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Progress in the Analysis of Complex Atmospheric Particles

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Abstract

This article presents an overview of recent advances in field and laboratory studies of atmospheric particles formed in processes of environmental air-surface 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 multimodal chemical characterization of particles with both molecular and lateral specificity. When combined, these approaches 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 the environmental effects of air-surface interactions.

Aerosol: mixture of airborne particles and gases at dynamic equilibrium

Radiative forcing of climate: difference in the amount of sunlight energy absorbed by the Earth and energy radiated back to space

1. INTRODUCTION

Atmospheric aerosols are complex multiphase chemical systems composed of a myriad of components from both natural (e.g., sea spray, dust storms, biological particle discharge, biogenic emissions of organic particles) 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 (internal mixing) and between (external mixing) individual particles. These result from components exchanging between different aerosol phases during atmospheric aging and transport (1). Aerosols profoundly impact environmental issues such as radiative forcing of 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 the 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 the multiphase chemistry of atmospheric aging, and the associated consequences for cloud-nucleating propensity and optical properties.

The field of aerosol analytical chemistry has advanced substantially over the last two decades, as summarized in comprehensive reviews (8–16) and texts (17, 18) that feature developments in state-of-the-art instruments and methodologies for online and off-line 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 to follow transformations as they occur in real-world field studies, test facilities, and environmental chambers. Unique advances in off-line techniques applied to particle samples include chemical imaging of individual particles and molecular-level speciation of complex organic constituents in bulk particle samples. Off-line techniques also offer a practical option for correlative multimodal characterization of particle samples.

This review highlights recent advances in aerosol chemistry revealed by off-line methods used to study air-surface interactions and processes 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 off-line 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 the elemental composition of particles, whereas the nature of elemental chemical bonding can be inferred from X-ray microscopy. Mass spectrometry techniques, in combination 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 and understanding their aging, reactivity, hygroscopicity, and cloud-forming propensity.

2.1. Chemical Imaging Techniques

Applications of microscopy, particularly scanning electron microscopy (SEM), microspectroscopy, and imaging mass spectrometry techniques [e.g., computer-controlled SEM (CCSEM)/energy-dispersed analyzer of X-rays (EDX), environmental SEM (ESEM), focused ion beam (FIB)/SEM, high-resolution transmission electron microscopy (HRTEM)/electron energy loss spectroscopy (EELS), scanning transmission X-ray microscopy (STXM)/near edge X-ray absorption fine structure spectroscopy (NEXAFS), time-of-flight secondary ionization mass spectrometry (TOF-SIMS), nano-SIMS, and micro-Raman and micro-Fourier transform infrared (FTIR) spectroscopy], have focused on aspects of multiphase atmospheric chemistry and physics using chemical imaging (elemental and molecular group mapping) of field and laboratory particle samples. Recent (2012–2015) literature 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 experiments (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 determination of the kinetics and mechanisms of atmospheric aging processes based on the isotope ratio measurements (65, 66) of individual particles.

SEM and transmission electron microscopy (TEM) coupled to EDX microanalysis are commonly used for analysis of particle morphology, size, elemental composition, and internal structures with nanometer (SEM) and subnanometer (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. The crystalline structure of 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 (e.g., 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

SEM: scanning electron microscopy

CCSEM: computer-controlled SEM

EDX: energy-dispersed analyzer of X-rays

ESEM: environmental SEM

FIB/SEM: focused ion beam system interfaced with SEM

EELS: electron energy loss spectroscopy

STXM: scanning transmission X-ray microscopy

NEXAFS: near edge X-ray absorption fine structure spectroscopy

Nano-secondary ion mass spectrometry (SIMS): SIMS instrument with magnetic sector mass analyzer optimized for ion probe imaging with high lateral resolution and accurate isotopic measurements

Micro-Raman and micro-Fourier transform infrared (FTIR)

spectrometry: Raman and FTIR spectrometers interfaced with optical microscopes for analysis of confined, micrometer-sized sample areas

TEM: transmission electron microscopy

RH: relative humidity

CCN: cloud condensation nuclei
IN: ice nuclei

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 also be investigated, depending on the specific STXM instrument. Selected features of NEXAFS spectra indicative of specific element functionalities are used to construct particle component maps and for 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, collecting secondary ions ejected from the sample (71). By using a TOF mass analyzer, a signature mass spectrum with lateral resolution of tens of 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 simultaneously detect a limited number (up to seven) of selected ions, 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 spectroscopy are complementary methods because vibrational modes that are not allowed in the infrared may be Raman active (76). When interfaced with optical microscopes, they allow chemical imaging of micrometer-sized particles (77, 78) and in situ monitoring of spectral bands correlated with physicochemical transformations of particles (58–60, 74). By using specially designed sample holders and flow reactor assemblies, water uptake by particles and their subsequent phase transformations and ice nucleation can be quantified. Due to the chemical complexity of these particles, many studies employ multimodal combinations of chemical imaging techniques to unravel their complex multiphase 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—all have profound impacts on particle hygroscopic and optical properties, viscosity and mixing states, reactivity, and the propensity to serve as cloud condensation nuclei (CCN) and ice nuclei (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 on board research aircraft in central California (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 multiphase chemistry driven by acid-displacement reactions and subsequent degassing of volatile products such as HCl or HNO₃ (see sidebar, Reactivity of Inorganic Particles with Weak Organic Acids). These chemical reactions are accelerated by particle dehydration cycling and result in changes in particle viscosity, hygroscopicity, and phase transitions and

