Solid organic-coated ammonium sulfate particles at high relative humidity in the summertime Arctic atmosphere

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The ability of atmospheric aerosols to impact climate through water uptake and cloud formation is fundamentally determined by the size, composition, and phase (liquid, semisolid, or solid) of individual particles. Particle phase is dependent on atmospheric conditions (relative humidity and temperature) and chemical composition and, importantly, solid particles can inhibit the uptake of water and other trace gases, even under humid conditions. Particles composed primarily of ammonium sulfate are presumed to be liquid at the relative humidities (67 to 98%) and temperatures (−2 to 4 °C) of the summertime Arctic. Under these atmospheric conditions, we report the observation of solid organic-coated ammonium sulfate particles representing 30% of particles, by number, in a key size range (<0.2 μm) for cloud activation within marine air masses from the Arctic Ocean at Utqiagvik, AK. The composition and size of the observed particles are consistent with recent Arctic modeling and observational results showing new particle formation and growth from dimethylsulfide oxidation to form sulfuric acid, reaction with ammonia, and condensation of marine biogenic sulfate and highly oxygenated organic molecules. Aqueous sulfate particles typically undergo efflorescence and solidify at relative humidities of less than 34%. Therefore, the observed solid phase is hypothesized to occur from contact efflorescence during collision of a newly formed Aitken mode sulfate particle with an organic-coated ammonium sulfate particle. With declining sea ice in the warming Arctic, this particle source is expected to increase with increasing open water and marine biogenic emissions.

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Despite the evidence for abundant solid or glassy organic particles (11, 12), ubiquitous hygroscopic inorganic components, such as ammonium sulfate, are presumed to be primarily present as ions dissolved in aqueous particles in the marine boundary layer due to the high relative humidity (RH) (13, 14). When considering the phase of ammonium sulfate at 293 K, there is a well-known hysteresis effect where a solid ammonium sulfate particle undergoes a phase transition to an aqueous liquid under typical tropospheric conditions, which is predicted to be liquid under typical tropospheric conditions in the summertime Arctic. Yet, we unexpectedly observed a significant concentration of solid particles composed of ammonium sulfate with an organic coating under conditions of high relative humidity and low temperature. These particle properties are consistent with marine biogenic-derived new particle formation and growth, with particle collision hypothesized to result in the solid phase. This particle source is predicted to have increasing relevance in the context of declining Arctic sea ice and increasing open water, with impacts on clouds, and therefore climate.

Significance

Physical and chemical properties of individual atmospheric particles determine their climate impacts. Hygroscopic inorganic salt particles mixed with trace amounts of organic material are predicted to be liquid under typical tropospheric conditions in the summertime Arctic. Yet, we unexpectedly observed a significant concentration of solid particles composed of ammonium sulfate with an organic coating under conditions of high relative humidity and low temperature. These particle properties are consistent with marine biogenic-derived new particle formation and growth, with particle collision hypothesized to result in the solid phase. This particle source is predicted to have increasing relevance in the context of declining Arctic sea ice and increasing open water, with impacts on clouds, and therefore climate.

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Particle at 78% RH when RH is increasing, while a liquid particle will not crystallize when drying until 34% RH (15). Thus, since one of the most common mechanisms for sulfate [SO$_4$$^{2-}$ (aq)] formation is aqueous phase oxidation of SO$_2$, and the RH over the Arctic Ocean does not go below 34% (16), it is commonly assumed that ammonium sulfate is present as dissolved ions in aqueous particles in the summertime Arctic. Even at temperatures near 0 °C, the phase transition to a solid is not predicted for pure ammonium sulfate at typical ambient RH values (~60 to 100%) by the ammonium sulfate phase diagram (15).

In this study we report the surprising observation of solid ammonium sulfate particles with organic coatings in the accumulation mode collected in marine air masses in the summertime Arctic at low temperatures (~2 to +4°C) and high RH (67 to 98%), for which ammonium sulfate is predicted to be present in aqueous particles. These particles were characterized using a multimodal microspectroscopic approach to determine their chemical composition, phase, and morphology. A combination of laboratory studies, thermodynamic modeling, and attribution of sources and formation processes is used to explain these unexpected results and their potential implications for atmospheric chemistry in cold, humid environments, including the summertime Arctic marine boundary layer.

