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1 Progress in the Analysis of Complex Atmospheric Particles

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25
26 **Keywords:** Aerosol, Chemical Imaging, Molecular-level, Multi-Phase Chemistry, Atmospheric Aging,
27 Environmental Interfaces

28

29 Manuscript in preparation for *Annual Reviews in Analytical Chemistry*

30 **Abstract**

31

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

45

46 1. Introduction

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

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

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

79

2. Multimodal Chemical Characterization of Particles

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

102

2.1. Chemical Imaging Techniques.

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

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

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

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

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

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

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

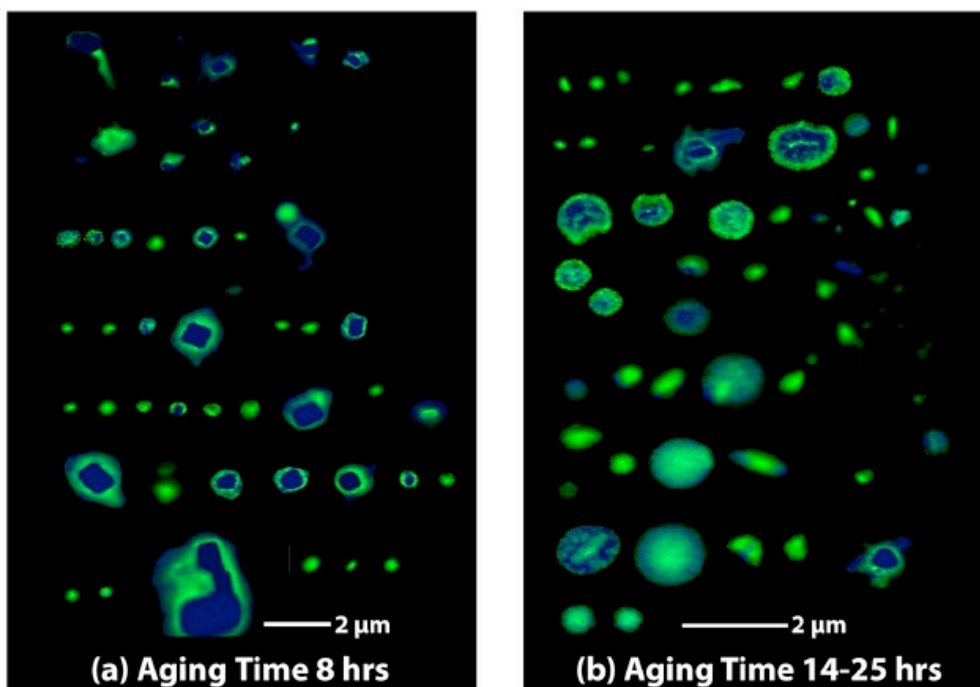
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164 2.2. Atmospheric Transformations of Particles

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

173 Chemical imaging approaches are used to elucidate transformations of specific particle
174 types collected in field and laboratory studies. Mechanisms are usually inferred from field
175 observations, which in turn guide follow-up laboratory studies designed to test a hypothesis.
176 Figure 1 compares STXM maps of relatively fresh and aged marine particles collected onboard
177 research aircraft in central California. Particle regions enriched in organic acids are shown in
178 green, and inorganic (mostly NaCl) components are shown in blue.(26) The maps indicate
179 morphology and internal composition changes due to in-particle reactions between organic
180 acids and NaCl components, as confirmed by laboratory studies.(39; 40) Complementary
181 multimodal STXM, CCSEM/EDX and micro-FTIR techniques showed that particles containing sea
182 salt and weak organic acids undergo irreversible transformations through multi-phase
183 chemistry driven by acid-displacement reactions and subsequent degassing of volatile products
184 HCl or HNO₃ products. These chemical reactions are accelerated by particle dehydration cycling
185 and result in changes in particle viscosity, hygroscopicity, phase transitions and separations,
186 and thereby modify particle environmental impacts and lifecycle.(44; 79; 80)

187



188
 189 **Figure 1.** STXM maps of particles of a marine origin with different transport (and hence, aging) times
 190 from the CARES 2010 field study.⁽⁸¹⁾ Areas dominated by organic carbon are green, and inorganic
 191 components are blue. (Reproduced with permission from reference (26). Copyright 2012 Wiley-
 192 Blackwell).