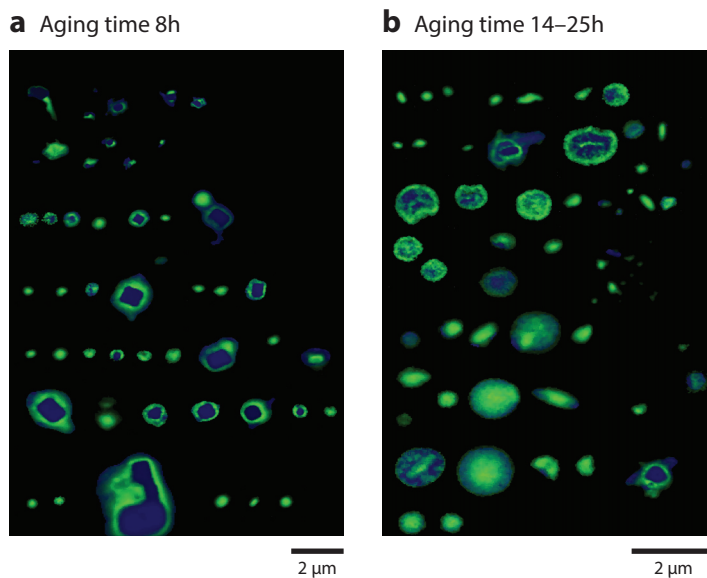


Figure 1

Scanning transmission X-ray microscopy 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. Figure reproduced with permission from Reference 26. Copyright 2012 Wiley-Blackwell. Abbreviation: CARES, Carbonaceous Aerosols and Radiative Effects Study.

separations and thereby modify the environmental impacts and life cycle of atmospheric particles (44, 79, 80).

The complementary combination of STXM/NEXAFS and CCSEM/EDX chemical imaging data sets has also provided a quantitative assessment of the mixing states of carbonaceous particles aged in the photochemical environment of urban plumes (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. Combining these techniques provided a quantitative assessment of the particle-type classes (23) and allowed

REACTIVITY OF INORGANIC PARTICLES WITH WEAK ORGANIC ACIDS

Unique atmospheric reactions of aerosolized particles were inferred from chemical imaging of individual marine particles (26). Chloride, carbonate, and nitrate components of inorganic particles (e.g., sea salt and selected components of mineral dust) may react with water-soluble organic acids, releasing volatile gas-phase products (HCl, CO₂, HNO₃) to the atmosphere and leaving behind particles enriched in the organic salts. Although these reactions are not thermodynamically favored for bulk aqueous chemistry, in aerosol they are driven by evaporation of the volatile products from drying particles. Field observations (26) of these particle transformations were corroborated in a number of laboratory experiments (39, 40) indicating substantial reactivity between inorganic and organic components within aged particles and suggesting its potential impact on the modification of hygroscopic and optical properties of aerosols.

determination of individual particle characteristics such as the particle-specific diversity, bulk population diversity, and mixing state index for particles with different atmospheric aging histories (24). It showed that the mixing states of urban particles in the Sacramento, California, 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 multimodal chemical imaging of particles.

Increasingly, chemical imaging methods are used for dynamic in situ laboratory studies that simulate atmospheric particle life cycles using specially designed microreactors. 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 (nanometer) 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 as particles undergo hygroscopic transformations. Instead, electron microprobe techniques are done under high vacuum (dry particle) conditions 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 a dehydration experiment, STXM/NEXAFS was used to determine the contributions of each component in the liquid phases and to monitor the dynamics of liquid-liquid phase separations. It was observed that both liquid phases contained inorganic and organic components, whereas their fractionation between the phases gradually increased at lower RH. Another study showed that multiple solid and liquid phases appear along with changes in the microstructures of field-collected particles during RH cycling (51). A recent multimodal 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 on an approximately $15\text{-}\mu\text{m}$ multicomponent sea salt particle at increasing values of RH (60). Dynamic transformation is assessed based on changes in Raman spectra indicative of water uptake and dissolution of sulfates in the outer particle layers; these are exhibited by an increase of hydrate ($3,400\text{ cm}^{-1}$) and aqueous sulfate (981 cm^{-1}) peaks. Binary chemical imaging maps that outline the locations of dissolved sulfate within the interior of a particle were constructed from the peak

