale bar is 2 μm.

3.3. Sea Spray Aerosol

The oceans cover about 71% of Earth surface and represent a continuous source of SSA, emitted through wave breaking and bubble bursting. Figure 6 illustrates how SSA impacts cloud formation, precipitation, atmospheric chemistry, and global climate.(91; 124) Recent studies, supported by laboratory mesocosm experiments(125-128), have demonstrated transport of organic material from the ocean to the atmosphere by SSA.(129-133) SSA particles show a strong enhancement of the organic fraction with decreasing aerosol size.(27; 125; 128; 133) Understanding SSA chemical composition is critical for predicting CCN activation and assessing their effects on cloud formation and climate.(134; 135) Due to their chemical complexity and variability in their external and internal mixing states, CCN activity of SSA is poorly constrained.(127; 136; 137) Recent applications of chemical imaging techniques combined with in-situ measurements revealed additional compositional details of SSA. Particles consisting of only organic carbon species dominate sizes smaller than 180 nm and their number concentration increases with increasing biological activity,(138) whereas SSA particles of larger sizes typically contain sea salt cores coated with organic material.(27) The presence of bacteria and phytoplankton in seawater affect the surfactant structure of large SSA, but have minor impact on smaller (~150 nm) particles.(139) SSA particles generated during bacteria metabolization indicate the presence of transition metals, likely due to bacterial bioaccumulation or colloids adhering to these metal ions.(140)