193
 194 The complementary combination of STXM/NEXAFS and CCSEM/EDX chemical imaging data
 195 sets has also provided a quantitative assessment of mixing states of carbonaceous particles
 196 aged in the photochemical environment of urban plume.^(23; 24) STXM provided experimental
 197 visualization of how soot and organic carbon constituents were mixed within individual
 198 particles and CCSEM provided corresponding information on the inorganic content. Combined,
 199 this unique study provided a quantitative assessment of the particle-type classes,⁽²³⁾ and
 200 individual particle characteristics such as the particle-specific diversity, bulk population
 201 diversity, and mixing state index determined for particles with different atmospheric aging
 202 history.⁽²⁴⁾ It showed that the mixing states of urban particles in the Sacramento, CA region
 203 were driven by local emissions of black carbon-containing particles that were coated by
 204 products from gas phase secondary chemistry and/or coagulated with sea spray, sulfate, and
 205 organic particles originating from refineries in the San Francisco Bay region. These unique
 206 results provided the first quantitative description of particle mixing state changes during
 207 transport parameterized for use in atmospheric modeling simulations. This allows additional
 208 model refinement based on the results of the multi-modal chemical imaging of particles.

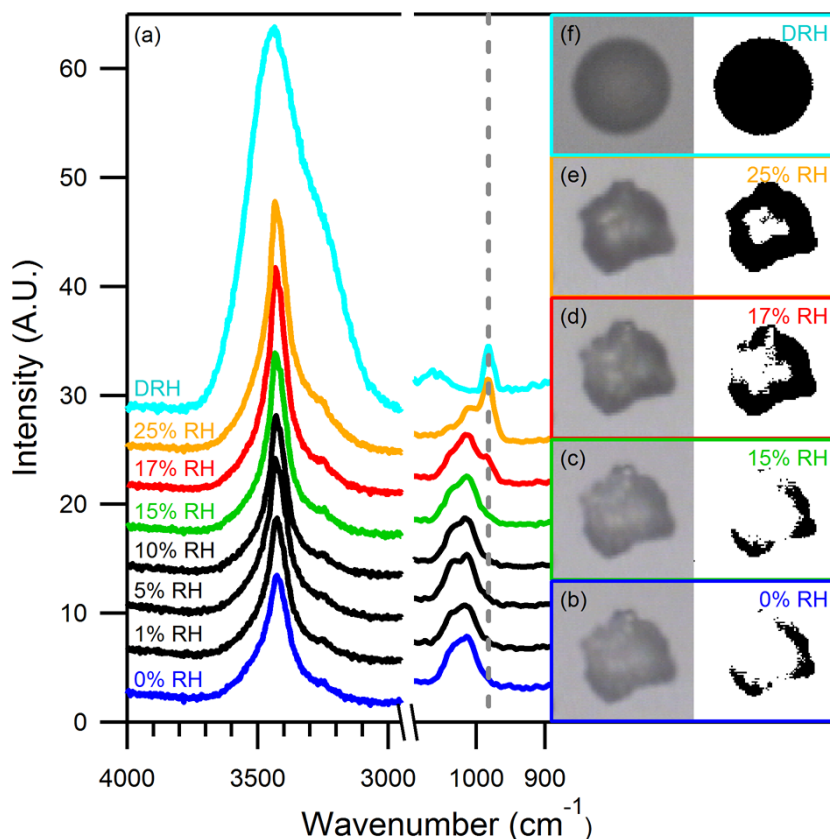
209 Increasingly, chemical imaging methods are used for dynamic in-situ laboratory studies that
 210 simulate the atmospheric particle life cycles using specially designed micro-reactors. Elucidating

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

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

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

252
253



254
255 **Figure 2.** Raman spectra (a) and optical images (b–e) of an approximately 15 μm mixed sea salt particle
256 captured during water uptake/ice nucleation experiments. Dynamic changes in particle composition
257 corresponding to water uptake and dissolution of sulfate components at the outer particle layers are
258 evidenced by differences in the spectra and the binary maps (right panels). For comparison, a fully
259 deliquesced sea salt particle is shown in (f). (Reproduced with permission from reference (60). Copyright
260 2014 American Chemical Society).