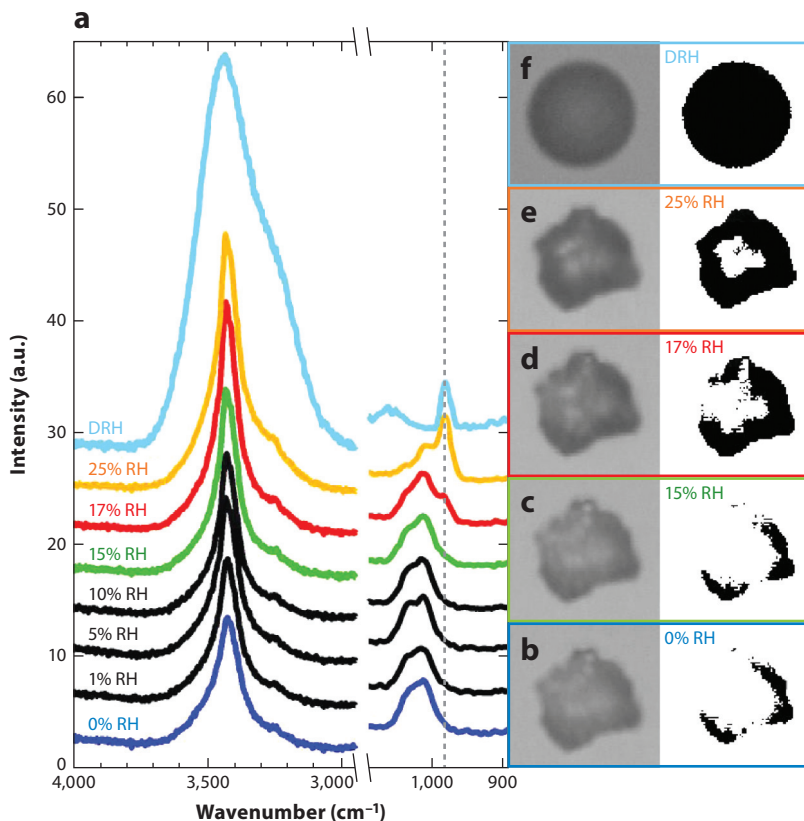


Figure 2

(a) Raman spectra and (b–e) optical images 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 (b–f, right) the binary maps. (f) For comparison, a fully deliquescent sea salt particle is shown. Figure reproduced with permission from Reference 60. Copyright 2014 American Chemical Society. Abbreviations: DRH, deliquescence relative humidity; RH, relative humidity.

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. Observations indicated that fresh and aged sea salt particles can induce ice crystal formation through both deposition and immersion nucleation modes (60).

2.3. Molecular-Level Characterization

Understanding molecular compositions and transformations of complex mixtures of organic aerosol (OA) components is arguably the most significant challenge in atmospheric aerosol research. Because of its ability to provide molecular-level information, high-resolution mass spectrometry (HRMS) assisted in combination with ambient pressure surface ionization is uniquely suited for chemical characterization of aerosol samples collected on substrates (11) (see sidebar, Molecular Identity of Organic Aerosols). For instance, a novel nanospray desorption electrospray ionization (nano-DESI)/HRMS approach enables rapid and sensitive (<10 ng) analysis of

OA: organic aerosol
HRMS: high-resolution mass spectrometry

MOLECULAR IDENTITY OF ORGANIC AEROSOLS

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

Nano-DESI:

nanospray desorption
electrospray ionization

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 MSⁿ experiments (84, 85). Such experiments involve mass selection of the ion of interest in the first MS stage, excitation of the ion followed by its dissociation, and mass analysis of the resulting fragments in the consequent MSⁿ ($n > 2$) stages. 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 of the nano-DESI technique and the HRMS spectra of ambient OA collected during the 2010 CalNex (California Research at the Nexus of Air Quality and Climate

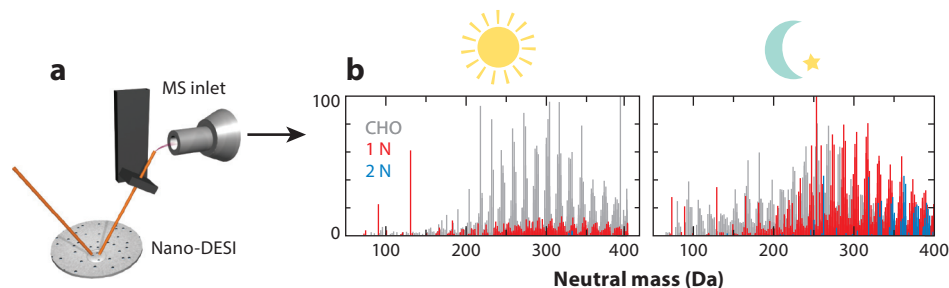


Figure 3

(a) 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. (b) Representative nano-DESI mass spectra of samples from Bakersfield, California, collected during the day and night. Colors correspond to the number of N atoms in the chemical formula: 0 N (gray), 1 N (red), and 2 N (blue). Figure reproduced with permission from Reference 86. Copyright 2013 Elsevier, Ltd. Abbreviations: MS, mass spectrometry; nano-DESI, nanospray desorption electrospray ionization.