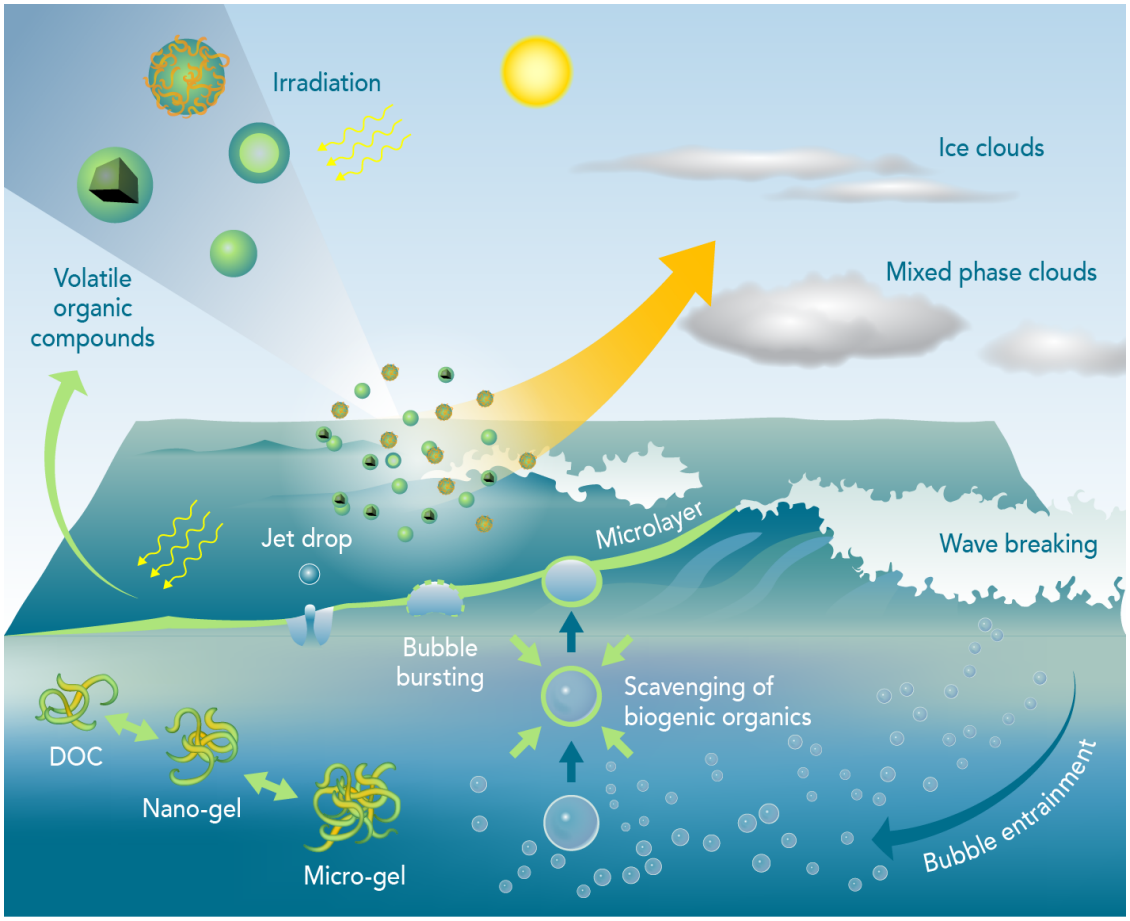

Figure 6. Schematic diagram showing the complex interactions between subsurface water and sea surface microlayer, generation and composition of SSA particles, and implications for their atmospheric chemical and physical processes of the environmental and climate forcing relevance.(5; 91; 95)

Colloids and aggregates exuded by phytoplankton contribute to water insoluble organic matter of SSA.(133) Such gel-like particles are composed of tangled macromolecules and colloids, preferentially from surface-active polysaccharides(141) and proteinaceous materials.(142) These marine nano- and micro-gels are ubiquitous at the ocean surface, and therefore, contribute to the SSA composition. Marine gels have been detected in cloud water which suggests they have a significant role in CCN activation.(131) However, chemical characterization of gels within individual SSA particles, and their molecular-level variability, are mostly unknown. Physicochemical properties such as phase state, optical properties, and responses to hydration, dehydration, and temperature changes are also poorly understood.

As inferred from field studies, laboratory experiments, and atmospheric models, specific types of SSA particles significantly affect atmospheric ice nucleation.(95; 143; 144) A recent study,(95) demonstrated enhanced ice nucleation activity in SSML water samples collected in

the Atlantic and Pacific oceans under typical cloud conditions. Specifically, it was shown that the ice nucleating components of SSA particles are < 200 nm in size and likely stem from phytoplankton exudates. Chemical imaging of individual particles nucleating ice suggests that aged marine particles can contribute to atmospheric ice crystal formation.(56) Wave channel generated SSA particles exhibited ice formation potential when the total organic content in seawater was similar to typical ocean background conditions.(128) All of these studies suggest that biogenic material ejected from oceans as SSA components can impact atmospheric ice nucleation. In addition to marine organisms such as viruses, marine gels may be potential IN candidates.(145) However, none of the compounds directly responsible for ice nucleation has been identified with a sufficient level of chemical specificity.

The composition of SSA particles defines their reactivity and transformations through heterogeneous and multiphase atmospheric chemistry involving gas- and aqueous phase oxidants. Photochemically induced reactions in the SSML change the nature of the organic molecules available for ejection.(92; 146) Furthermore, photochemical reactions occurring in SSA, lead to changes in the physicochemical properties of particles and in the gas-particle partitioning of the products.(147) The mixing state and amount of organic material distributed among different SSA particles may impact the underlying multiphase reaction mechanisms and their kinetics. For example, laboratory studies of SSA reacting with HNO_3 demonstrated that particle reactivity was correlated with the crystalline structure of the salt core and the amount of organic carbon.(41) Reactive uptake by HNO_3 resulted in a redistribution of inorganic cations and a layer of organic matter concentrated at the surface of the particle suggest that specific ion and pH effects impact the physicochemical structures of SSA particles.(42) Atmospheric aging and transformation of SSA through reactions with other common oxidants such as O_3 and OH are not sufficiently known. The origin and composition of the organic matter in SSA is substantially different from biogenic and anthropogenic OA. Hence, understanding atmospheric chemistry and transformations of OA in the marine environment requires additional studies.

3.4. Airborne Soil Organic Particles

Until recently, it was believed that the primary processes for aerosolizing soils and entraining their SOM constituents into the Earth's atmosphere were natural wind erosion and human mechanical activities such as agricultural tilling or harvesting. However, recent field observations provided evidence of a previously unrecognized mechanism of atmosphere – land surface interactions that result in ejection of submicron ASOP after intensive precipitation events such as rainfall or irrigation.(96) These observations were corroborated by a separately reported laboratory study(148) showing that droplets impinging on wet mineral surfaces generated fine aqueous mist. Figure 7 displays images, captured by a high-speed camera, showing raindrop induced frenetic generation of bubbles within a layer of the surface accumulated water followed by ejection of very fine aqueous particles upon bubble bursting.