Results and Discussion

Solid Particles Observed at Low Temperature and High RH. Ambient particles were collected at the coastal Arctic location of Utqiaġvik, AK during August to September 2015, at ambient temperatures from ~2 to +4°C and RHs between 67 and 98% within marine air masses. Microscopic analysis revealed a unique type of particle that was predominantly ammonium sulfate, the phase of which was unexpectedly solid with a complex morphology (Fig. 1A). The physical properties of these particles were investigated using atomic force microscopy (AFM), which demonstrated the tall nature of the particles, with heights of 150 to 200 nm measured for 130- to 500-nm projected area (Fig. 1A and B). Upon impaction, these particles spread a similar amount as solid particles and far less than aqueous particles (17, 18), indicating these ambient particles existed in a solid or viscous phase. AFM phase images revealed particles with complex structure, showing a difference in particle phase (19) between the main particle and distinct smaller particle(s) on its surface (Fig. 1C). Scanning electron microscopy (SEM) imaging in transmission mode showed that most of these round particles contained small (~20 nm) cubic sulfate particles on the surface (Fig. 1D), distinct from the ammonium sulfate in the core (20). SEM images collected at a 75° tilt in back-scattering mode further demonstrated the tall, hemispherical nature of these particles (Fig. 1F), in comparison to other flat, liquid ambient particle types observed within the same samples (SI Appendix, Fig. S1). This tilt method has previously been used to show solid organic particles formed in agricultural areas (10). To our knowledge, this tall morphology has not been previously observed for ambient particles in the Arctic or beyond, suggesting it is unique to the particle composition, observed atmospheric conditions, and particle’s history since its formation.

The physical properties of these ambient particles were compared to the morphology of laboratory-generated solid (RH = 15%, effloresced) ammonium sulfate particles, as well as liquid (RH = 50%, deliquesced) inorganic sulfate particles from Olson et al. (18) (Fig. 2). Particle phase can be inferred by the extent of spreading, determined by the particle radius and height following inertial impaction onto a substrate at ambient pressure. AFM height traces (25 to 72 particles per trace) showed that the tall ambient particles were comparable to similar diameter solid laboratory-generated ammonium sulfate particles, while the aqueous laboratory-generated sulfate particles were much shorter (Fig. 24). Spreading ratios are similar for the ambient (2.0 ± 0.1) and solid laboratory (1.43 ± 0.08)
particles and far less than for the aqueous laboratory particles (7 ± 1) (Fig. 2B). Three-dimensional AFM height images further demonstrated the similar morphology of the tall ambient (Fig. 2C) and solid laboratory-generated ammonium sulfate particles (Fig. 2D), indicating the ambient particles exhibited a solid phase (21). To examine whether the ambient particles were capable of deliquescing and spreading substantially on the substrate, RH cycling experiments were conducted for the ambient particles where RH was increased up to 85%, above the deliquescence RH of ammonium sulfate, and then decreased to 30%. Low spreading ratios were still observed after cycling, confirming the particles did not deliquesc to fully liquid particles on the substrate and spread (see details in SI Appendix and SI Appendix, Fig. S1).

Chemical Composition and Phase Separation. The chemical composition of the individual particles was determined to investigate its role in the observed morphology and phase. SEM coupled with energy dispersive X-ray spectroscopy (SEMEDX) identified carbon, oxygen, and sulfur in the individual particles (Fig. S4 and Fig. S5), indicative of sulfate and organic. Notably, these particles were extremely sensitive to the electron beam, characteristic of ammonium sulfate (22). Other elements associated with sea spray (e.g., Na, Mg, K, Ca, and Cl) were not observed in these particles. Scanning transmission electron microscopy with near-edge X-ray absorption fine structure (STXM-NEXAFS) spectra of individual particles over the sulfur L-edge confirmed the presence of inorganic sulfate [S(VI)] in the particles (Fig. S4) (23). AFM coupled with photothermal infrared spectroscopy (AFM-PTIR) was used to identify functional groups present in particles smaller than the optical diffraction limit (17, 24). AFM-PTIR analysis of individual particles identified ammonium sulfate, with characteristic νca(SΟ42−) and δ(NH4+) modes at 1,098 cm−1 and 1,420 cm−1, respectively (13, 17), a bisulfate νca(HSO4−) mode at 1,260 cm−1, and a δ(H2O) mode at 1,726 cm−1 (13) (Fig. 3B and additional PTIR spectra in Fig. S5). The location of an ammonium δ(NH4+) mode at 1,420 cm−1 is consistent with solid ammonium sulfate, based on prior efflorescence studies (13).