Change) campaign at Bakersfield, California (86). For comparison, characteristic HRMS spectra collected during both day- and nighttime are shown.

The high fraction of CHO compounds, characteristic of fresh OA produced by photochemistry and ozonolysis, dominate the daytime spectrum. The increased fractions of nitrogen-containing CHON₁₋₂ 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 CHON₁₋₂ 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.

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 articles summarized existing knowledge on aerosol sources, composition, transformations, and impacts (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 in this section is not intended as an inclusive review of environmental processes at air-surface interfaces. Rather, we embrace selected topics in which off-line analysis methods are best suited to provide key advances to examine unrecognized processes of particle ejection and transformation.

3.1. Windblown Dust

Windblown mineral dust is one of the major sources of primary atmospheric particles that affect the atmospheric environment and climate through light absorption and scattering and by 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 photochemical reactions with organic compounds in the presence of sunlight, where Fe(III) can act as either a reactant or 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 and reactivity. On regional and global scales, the reactions of Fe-containing particles transported over long ranges are of significant interest because they impact biological productivity

of phytoplankton in the oceans and, consequently, the biogeochemical cycling of carbon and sulfur (101).

As discussed in Section 2.2, in marine particles, organic acid components of OA can react with inorganic components through multiphase 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 the outer layers of particles. 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 ultraviolet-visible (UV-Vis) radiation because of the unique chelating and photocatalytic activity of Fe(III). Specifically, chelated [Fe(III)-R-COOH] complexes absorb light in the UV-Vis range and decompose into Fe(II) and •R-COOH pairs (103). •R-COOH radicals can subsequently decompose into smaller oxygenated organic compounds, CO₂, and peroxides. The radicals may participate in oligomerization processes, whereas CO₂ and high-volatility oxygenated organics can partition into the gas phase. Peroxides can drive Fenton chemistry, Fe(II) to Fe(III) reoxidation, creating a photocatalytic cycle in which organic acid components are continuously converted into reactive products, followed by their decomposition and oligomerization reactions. Modeling these photocatalytic processes suggests that 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, multiphase photochemistry of mixed OA/dust particles may also contribute to new particle formation and growth in dust plumes mixed with anthropogenic pollution (see sidebar, Surface-Mediated Reactions of Dust Promote New Particle Formation). **Figure 4** illustrates Asian dust transformation in a context of photoinduced, dust surface-mediated reactions inducing new particle formation as reported in recent field measurements (97). Complementary to the known heterogeneous atmospheric chemistry of dust, the photocatalytic 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.

As a result of the OA/Fe(III) multiphase 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

SURFACE-MEDIATED REACTIONS OF DUST PROMOTE NEW PARTICLE FORMATION

Field observations at a mountain site in South China reported an unexpected impact of mineral dust on new particle formation and growth (97). Enhanced events of new particle formation and growth were systematically observed during high-loading episodes of mineral dust aged by anthropogenic pollution. These observations were ascribed to plausible dust-induced multifacet photochemistry, where photolytic decomposition of complex organic compounds releasing volatile nucleating products was suggested. These findings challenge the traditional wisdom that mineral dust acts mostly as a sink for atmospheric oxidants and suggest that when mineral dust and pollution are mixed, they may have photocatalytic feedback that provides an unrecognized source of OH radical and other oxidants.