Similar to generation of organic sea spray particles, discussed in section 3.3., dissolved organic matter from wet soils is aerosolized by bursting of entrained bubbles at the air-water interface.

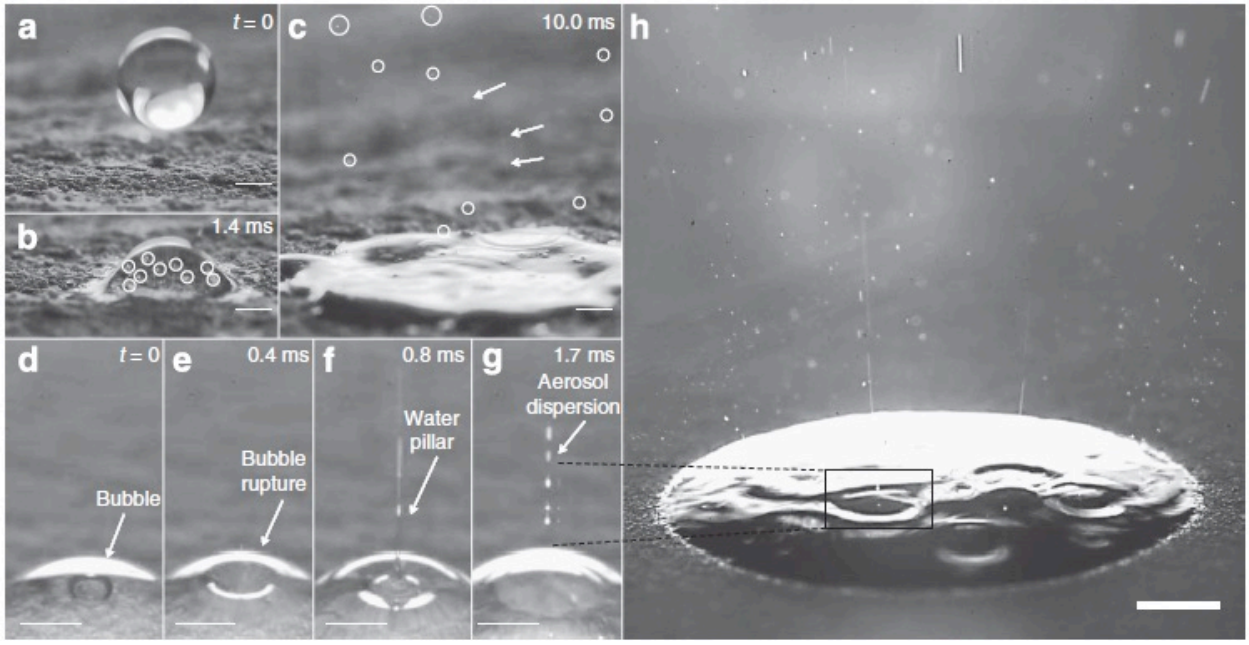

Figure 7. High-speed images capturing the "raindrop mechanism" of aerosol generation. (a-c) Impingement of a droplet onto solid mineral surface and formation of air bubbles inside of the aqueous layer formed on the surface. (d-e) Dynamic ejection of a fine aqueous mist upon bursting of the air bubbles at the air-water interface. (Reproduced with permission from reference (148). Copyright 2015 Nature Publishing Group).

Micro-spectroscopic chemical imaging and microanalysis of ASOP collected in a field study in Oklahoma indicate that they appear as unusual spherical glassy organic solids, and their characteristic X-ray absorption spectra match those of dissolved soil organic matter. Figure 8 illustrates their visual appearance in the SEM images taken at tilted angle.(96) The soil-derived source and mechanism of ASOP formation were inferred based on the notable similarity of their NEXAFS spectra to that of SOM. Typical molecular constituents of SOM are substantially larger than common atmospheric organics. Therefore, evaporation of water from SOM-containing aqueous mist results in solidification of resulting ASOP at ambient conditions, as confirmed by the observed glassy-like spherical morphology. This additional, previously unrecognized type of OA may have significant impacts on the atmospheric environment in areas where soils are exposed to strong, episodic precipitation events such as agricultural systems or natural grasslands.