Trace organic compounds impact the phase (25) and physical properties [deliquescence, efflorescence, and crystallization (15, 26–28)] of ammonium sulfate particles. The presence of organics in the ambient particles was confirmed by STXM-NEXAFS mapping over the carbon K-edge, which showed organic components coating the primarily inorganic particles (Fig. 3C). Inclusions of sp2 carbon were also observed on the organic/inorganic interface of a few particles (Fig. 3C), indicative of material not soluble in the organic phase and further demonstrating the complex multiphase nature of these particles. Though commonly associated with soot, sp2 carbon has also been attributed to marine biogenic sources (29, 30). Organic coatings on ammonium sulfate particles were recently observed during summertime in the Norwegian Arctic, including some particles with soot inclusions in the organic coating, though these particles were liquid when collected based on extensive spreading (31). Organic volume fractions within the individual ambient particles in this study were determined based on the STXM-NEXAFS data. Two distinct components were defined: an organic coating (average 89% organic, 11% inorganic) and an inorganic core (average 3% organic, 97% inorganic) (Fig. 3D and E). The thickness of the inorganic and organic components from the edge to center of each particle was determined based on the organic volume fraction, further demonstrating the presence of an organic dominant coating (100- to 150-nm thickness) and inorganic dominant core (Fig. 3 D and E). The solubility of organic compounds decreases with temperature (32); therefore, at the observed temperatures (−2° to +4°C), the organic coatings likely formed via liquid–liquid phase separations due to the lower surface energy of that structure (33). However, the sampled particles observed herein were solid, which means the ammonium sulfate core effloresced in the atmosphere prior to collection. This efflorescence likely concentrated the organic material at the surface, leading to the formation of a more viscous organic phase.

For each time period when the solid particles were collected, RH <81% was observed during a portion of the air mass trajectory (SI Appendix, Discussion of Impaction and Analysis of Solid Particles and Fig. S6). During Arctic Ocean air mass sampling, ambient RH ranged from 67 to 98%, with 38% of the sampling time at RH <81%. Aqueous ammonium sulfate is metastable (i.e., supersaturated) at RH <81% (13), the deliquescence RH of ammonium sulfate for the sampling temperatures (15, 34). In a metastable phase, it is thermodynamically favorable for particles to effloresce and form a solid phase, but without a surface to overcome the free energy barrier necessary to nucleate a new phase (35), the particles remain aqueous. Contact
efflorescence occurs when a solid particle collides with a metastable particle and provides a surface that facilitates efflorescence at an RH much higher than the efflorescence RH (34) [40% for ammonium sulfate at the sampling temperatures (15)]. Recently, it has been shown in laboratory experiments that solid ammonium sulfate particles induce efflorescence when they collide with phase-separated particles composed of an organic shell and aqueous ammonium sulfate core (36). Therefore, small, solid sulfate particles, formed at RH <81%, colliding with larger core-shell (ammonium sulfate-organic) particles at <81%, can explain the solid organic-coated ammonium sulfate particle structure with cubic sulfate protrusions at the surface observed by AFM and SEM (Fig. 1). Therefore, we hypothesize that contact efflorescence led to these unexpected solid sulfate particles.

Proposed Marine Biogenic Source and Formation Mechanism. The organic-coated ammonium sulfate particles were primarily observed under Arctic Ocean air mass influence from the Beaufort Sea (SI Appendix, Fig. S6), with minimal anthropogenic influence (37). Bulk aerosol composition, including sulfur isotope analysis, supports a marine biogenic aerosol source, as discussed in SI Appendix. During these marine air masses, the full aerosol size distribution has modes in both the Aitken and accumulation diameter ranges (SI Appendix, Fig. S2), which is representative and typical of the summertime Arctic (38). The number fraction of the observed solid organic-coated ammonium sulfate particles increased with decreasing particle diameter from 0.56 ± 0.04 μm (5 ± 2%, by number) to 0.13 μm diameter (23 ± 5%, by number) (SI Appendix, Fig. S2) (37). At less than 0.2 μm dp, ~30% of the total particles, by number, corresponded to these solid, organic-coated ammonium sulfate particles, associated with a peak in the size distribution at ~120 nm (SI Appendix, Fig. S2) (37), indicating that a significant fraction of the observed particle number concentration exhibited a solid phase in a key size range for CCN activation. The Aitken mode particles were below the lower size collection limit, which prohibited microscopic analysis; however, these particles (mode diameter ~25 nm) are notably similar in size to the sulfate edge protrusions on the larger solid particles, supporting the hypothesis of Aitken mode particles colliding with accumulation mode particles.