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262

2.3. Molecular-level Characterization

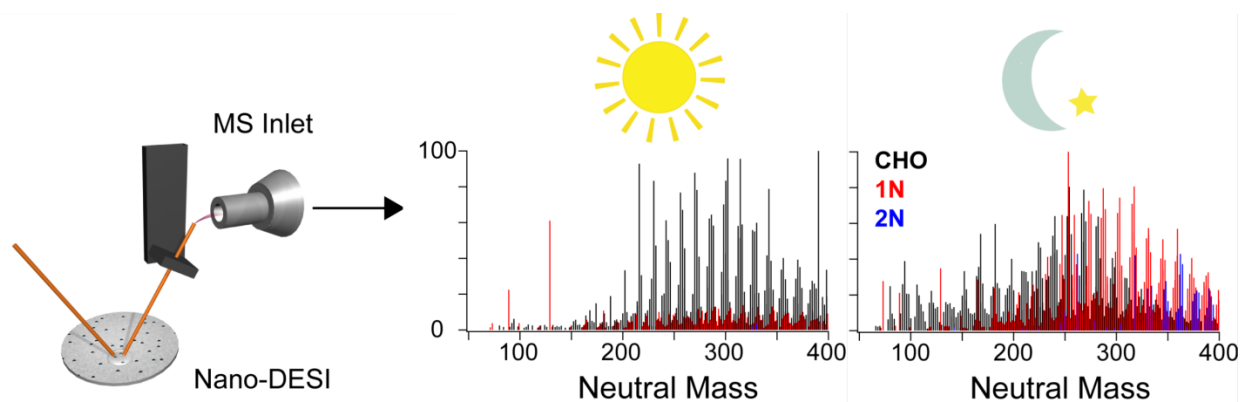
263 Understanding molecular compositions and transformations of complex mixtures of OA
264 components is arguably the most significant challenge in atmospheric aerosol research.
265 Because of its ability to provide molecular-level information, HRMS assisted with ambient
266 pressure surface ionization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

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

279 Figure 3 shows a schematic drawing of the nano-DESI technique and the HRMS spectra of
280 ambient OA collected during the 2010 CalNex campaign at Bakersfield, CA.(86) For comparison,
281 characteristic HRMS spectra collected at the daytime and the nighttime are shown.
282 The high fraction of CHO compounds, characteristic for fresh OA produced by photochemistry
283 and ozonolysis, dominate the daytime spectrum. The increased fractions of nitrogen-containing
284 CHON₁₋₂ compounds are evident in the nighttime spectrum. By comparing plausible reactant-
285 product pairs within molecular species identified in the mass spectra, changes in the OA
286 chemical composition between day and night were assessed. Over 50% of the CHON₁₋₂ species
287 had CHO precursor product pairs consistent with imidization reactions and formation of species
288 with –C=N–C=C– chemical bonds (Schiff bases). These reactions involve ammonia and carbonyl
289 groups on the precursor species, and they suggest a potential role of the Schiff bases in forming
290 nitrogen-containing OA.(86) Formation of these low-volatility and potentially light absorbing
291 compounds may play an important role in OA atmospheric transformations that remain poorly
292 understood.

293

294



295
 296 **Figure 3.** Left panel: Schematic of the nano-DESI analysis of organic aerosol. In nano-DESI, the analyte
 297 deposited on a substrate is probed by an online liquid extraction followed by soft nanoelectrospray
 298 ionization. Right plots: Representative nano-DESI mass spectra of samples from Bakersfield, CA collected
 299 during day and night, respectively. The colors correspond to the number of N atoms in the chemical
 300 formula with black = 0 N, red = 1 N, blue = 2 N. (Reproduced with permission from reference (86).
 301 Copyright 2013 Elsevier, Ltd.).