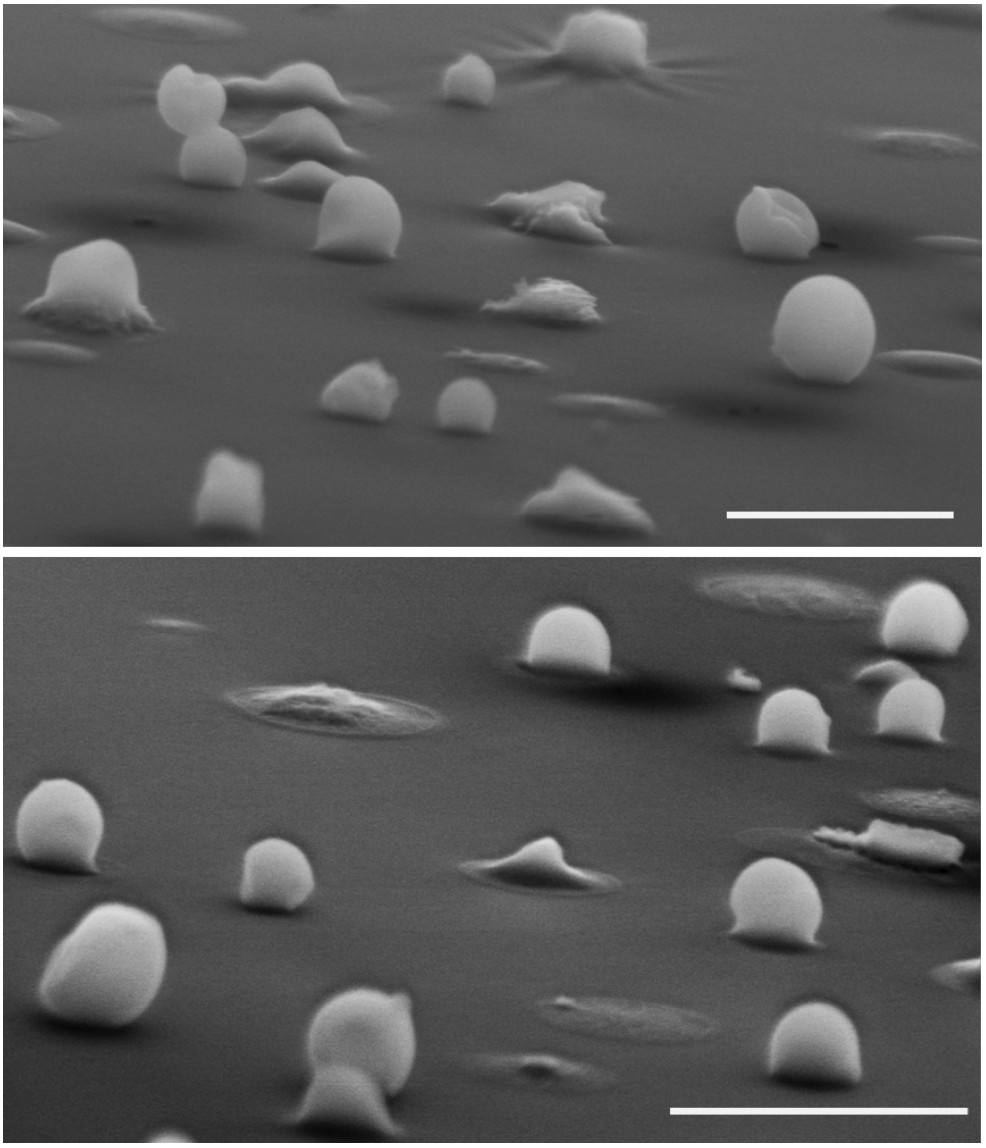

Figure 8. SEM images at 75° tilt angle of solid ASOP sampled by the impaction method. High vertical dimension of ASOP is indicative of their solid (glassy) phase.(96)

Inherent with their soil-derived composition and substantial content of carbon with sp^2 hybridization (C=C double bonds), ASOP may contribute substantially to atmospheric brown carbon and its associated light absorption and scattering. ASOP advected aloft may ultimately impact cloud properties and subsequent precipitation. Dynamic ESEM imaging of hydrating ASOP confirmed that they remain water-soluble and CCN-active.(96) Furthermore, because of their glassy phase, ASOP would provide solid surfaces for heterogeneous ice nucleation in cold and mixed-phase clouds. Interestingly, the importance of SOM as strong IN has been highlighted in numerous field and laboratory studies.(149-151) However, previously, airborne

SOM has always been attributed to the wind-blown erosion of soil, whereas direct emissions in a form of ASOP were never considered.

