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Other Journal Item**Author(s):**

Marcolli, Claudia ; Krieger, Ulrich K.

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Spotlight

Relevance of Particle Morphology for Atmospheric Aerosol Processing

Claudia Marcolli^{1,*}
and Ulrich K. Krieger¹

Recent laboratory and modeling studies suggest high relevance of aerosol mixing state and particle morphology for the life cycle of atmospheric aerosols. A new article by [Gorkowski and colleagues](#) presents a framework to predict morphologies of aerosol particles based on O:C ratio for incorporation into chemical transport models.

Over the past few decades, considerable progress has been made in establishing the composition and physical properties of atmospheric aerosols and assessing their impact on air pollution, human health, and the Earth's radiative balance. To understand how anthropogenic and biogenic emissions play together to affect climate and health, a holistic view is needed. Exceptionally challenging is the organic aerosol fraction consisting of hydrocarbons and aromatic compounds with varying degree of oxidation, resulting in alcohols, peroxides, organic acids, and aldehydes. Atmospheric organic compounds cover orders of magnitude in volatility and range from highly to hardly reactive. The organic aerosol fraction is emitted directly into the atmosphere as primary organic aerosol (POA) or forms through oxidation of organic vapors [secondary organic aerosol (SOA)] [1]. Given the large range of organic compounds, from very hydrophobic to strongly hydrophilic, their miscibility is limited, which may lead to liquid-liquid phase separation (LLPS) within particles. The morphol-

ogies arising from LLPS are partially engulfed when both phases have access to the gas phase and core-shell when the inner phase is shielded from the gas phase by the surrounding outer phase. Particle morphology influences heterogeneous and multiphase chemistry and thermodynamic equilibration between the gas and the condensed phases [2].

A new article by Gorkowski, Donahue, and Sullivan [3] presents aerosol optical tweezer (AOT) experiments to study the resulting morphologies when SOA particles collide with a levitated micrometer-sized droplet under controlled temperature and relative humidity (RH) conditions. The morphology of the levitated droplet is not directly visible, yet it can be inferred making use of the whispering gallery modes (WGMs), that arise in Raman spectra when a spherical droplet acts as optical cavity amplifying the scattered light [2,4]. For this to happen, the size of the droplet needs to match the laser's wavelength so that resonance conditions near the droplet's surface arise. Core-shell and homogeneous droplets both exhibit WGMs, while partially engulfed droplets do not. Applying Mie theory, Gorkowski and coworkers discriminated between core-shell and partially engulfed morphologies and retrieved refractive indices and droplet size. Morphologies can be distinguished by the way WGMs shift in evaporating droplets: the WGMs in a homogeneous droplet evolve parallel to each other, whereas WGMs in a core-shell droplet do not because different modes have different characteristic penetration depths and thus experience different average indices of refraction. In this and a previous study [5], Gorkowski and coworkers make use of this technique to study the resulting morphologies when SOA particles from α -pinene ozonolysis (~200 nm in diam-

eter) that nucleated directly in the AOT chamber coagulate with the levitated droplet. They found that the SOA spread on levitated squalane droplets at low and high RH (12% and 80%) forming the shell around the squalane core, indicating immiscibility and low viscosity of the SOA. When the same SOA coagulated with a levitated glycerol droplet, it mixed at low (12%) but not at high RH (73%), showing that an increase in RH can induce LLPS in droplets that contain constituents of different hydrophilicity. To rationalize their results, Gorkowski and coworkers used spreading coefficients to predict morphologies. Based on their own and literature data they propose a framework for incorporation in chemical transport models that predicts LLPS and morphology based on the degree of oxidation captured by the oxygen-to-carbon atomic ratio (O:C) and RH.

What are the implications of the findings by Gorkowski and coworkers for atmospheric aging of air masses? [Figure 1](#) illustrates an atmospheric scenario where background aerosol first mixes with traffic and biogenic emissions followed by cloud processing. Background particles are assumed to consist of sulfates and nitrates partially neutralized by ammonia and homogeneously mixed with aged organic compounds with average O:C > 0.8. Traffic emits particles (POA) that partially volatilize while they dilute [6]. Since freshly emitted POA is barely oxidized (O:C < 0.36), its semivolatile vapors are hardly absorbed by oxidized background particles (trajectory 1), yet, some POA may coagulate with background particles yielding partially engulfed morphology (trajectory 3). Vegetation emits volatile organic compounds such as isoprene and monoterpenes, which are oxidized in the gas phase to semivolatile products. These oxidation products may form