302 3. Exchange of Chemical Constituents at Air-Surface Interfaces

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

318 3.1. Wind Blown Dust

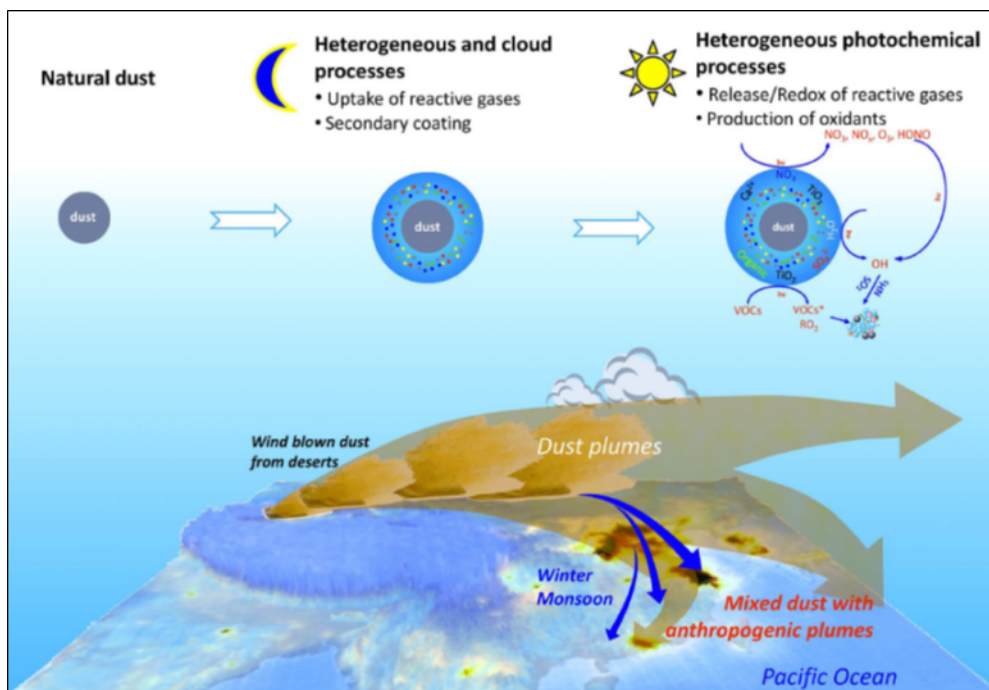
319 Wind-blown mineral dust is one of the major sources of primary atmospheric particles that
 320 affect atmospheric environment and climate through light absorption and scattering, and acting
 321 as either CCN or IN.(98) Atmospheric aging of dust particles, through multiphase chemistry
 322 during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

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

335 As discussed in section 2.2., in marine particles, organic acid components of OA can react
336 with inorganic components through multi-phase aqueous chemistry where the reaction
337 equilibrium is shifted to the products by rapid irreversible degassing of volatile products.(26;
338 39; 40) These reactions are common for a broad class of water-soluble organic acids present in
339 both biogenic and anthropogenic OA. Analogous reactions and formation of organic salts are
340 reported for particles containing calcite components of mineral dust.(80; 102) Considering this
341 reactivity for Fe(III)-containing dust components, the organic salts produced would
342 preferentially form on particle outer layers. For instance, the (oxyhydr)oxide surface of
343 hematite can be eroded by carboxylic acids (R-COOH) driven by evaporation of water (a
344 reaction product). The hematite degradation processes may be further enhanced in the
345 presence of UV-Vis radiation because of the unique chelating and photo-catalytic activity of
346 Fe(III). Specifically, chelated [Fe(III) - R-COOH] complexes absorb light in the UV-Vis range and
347 decompose into Fe(II) and \cdot R-COOH pairs.(103) \cdot R-COOH radicals can subsequently decompose
348 into smaller oxygenated organic compounds, CO₂ and peroxides. The radicals may participate in
349 oligomerization processes, while CO₂ and high volatility oxygenated organics can partition into
350 the gas phase. Peroxides can drive Fenton chemistry, Fe(II) to Fe(III) re-oxidation, creating a
351 photo-catalytic cycle in which organic acid components are continuously converted into
352 reactive products, followed by their decomposition and oligomerization reactions. Modeling
353 these photo-catalytic processes suggests they may drive aqueous phase aging of atmospheric
354 organics in the presence of Fe(III), a topic requiring further study.(104)

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

361 on the environment. Specifically, gas-phase partitioning of volatile oxygenated organics
362 produced through photochemistry in mixed OA/Fe(III) particles may be an unrecognized source
363 of nucleating vapors contributing to new particle formation and growth.
364



365
366
367 **Figure 4.** Schematic Transformations of Asian dust during its atmospheric transport: 1) Fine mineral dust
368 is aerosolized by winds in the remote Gobi desert area, 2) dust particles acquire secondary coatings
369 when transported over industrial regions with anthropogenic pollution, 3) aged dust particles are
370 transported into the Pacific region and experience multi-phase photochemistry that releases reactive
371 gases relevant to new particle formation and growth. (Reproduced with permission from reference (97)
372 Copyright 2014 Nature Publishing Group).

373
374 As a result of the OA/Fe(III) multi-phase chemistry discussed above, multiple changes in
375 particle properties are expected. First, the optical properties of these systems would be altered
376 depending upon different scenarios of atmospheric aging and specific OA composition (e.g.
377 biogenic - less aromatic versus anthropogenic - higher aromatic precursors; chelated Fe(III)-
378 organic complexes are strong chromophores). Second, changes in particle viscosity are
379 expected because of the gas-phase partitioning of CO₂ and volatile organic products on one
380 side, and resulting oligomerization processes on the other side. These factors strongly affect
381 particles' CCN and IN ability. The degree to which these combined processes alter OA
382 composition, particle optical properties, and their CCN and IN ability remain an open question.
383 These questions can be addressed through complementary applications of off-line techniques
384 that probe particle samples collected in field and laboratory studies.