Understanding sources and the chemical composition of solid organic particles lies at the research forefront for the atmospheric chemistry community because of their unique physicochemical properties that are directly relevant to climate change and public health. The phase state of atmospheric organic particles plays a key role in their physicochemical properties, interactions with water vapor, gas-particle partitioning, and reactivity, and thus, has important implications in various environmental processes.(40; 152-156) Currently, research efforts on the phase of OA are concentrated on atmospheric processes that solidify liquid-like secondary organic particles produced through multi-phase atmospheric chemistry.(13; 157; 158) The concept of direct emissions of solid ASOP is not even considered.

Additionally, ASOP may impact the atmospheric environment as a carrier to transport water-soluble nitrites from soils to airborne aqueous particles, where nitrite can be protonated to form HONO and partition into the gas-phase. HONO is an important source of hydroxyl (OH) radicals that control the oxidative capacity of the atmosphere. Release of HONO from soil nitrites may substantially influence HONO and OH production in the atmosphere, and impact the biogeochemical nitrogen cycle.(159; 160) The large surface area of ASOP may drastically accelerate gas-phase release of HONO, and consequently affect processes influencing the oxidative atmospheric environment.

Future studies should assess the relationship between rainfall intensity and efficiency of the ASOP generation, evaluate and constrain ASOP budgets specific to different geographic regions, describe region-specific variability in ASOP composition, understand their atmospheric transformations, and quantify their optical and cloud nucleation properties.

Notably, ASOP are refractory and do not volatilize substantially upon heating up to 600 $^{\circ}$C.(96) Hence, they would not be detected by common methods of in-situ particle speciation based on thermal evaporation. Methods of laser ablation MS can certainly detect ASOP; however, extensive fragmentation upon ablation could generate mass spectra that would be confused with other organic particles. The solid (glassy) phase, and refractory carbonaceous composition of ASOP make spectro-microscopy methods the most effective detection techniques, and for assessing optical and hygroscopic properties. The structures of the high-molecular weight constituents of ASOP are of particular interest because they control their chemical and physical properties. Size-selected sampling of ASOP during events of their high abundance, followed by advanced analysis using nano-DESI/HRMS can be utilized for probing the molecular-level speciation of ASOP and ultimately for understanding their atmospheric transformations.

4. Summary

Multi-modal applications of novel analytical platforms highlighted in this manuscript facilitated in-depth chemical analysis of complex atmospheric particles. Methods of chemical imaging and molecular-level analysis described herein provide experimental means to improve fundamental knowledge of particle effects on cloud microphysics, their dependence on variables (relative humidity, temperature, multi-phase reactions), and distinguishing chemistry of natural and anthropogenic particles. The complex issues of aerosol chemistry and physics utilize a consortium of expertise, methods and measurements that require a collaborative framework and shared resources to provide coordinated, comprehensive, and multidisciplinary approaches to advance our fundamental understanding of aerosol impact on climate change, air quality, visibility and health issues. In recent years, we observed tremendous expansion and growth of research in this area; a trend that likely will continue.

We highlighted several scientific challenges related to complex, multi-phase chemistry and physics of atmospheric particles that could uniquely benefit from multi-modal experimental approaches of chemical imaging and molecular-level analysis. The atmospheric processes associated with these particles and their impacts on environment and climate remain insufficiently understood, even at the phenomenological level, largely due to incomplete information on the fundamental physicochemical properties of particles. These selected examples highlight exciting opportunities in the field of aerosol environmental chemistry, where multi-modal characterization of particles would significantly impact our fundamental understanding of various air- surface interactions, and their influence on climate and air quality.

5. Disclosure Statement

The authors are not aware of any issues that might be perceived as affecting the objectivity of this review.