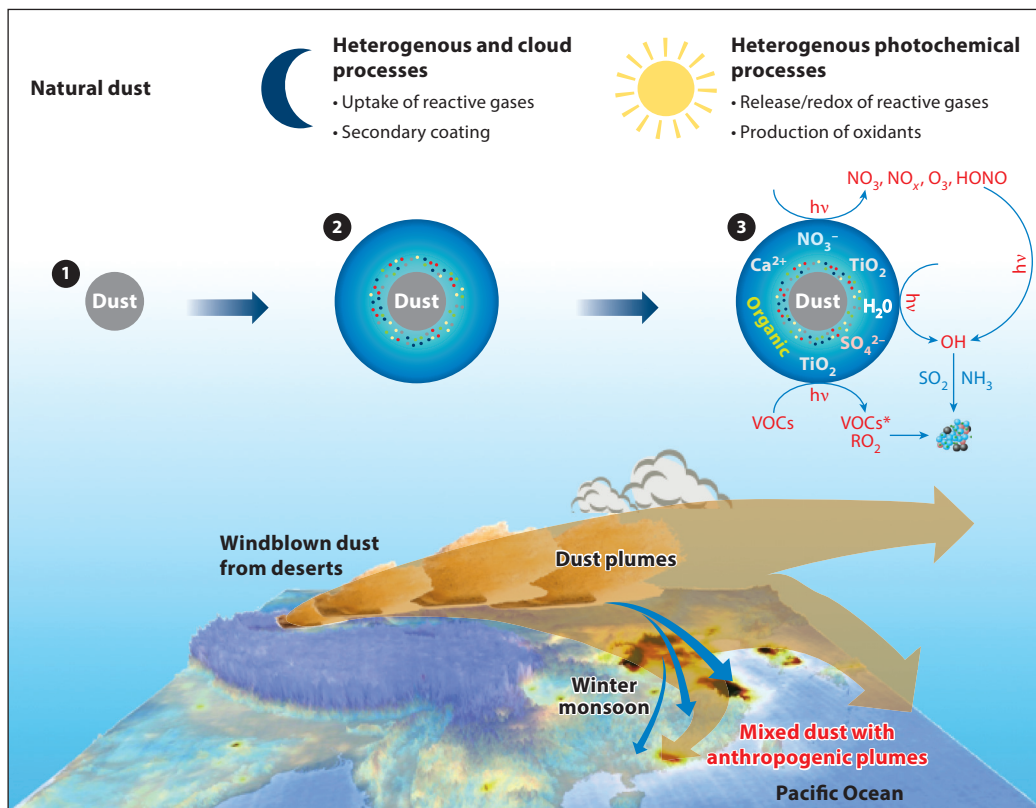


Figure 4

Schematic showing transformation 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; and **3** aged particles are transported into the Pacific region and experience multiphase photochemistry that releases reactive gases relevant to new particle formation and growth. Figure reproduced with permission from Reference 97. Copyright 2014 Nature Publishing Group. Abbreviation: VOC, volatile organic compounds.

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 the resulting oligomerization processes on the other side. These factors strongly affect particles' ability to serve as CCN and IN. The degree to which these combined processes alter OA composition, particle optical properties, and their ability as CCN and IN remains 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. 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 the 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, and the debris of dead organisms. Atmospheric biological particles can be found in a broad size range, with diameters varying from nanometers (e.g., viruses, macromolecules) up to a few hundred micrometers (pollens, plant debris) (5, 90). Estimated mass emissions into the atmosphere range from 10 to 10^3 Tg year⁻¹ (109) and are believed to be the dominant source of OA in the tropics (110).

Fungal spores are major contributors to biological particles, and their emission estimates range between 8 and 186 Tg year⁻¹ (105, 106, 110). Global model simulations estimated that fungal spores contribute 23% of the total primary emissions of OA 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, RH, wind, 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's surface (5). Summer rain in boreal and semiarid forests leads to an increase in both biological particle and total particle concentrations (114). One hypothesis is that fungal spores and other biological particles are lofted from the splashing of rain droplets encountering soil and leaf surfaces (114).

Due to the similarities between biological particles and other carbonaceous particles, measuring and detecting biological particles by in situ aerosol characterization methods are challenging. This results in ambiguous data on the atmospheric concentrations and chemical composition of these particles (115), which produces large uncertainties in estimates of the global budget of biological particles (105). Off-line microspectroscopy techniques, such as 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 the 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 ranging from a few nanometers to several micrometers in size (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 a climate perspective, these fragmented particles can act as CCN (120) and IN (121); however, from a health perspective, they may have an adverse impact on air quality.

Fungal spores are smaller than pollen grains (1–6 versus 5–150 μm in diameter) and have a higher concentration (number: approximately 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 supermicrometer aerosol particles (105). Recent studies show that, similar to pollens, fungal spores can rupture when exposed to high RH and subsequent drying (see sidebar, New Particles from Fragmentation of Biological Spores). **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 submicrometer particles from fungal spores under moist conditions in the Amazon basin (RH >70%) and/or outflow from deep convective clouds (in-cloud processing of fungal spores) can be

NEW PARTICLES FROM FRAGMENTATION OF BIOLOGICAL SPORES

Observations from our ongoing experiments show that fungal spores can rupture when exposed to high RH (approximately 98%) and subsequent drying. In one case, we investigated biological particles collected during the wet season in 2015 at a pristine rainforest site in central Amazonia. **Figure 5** shows an example of fragmented and expelled fungal spores after wet and drying cycles. The rupture process expels tens to hundreds of fine subfungal particles ranging from a few to hundreds of nanometers in size. In particular, a substantial variation in number, size, and composition was observed for fragmented particles from the ruptured fungal spores.