385

386 3.2. Air-Surface Interfaces of Biological Particles

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

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

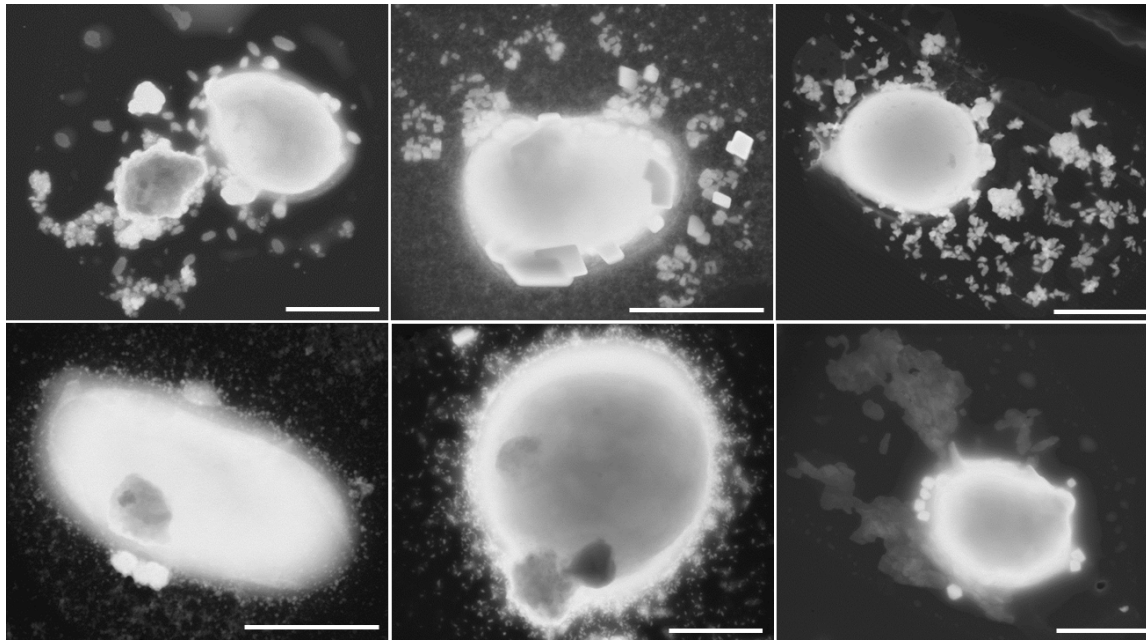
411 Due to their similarities with other carbonaceous particles, measuring and detecting
412 biological particles by in-situ aerosol characterization methods is challenging. This results in
413 ambiguous data on their atmospheric concentrations and chemical composition(115), which
414 produces large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