6. Acknowledgements

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Acronyms and Definitions

Aerosol: mixture of airborne particles and gases at dynamic equilibrium.
(typeset next to the text lines 47-50)

Radiative forcing of climate: difference in the amount of sunlight energy absorbed by the Earth and energy radiated back to space
(typeset next to the text lines 55-56)

SEM: scanning electron microscope; CCSEM – computer controlled SEM, ESEM – environmental SEM, FIB/SEM – Focused ion beam system interfaced with SEM
(typeset next to the text lines 105-106)

EDX: Energy dispersed analyzer of X-rays
(typeset next to the text lines 105-106)

HRTEM: High resolution transmission electron microscope
(typeset next to the text lines 105-106)

EELS: Electron energy loss spectroscopy
(typeset next to the text lines 105-106)

STXM/NEXAFS: Scanning transmission x-ray microscope with near edges X-ray absorption fine structure spectroscopy
(typeset next to the text lines 105-106)

TOF-SIMS: Time-of-flight secondary ionization mass spectrometer
(typeset next to the text lines 105-106)

nano-SIMS: SIMS instrument with magnetic sector mass analyzer optimized for ion probe imaging with high lateral resolution and accurate isotopic measurements.
(typeset next to the text lines 105-106)

Micro-Raman and Micro-FTIR: Raman and Fourier transform infrared spectrometers interfaced with optical microscopes for analysis of confined micrometer-size sample areas.
(typeset next to the text lines 105-106)

CCN and **IN:** cloud condensation nuclei and ice nuclei
(typeset next to the text line 172)

RH: relative humidity
(typeset next to the text line 243)

OA: organic aerosol
(typeset next to the text line 263)

HRMS: high resolution mass spectrometry
(typeset next to the text line 265)

Nano-DESI: nanospray electrospray ionization
(typeset next to the text line 267)

SSA: sea spray aerosol
(typeset next to the text line 451)

SSML: sea surface microlayer
(typeset next to the text line 486)

SOM: soil organic matter
(typeset next to the text line 516)

ASOP: airborne soil organic particles
(typeset next to the text line 519)

683 **Side Bars**

684 REACTIVITY OF INORGANIC PARTICLES WITH WEAK ORGANIC ACIDS
685 (typeset next to section 2.2)

686 Unique atmospheric reactions of aerosolized particles were inferred from chemical imaging of
687 individual marine particles.(26) Chloride, carbonate, and nitrate components of inorganic
688 particles (e.g. sea salt and selected components of mineral dust) may react with water soluble
689 organic acids releasing volatile gas-phase products (HCl, CO_2, HNO_3) to the atmosphere, leaving
690 behind particles enriched in the organic salts. While these reactions are not thermodynamically
691 favored for bulk aqueous chemistry, these reactions in aerosol are driven by evaporation of the
692 volatile products from drying particles. Field observations(26) of these particle transformations
693 were corroborated in a number of laboratory experiments(39; 40) indicating that substantial
694 reactivity between inorganic and organics components within aged particles and its potential
695 impact on the modification of hygroscopic and optical properties of aerosols.

696

697 MOLECULAR IDENTITY OF ORGANIC AEROSOLS
698 (typeset next to section 2.3)

699 Recent advances in molecular-level characterization of OA facilitate new opportunities for
700 improved understanding of its formation mechanisms, source apportionment and atmospheric
701 transformations. Here, we highlight several new studies where deciphering molecular identity
702 of OA identifies perspective areas for future research. Specifically, the molecular-level HRMS
703 data can be used as a fingerprint for advanced source apportionment of ambient OA based on
704 the comparative analysis with its laboratory mimics,(87) or by identifying molecular markers of
705 the source specific precursors.(93) Multiple reports suggest that selected OA components may
706 have a distinct effect on its overall “brown carbon” properties evoking additional studies
707 focused on the molecular characterization of light-absorbing components within complex matrix
708 of OA.(22) Explicit description of OA molecular components can be used for model
709 estimates(161) of particle viscosity and phase state providing critical insights into
710 transformation of OA physicochemical properties and atmospheric life cycle.