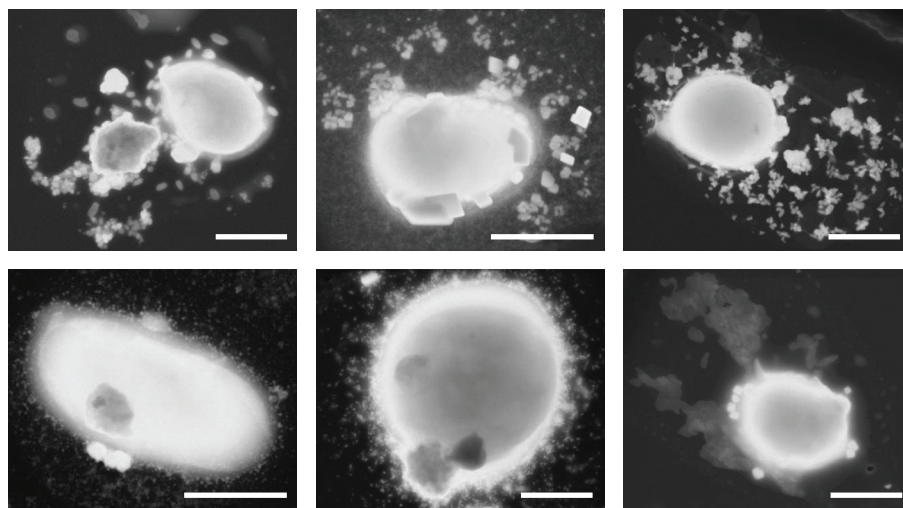


Figure 5

Scanning electron micrographs of fragmented fungal spores and expulsion of subfungal spore particles. The examples shown are fungal spores collected in Amazonia. Images reveal that the size of the expelled fungal spores varies substantially, ranging from a few to hundreds of nanometers. Scale bars are 2 μm .

common in other tropical areas and may provide insight into new particle formation. Chemical imaging and microscopy characterization of substrate-deposited particles and monitoring of their transformations using environmental cells are among the most promising methods to study spore fragmentation phenomena and their climatic impacts.

3.3. Sea Spray Aerosol

The oceans cover approximately 71% of the Earth's surface and represent a continuous source of sea spray aerosol (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 the chemical

SSA: sea spray aerosol

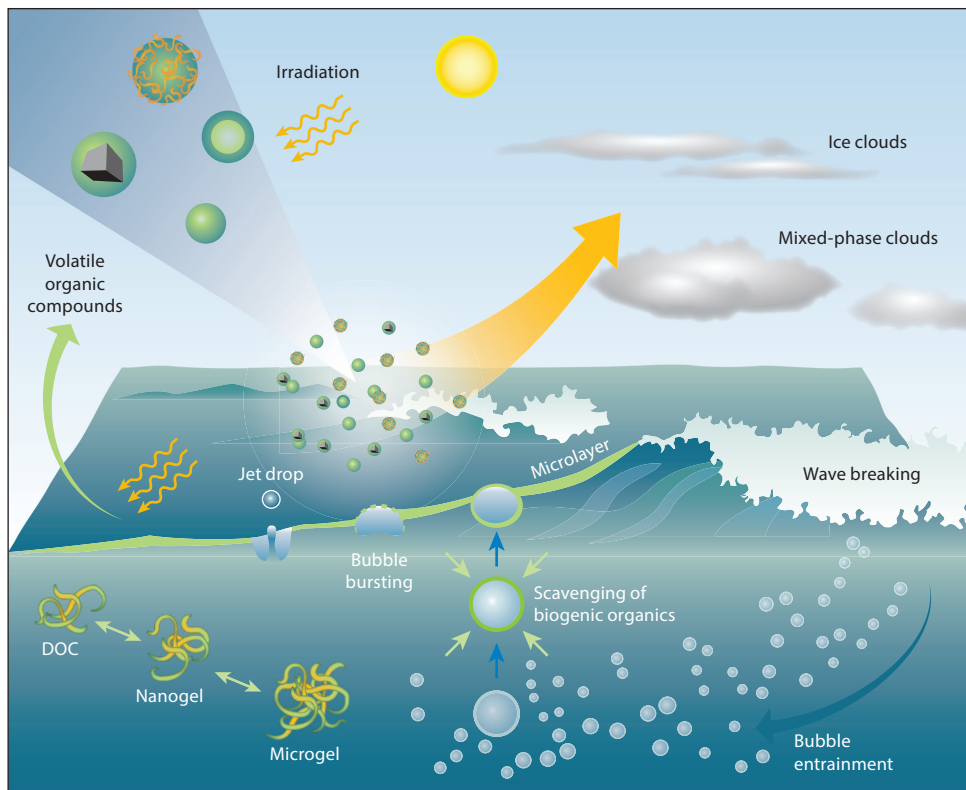


Figure 6

Schematic showing the complex interactions between subsurface water and the sea surface microlayer, generation and composition of sea spray aerosol particles, and implications for their atmospheric chemical and physical processes relevant to the environment and climate forcing (5, 91, 95). Abbreviation: DOC, dissolved organic carbon.

complexity and variability in CCN 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 larger-sized SSA particles typically contain sea salt cores coated with organic material (27). The presence of bacteria and phytoplankton in seawater affects the surfactant structure of large SSA particles but has minor impact on smaller (approximately 150 nm) particles (139). SSA particles generated during bacterial metabolism indicate the presence of transition metals, likely due to bacterial bioaccumulation or colloids adhering to these metal ions (140).