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

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

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

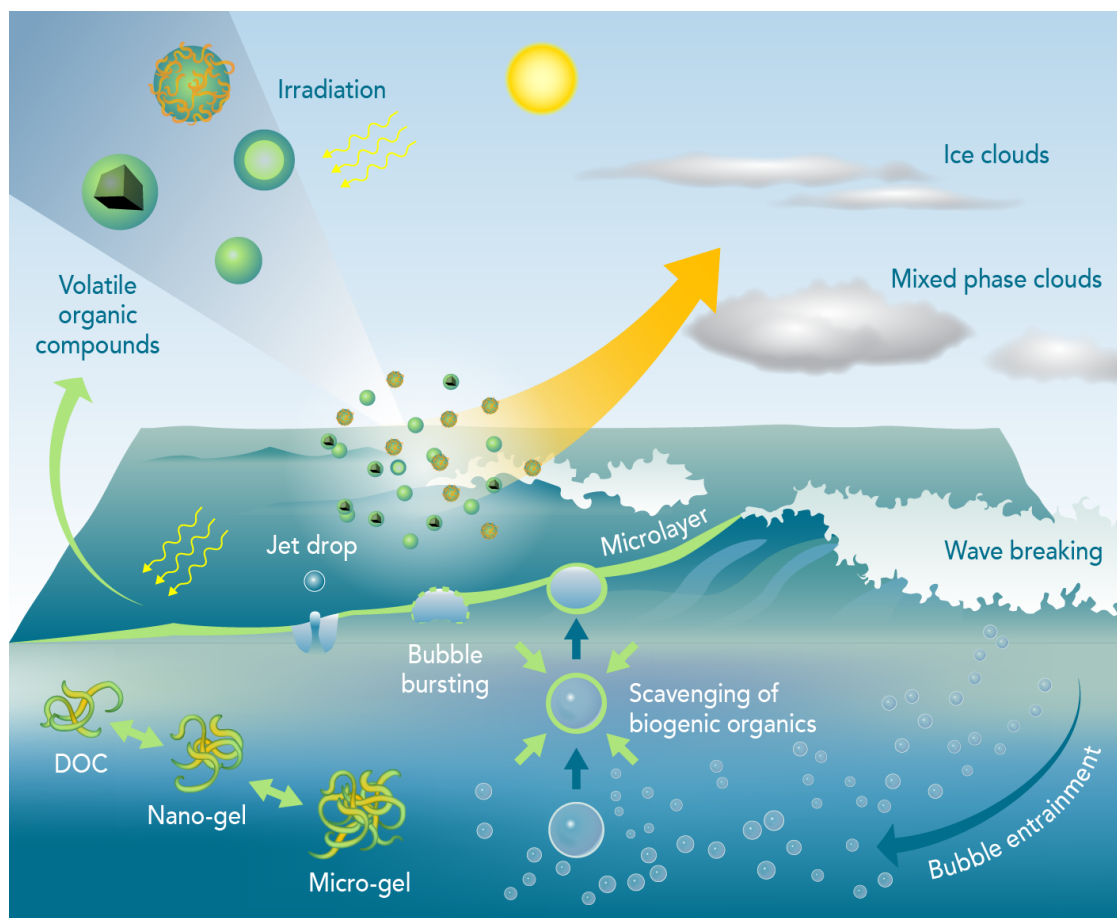
444



445
 446 **Figure 5.** SEM images of fragmented fungal spores and expulsion of subfungal spore particles. The
 447 examples shown in the images are fungal spores collected in the Amazonia. Images revealed that size of
 448 the expelled fungal spores vary substantially, ranging from a few to hundreds nanometers. Scale bar is 2
 449 μm .

450 3.3. Sea Spray Aerosol

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



470

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

474

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

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

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

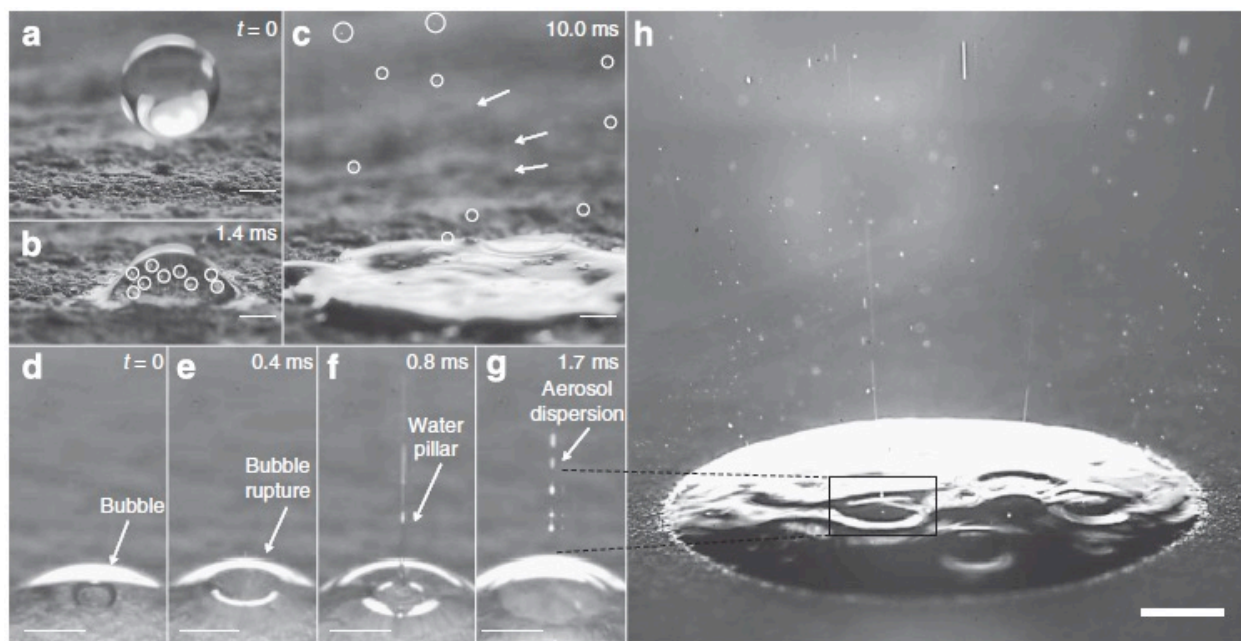
497 The composition of SSA particles defines their reactivity and transformations through
498 heterogeneous and multiphase atmospheric chemistry involving gas- and aqueous phase
499 oxidants. Photochemically induced reactions in the SSML change the nature of the organic
500 molecules available for ejection.(92; 146) Furthermore, photochemical reactions occurring in
501 SSA, lead to changes in the physicochemical properties of particles and in the gas-particle
502 partitioning of the products.(147) The mixing state and amount of organic material distributed
503 among different SSA particles may impact the underlying multiphase reaction mechanisms and
504 their kinetics. For example, laboratory studies of SSA reacting with HNO₃ demonstrated that
505 particle reactivity was correlated with the crystalline structure of the salt core and the amount
506 of organic carbon.(41) Reactive uptake by HNO₃ resulted in a redistribution of inorganic cations
507 and a layer of organic matter concentrated at the surface of the particle suggest that specific
508 ion and pH effects impact the physicochemical structures of SSA particles.(42) Atmospheric
509 aging and transformation of SSA through reactions with other common oxidants such as O₃ and
510 OH are not sufficiently known. The origin and composition of the organic matter in SSA is
511 substantially different from biogenic and anthropogenic OA. Hence, understanding atmospheric
512 chemistry and transformations of OA in the marine environment requires additional studies.