711

712 SURFACE-MEDIATED REACTIOS OF DUST PROMOTE NEW PARTICLE FORMATION
713 (typeset next to section 3.1)

714 Field observations at a mountain site in South China reported an unexpected impact of mineral
715 dust on new particle formation and growth.(97) Enhanced events of new particle formation and

716 growth were systematically observed during high-loading episodes of mineral dust aged by
717 anthropogenic pollution. These observations were ascribed to plausible dust induced multi-
718 facet photochemistry, where photolytic decomposition of complex organic compounds
719 releasing volatile nucleating products was suggested. These findings challenge the traditional
720 wisdom that mineral dust acts mostly as a sink for atmospheric oxidants, and suggested that
721 when mineral dust and pollution are mixed they may have photocatalytic feedback that
722 provides an unrecognized source of OH radical and other oxidants.

723

724 NEW PARTICLES FROM FRAGMENTATION OF BIOLOGICAL SPORES
725 (typeset next to section 3.2)

726 Observations from our ongoing experiments show that fungal spores can rupture when
727 exposed to high relative humidity (~98% RH) and subsequent drying. In this study, we are
728 investigating biological particles collected during the wet season in 2015 at a pristine rainforest
729 site in Central Amazonia. Figure 5 shows an example of fragmented and expelled fungal spores
730 after wet and drying cycles. The rupture process expels tens to hundreds of fine subfungal
731 particles ranging from a few to hundreds of nanometers in size. In particular, a substantial
732 variation in number, size, and composition was observed for fragmented particles from the
733 ruptured fungal spores.

734

735 ICE-NUCLEATING PROPENSITY OF ORGANIC PARTICLES

736 (typeset next to section 3.3)

737 Ice nucleation experiments using a controlled vapor cooling-stage microscope system and
738 complemented by chemical imaging(56; 95; 143) indicate substantial presence of organics in
739 ice-nucleating particles. Experiments with SSA particles collected at different locations above
740 the ocean surf zone, laboratory mesocosm experiments, and Atlantic ocean show that particles
741 larger than 300 nm in diameter initiate ice nucleation under conditions relevant to mixed-phase
742 and cirrus clouds. Identified ice-nucleating particles contain inorganic cores of sea salt
743 surrounded by organic outer layers. Chemical imaging reveals alcohol and carboxyl
744 functionalities in the organic material and suggests that the organic coating is highly viscous.
745 These observations support the potential for organic particles to affect ice nucleation in the
746 atmosphere.

747

748 RAINFALL GENERATES SOLID ORGANIC PARTICLES

(typeset next to section 3.4)

Solidified ASOP – airborne soil organic particles can be generated as a result of atmosphere – land surface interactions through a recently revealed “raindrop mechanism”(148) when water droplets, during precipitation or irrigation events, hit open soil surfaces.(96) Field observations showed a dominant presence of solid ASOP (60% by number) after an intensive rain event at Southern Great Plains, Oklahoma, USA – an agricultural region where large areas of cultivated land are exposed to ambient air. Physicochemical properties of ASOP, investigated by chemical imaging and microanalysis techniques, suggest that they may serve as cloud condensation and ice nuclei, absorb solar radiation, and impact the atmospheric environment and carbon cycle at local and regional scales.

7. Literature Cited

Annotated references:

Ref 1 An excellent review of aerosol chemistry highlighting synergism between laboratory studies, field measurements and modeling analysis.

Ref 5. Comprehensive review of aerosol multiphase chemistry influencing the Earth system, climate, air quality, and public health.

Ref 16. A review manuscript featuring applications and perspectives of the HRMS analysis for molecular-level studies of organic aerosols.

Ref 17. An edited book offering the comprehensive overview of the spectroscopy of aerosols, including fundamental aspects and applications.

Ref 22. Thorough review focused on the current understanding of the chemistry of atmospheric brown carbon, including highlights of areas that need further studies.

Ref 91. A comprehensive review of the results of field and laboratory studies performed to characterize the properties of SSA, with an emphasis on the organic fraction.

Ref 92. A comprehensive review of photochemical processes occurring at the air-surface interfaces of aerosols, environmental surfaces and atmospheric ice.

Ref 96. The field evidence report of solid ASOP emitted to the atmosphere through atmosphere – land surface interactions following rainfall.

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