The typical summertime Arctic bimodal aerosol size distribution has been explained, through observations and modeling by Croft et al. (38), by new particle formation and growth resulting in Arctic Aitken mode particles (<0.1 μm) and further condensation leading to the accumulation mode (0.1 to 1.0 μm). Recently, Beck et al. (39) showed summertime observations at Svalbard of particle nucleation via sulfuric acid (from marine dimethylsulfide [DMS] oxidation) and ammonia, followed by condensation of sulfate, methanesulfonate, and highly oxygenated organic molecules, with growth to CCN sizes. Earlier measurements showed that ammonium sulfate is the main component of new particles during summertime at Svalbard (40) and that oxygenated volatile organic compounds are emitted from open water during summer in the Canadian Archipelago (41). Modeling has shown that ammonia emissions from sea birds react with sulfuric acid, from DMS oxidation, and contribute to new particle formation and increased cloud droplet number concentrations across the Arctic, including over the Beaufort Sea, an area where elevated ammonia concentrations were previously observed (42). Further Arctic air quality modeling by Ghahremaninezhad et al. (43) suggests that DMS oxidation and resulting new particle formation and growth leads to significant enhancements in sulfate particles up to 0.2 μm at high latitudes (>70°N), with strong enhancements up to 1 μm at lower latitudes (<70°N). Indeed, frequent aerosol growth events, with >0.1-μm particles consisting primarily of organics and sulfate, were observed simultaneously at the Canadian Archipelago Arctic sites of Eureka and Alert, located 480 km apart, during August to September 2015 (44). The observed bimodal aerosol size distribution (SI Appendix, Fig. S2) resulting from the regional new particle formation and growth events supports the hypothesized contact efflorescence occurring when a newly formed Aitken mode sulfate particle, formed at a portion of the air mass trajectory at <81% RH (SI Appendix, Fig. S6), collides with an accumulation mode organic-coated ammonium sulfate particle at RH <81%. Therefore, this new particle formation and growth mechanism, dominated by marine biogenic sulfate, is consistent with the particle properties measured in our study at Utqiagvik, AK (71°N) with marine air mass influence from the Beaufort Sea (Fig. 4).

Conclusions

The observation of solid, organic-coated ammonium sulfate particles in the Arctic boundary layer has significant implications for regional atmospheric chemistry, cloud formation, and climate feedbacks. The solid phase of these particles is hypothesized to have formed through contact efflorescence when an Aitken mode solid sulfate particle collided with an accumulation mode organic-coated ammonium sulfate particle, with the ammonium sulfate core in a metastable (i.e., supersaturated) state, which has recently been observed in the laboratory (36). The unexpected solid phase and solid organic coating on these particles likely inhibited trace gas and water uptake at subsaturated RH (45, 46). Despite the increased timescale expected for water uptake, glassy organic particles with ammonium sulfate cores are expected to activate as CCN at elevated water supersaturation, based on room-temperature measurements (47). Notably, solid ammonium sulfate particles also have a higher refractive index than liquid particles and can serve as INPs via deposition freezing (48). These particles may be a previously unconsidered source of INPs in the Arctic, where mixed-phase clouds are important for the surface energy budget and yet challenging to simulate (49). Recent incorporation of inferred viscosity into a global model predicted secondary
Single-Particle Microscopy Measurements. The individual particle MPS samples on TEM grid substrates were analyzed by computer-controlled SEM-EDX using an FEI Quanta scanning electron microscope with field emission gun operating at 20-keV accelerating voltage. The instrument is equipped with a high angle annular dark field detector and energy-dispersive X-ray detector (EDAX, Inc.) to provide information on the size, morphology, and elemental composition of individual particles. K-means clustering of the EDX data identified unique particle classes, as described by Gunsch et al. (37) and references therein. Additional SEM images were collected using a secondary electron detector with the sample tilted 75° to provide additional information on particle three-dimensional morphology (10).

AFM-PTIR was used to further probe the morphology and chemical composition of individual particles using a nanoIR2 (Anasys Instruments). AFM images were collected in contact mode at a 0.75-Hz scan rate over a 5-μm x 5-μm area on the copper grid bar of the TEM grid substrate in order to measure the diameter and height of individual particles, according to an established method for AFM-PTIR application to aerosol particles (17, 53). Spreading ratios and associated errors (95% confidence interval) were calculated following the method in Olson et al. (18). IR spectra were collected over the 900 to 3,600 cm⁻¹ range at 4 cm⁻¹ per point resolution. Additional AFM images were collected in tapping mode to provide information on particle phase (SI Appendix).

STXM-NEXAFS was conducted at the Canadian Light Source Beamline 10ID-1. Analysis was conducted over the carbon K-absorption edge and sulfur L-absorption edge to distinguish carbon and sulfur oxidation states present in the individual particles, using a previously described method (23, 54). Briefly, X-ray energies are selected with a monochromator and raster-scanned across the sample. Images at closely spaced X-ray energies are combined to create an image stack, and X-ray spectra are then calculated by deconvoluting intensity using the Beer–Lambert law. Pre-edge/postedge ratios of X-ray absorption over the carbon K-absorption edge (280 to 320 eV) were used to create a map showing the relative contribution of organic and inorganic components in individual particles. Sulfur L-absorption edge spectra were collected over the 168- to 176-eV range. The ratio of peaks at 173.2 and 171.1 eV was used to assess the relative contribution of different sulfur oxidation states (S(V) and S(VI)).

Data Availability. All study data are included in the article and/or SI Appendix.

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