513

514 **3.4. Airborne Soil Organic Particles**

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

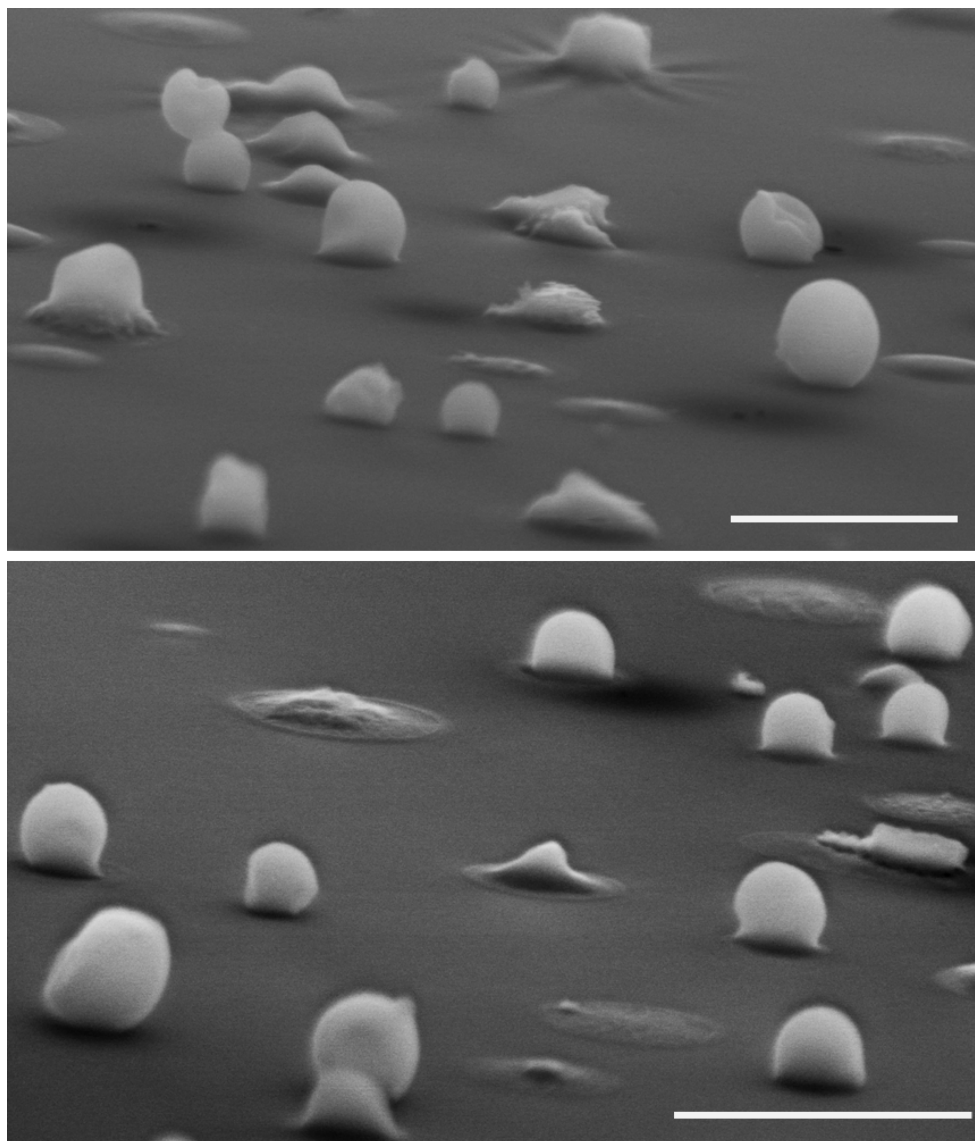
525 Similar to generation of organic sea spray particles, discussed in section 3.3., dissolved organic
526 matter from wet soils is aerosolized by bursting of entrained bubbles at the air-water interface.
527