Colloids and aggregates exuded by phytoplankton contribute to the water-insoluble organic matter of SSA (133). Such gel-like particles are composed of tangled macromolecules and colloids, derived preferentially from surface-active polysaccharides (141) and proteinaceous materials (142). These marine nano- and microgels are ubiquitous at the ocean surface, and therefore contribute to SSA composition. Marine gels have been detected in cloud water, which suggests that they have a significant role in CCN activation (131). However, chemical characterization of

ICE-NUCLEATING PROPENSITY OF ORGANIC PARTICLES

Ice nucleation experiments using a microscope system with a controlled vapor-cooling stage complemented by chemical imaging (56, 95, 143) indicate the substantial presence of organics in ice-nucleating particles. Experiments with SSA particles collected at different locations above the ocean surf zone, laboratory mesocosm experiments, and Atlantic Ocean showed that particles larger than 300 nm in diameter initiate ice nucleation under conditions relevant to mixed-phase and cirrus clouds. The identified ice-nucleating particles contained inorganic cores of sea salt surrounded by organic outer layers. Chemical imaging revealed alcohol and carboxyl functionalities in the organic material, suggesting that the organic coating is highly viscous. These observations support the potential for organic particles to affect ice nucleation in the atmosphere.

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) (see sidebar, Ice-Nucleating Propensity of Organic Particles). A recent study (95) demonstrated enhanced ice nucleation activity in sea surface microlayer (SML) 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 greatest 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 SML 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, suggesting 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 are substantially different from those in biogenic and anthropogenic OA. Hence, understanding atmospheric chemistry and transformations of OA in the marine environment requires additional studies.

SML: sea surface microlayer

SOLID ORGANIC PARTICLES GENERATED BY RAINFALL

Solidified ASOP can be generated as a result of atmosphere–land surface interactions through a recently revealed raindrop mechanism (148) occurring when water droplets hit open soil surfaces during precipitation or irrigation events (96). Field observations showed a dominant presence of solid ASOP (60% by number) after an intensive rain event in the southern Great Plains in Oklahoma, 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 on local and regional scales.

3.4. Airborne Soil Organic Particles

Until recently, it was believed that the primary processes for aerosolizing soils and entraining their soil organic matter (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 the ejection of submicrometer airborne soil organic particles (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 surface-accumulated water followed by ejection of very fine aqueous particles upon bubble bursting. Similar to the generation of organic sea spray particles, discussed in Section 3.3, dissolved organic matter from wet soils is aerosolized by the bursting of entrained bubbles at the air–water interface (see sidebar, Solid Organic Particles Generated by Rainfall).

Microspectroscopic chemical imaging and microanalysis of ASOP collected in a field study in Oklahoma indicate that they appear as unusual glassy, spherical organic solids, and their characteristic X-ray absorption spectra match those of dissolved SOM. **Figure 8** shows their visual appearance in SEM images taken at a tilted angle (96). The soil-derived source and mechanism of ASOP formation were inferred based on the notable similarity between their NEXAFS spectra and those 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 the resulting ASOP at ambient conditions, as confirmed by the observed glassy, 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.

Due to 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 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 was attributed to the wind erosion of soil, whereas direct emissions in the form of ASOP were never considered.