528
529 **Figure 7.** High-speed images capturing the “raindrop mechanism” of aerosol generation. (a-c)
530 Impingement of a droplet onto solid mineral surface and formation of air bubbles inside of the aqueous
531 layer formed on the surface. (d-e) Dynamic ejection of a fine aqueous mist upon bursting of the air
532 bubbles at the air-water interface. (Reproduced with permission from reference (148). Copyright 2015
533 Nature Publishing Group).

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

546
547



548
549

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

552

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

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

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

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

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

584 Notably, ASOP are refractory and do not volatilize substantially upon heating up to 600
585 °C.(96) Hence, they would not be detected by common methods of in-situ particle speciation
586 based on thermal evaporation. Methods of laser ablation MS can certainly detect ASOP;
587 however, extensive fragmentation upon ablation could generate mass spectra that would be
588 confused with other organic particles. The solid (glassy) phase, and refractory carbonaceous
589 composition of ASOP make spectro-microscopy methods the most effective detection
590 techniques, and for assessing optical and hygroscopic properties. The structures of the high-
591 molecular weight constituents of ASOP are of particular interest because they control their
592 chemical and physical properties. Size-selected sampling of ASOP during events of their high
593 abundance, followed by advanced analysis using nano-DESI/HRMS can be utilized for probing
594 the molecular-level speciation of ASOP and ultimately for understanding their atmospheric
595 transformations.

596

597 **4. Summary**

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

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

618 **5. Disclosure Statement**

619 The authors are not aware of any issues that might be perceived as affecting the
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636

637 **Acronyms and Definitions**

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

681

682

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, CO₂, HNO₃) 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

749 (typeset next to section 3.4)

750

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

760

761

762

763

764

765 7. Literature Cited

766 Annotated references:

- 767 **Ref 1** An excellent review of aerosol chemistry highlighting synergism between laboratory studies,
768 field measurements and modeling analysis.
- 769 **Ref 5.** Comprehensive review of aerosol multiphase chemistry influencing the Earth system, climate,
770 air quality, and public health.
- 771 **Ref 16.** A review manuscript featuring applications and perspectives of the HRMS analysis for
772 molecular-level studies of organic aerosols.
- 773 **Ref 17.** An edited book offering the comprehensive overview of the spectroscopy of aerosols,
774 including fundamental aspects and applications.
- 775 **Ref 22.** Thorough review focused on the current understanding of the chemistry of atmospheric
776 brown carbon, including highlights of areas that need further studies.
- 777 **Ref 91.** A comprehensive review of the results of field and laboratory studies performed to
778 characterize the properties of SSA, with an emphasis on the organic fraction.
- 779 **Ref 92.** A comprehensive review of photochemical processes occurring at the air-surface interfaces of
780 aerosols, environmental surfaces and atmospheric ice.
- 781 **Ref 96.** The field evidence report of solid ASOP emitted to the atmosphere through atmosphere – land
782 surface interactions following rainfall.
- 783 **Ref 98.** An edited book offering the comprehensive overview of the chemistry and physics of
784 atmospheric mineral dust.
- 785 **Refs 106,107.** Comprehensive reviews focused on the airborne biological particles, theirs atmospheric
786 lifecycles and impacts on air quality and climate.
- 787
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