SOM: soil organic matter

ASOP: airborne soil organic particles

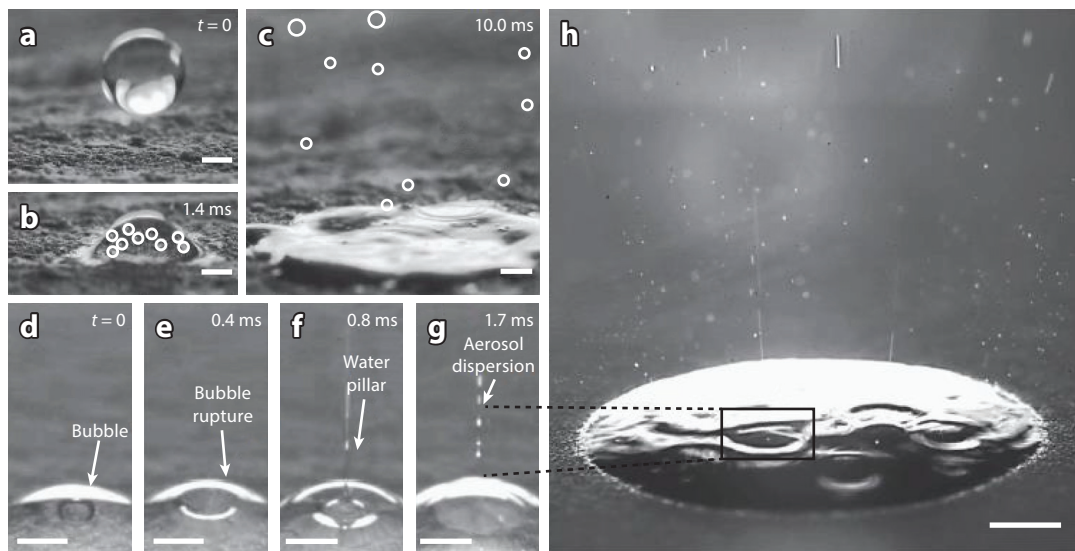


Figure 7

High-speed photographic images capturing the raindrop mechanism of aerosol generation. (*a–c*) Impingement of a droplet onto a 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. Scale bars are 1 mm. Figure reproduced with permission from Reference 148. Copyright 2015 Nature Publishing Group.

Understanding the sources and chemical composition of ASOP 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 phases of OA are concentrated on atmospheric processes that solidify liquid-like secondary organic particles produced through multiphase 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 the efficiency of 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 and ice nucleation properties.

Notably, ASOP are refractory and do not volatilize substantially upon heating (up to 600°C) (96). Hence, they would not be detected by common methods of in situ particle speciation based on thermal evaporation. Methods of laser ablation mass spectrometry can certainly detect ASOP;

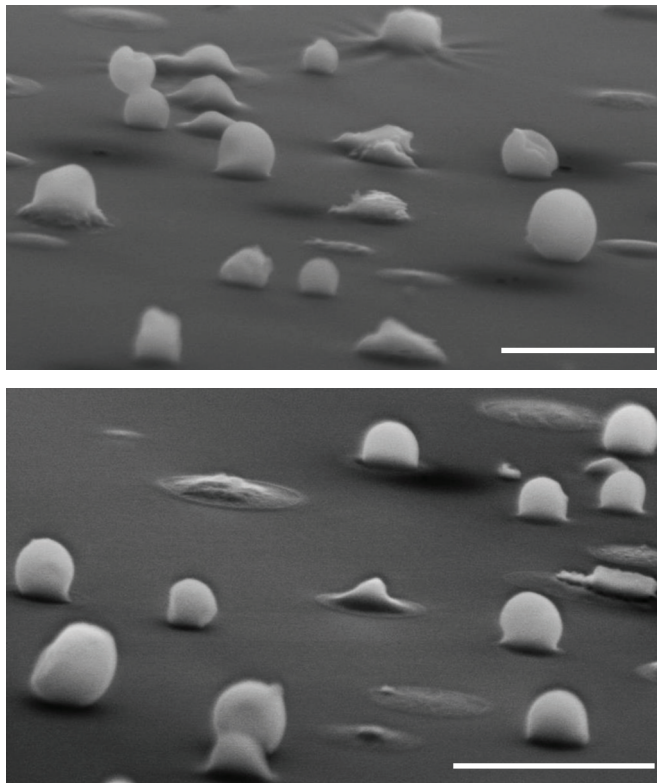


Figure 8

Scanning electron micrographs (at a 75° tilt angle) of solid airborne soil organic particles (ASOP) sampled by the impaction method. The high vertical dimension of ASOP is indicative of their solid (glassy) phase (96). Scale bars are 2 μm .

however, extensive fragmentation upon ablation could generate mass spectra that could be confused with other organic particles. The solid (glassy) phase and refractory carbonaceous composition of ASOP make spectromicroscopy methods the most effective techniques for detection and for assessment of optical and hygroscopic properties. The structures of the high-molecular-weight constituents of ASOP are of particular interest because they control the chemical and physical properties of ASOP. 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

Multimodal applications of novel analytical platforms highlighted in this review have facilitated in-depth chemical analyses of complex atmospheric particles. Methods of chemical imaging and molecular-level analysis described herein provide the experimental means to improve our fundamental knowledge of particle effects on cloud microphysics and particles' dependence on variables (e.g., RH, temperature, multiphase reactions) and to distinguish the 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 the impact of aerosols on climate change, air quality, visibility, and health issues. In recent years, we have observed a tremendous expansion and growth of research in this area, a trend that likely will continue.

Developments of the new instrumentation and novel analytical methodologies allow investigations on the chemical complexity of the atmospheric particles and their transformations with a level of detail that was unprecedented just a few years ago. However, additional analytical chemistry developments are needed, in particular with higher time resolution, to make rapid measurements of particle heterogeneity, gas-particle interfaces, internal mixing, and phase separations at nano scale to better understand the processes controlling particles' life cycle and their physicochemical properties. These developments will broaden the scope of future studies and will ultimately allow for better parameterization of particle chemistry in atmospheric models.

We highlighted several scientific challenges related to the complex, multiphase chemistry and physics of atmospheric particles that could uniquely benefit from multimodal experimental approaches to 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, in which multimodal characterization of particles would significantly impact our fundamental understanding of various air-surface interactions and their influence on climate and air quality.

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The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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