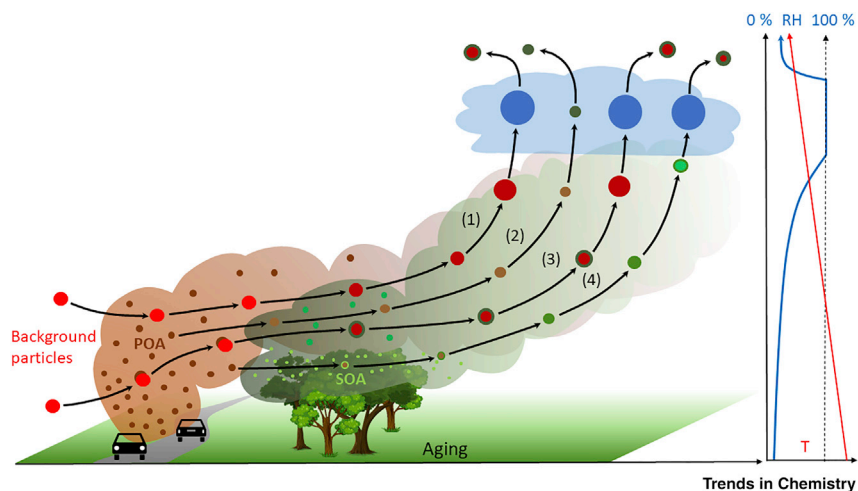


Figure 1. Mixing and Particle Morphologies of an Air Mass as it Passes through Traffic Emissions [Primary Organic Aerosol (POA)], Mixes with Biogenic Secondary Organic Aerosol (SOA), and Passes through a Cloud.

In trajectory (1), the background particle hardly absorbs the hydrophobic hydrocarbons [oxygen-to-carbon atomic ratio (O:C) < 0.36] of POA vapors (brown). Strongly oxidized semivolatile SOA species (green) partition into the background particle, yet without inducing liquid–liquid phase separation (LLPS). With increasing relative humidity (RH), the particle takes up water and grows in size. When RH exceeds 100%, the particle activates to a cloud droplet. Cloud processing results in an organic fraction with O:C of about 0.6, making LLPS with core-shell morphology likely after the cloud has dissipated. Trajectory (2) depicts a POA particle that absorbs hydrophobic semivolatile vapors stemming from vegetation emissions. It remains interstitial while it passes through the cloud. As the background particle in trajectory (3) passes close to the POA emissions, it is assumed to coagulate with primary particles acquiring a partially engulfed morphology. Condensation of SOA shifts the morphology to core-shell. As RH increases, water uptake renders the phases miscible, resulting in a homogeneous particle that activates readily to a cloud droplet. Cloud processing is likely to lead to core-shell morphology after the passage through the cloud. In trajectory (4), a POA particle passes close to the location of SOA formation and acquires an SOA coating through coagulation. As the air mass ages, further oxidation renders the SOA and POA phases miscible. This particle activates less readily than the background particles. If it activates, it is likely to pass through LLPS during hygroscopic growth. Within the cloud, may acquire sulfate through SO₂ oxidation, resulting in LLPS after the cloud has dissipated.

new particles through nucleation or coagulate with existing particles resulting in core-shell morphology (trajectory 4). Thermodynamic equilibration of semivolatile species between particles of different sources occurs readily [7], but condensation only occurs if they are miscible. Therefore, this process alone is unlikely to lead to phase-separated particles. Yet, LLPS may occur through variation of RH since miscibility depends on water content. Mixtures of moderately hydrophilic organic compounds with inorganic salts are immiscible at low RH and become miscible as RH increases.

When RH decreases again, LLPS may result because organic compounds that partitioned to the particle at elevated RH become immiscible at low RH. Likewise, cloud processing promotes internal mixing of organic and inorganic species (trajectories 1, 3, and 4) as clouds shift gas-particle partitioning of semivolatile species to the condensed phase. Photo-oxidation and fragmentation reactions within cloud droplets result in organic aerosol composition with O:C ratios of about 0.6 [8]. Hence, after the cloud has dissipated, inorganic salts and organic species end up internally mixed

in phase-separated particles with an aqueous core surrounded by an organic shell. SOA-dominated particles may also activate to cloud droplets by passing through a phase separated state (trajectory 4) [9]. When temperature decreases, partitioning shifts to the condensed phases [6] and the organic aerosol fraction tends to turn viscous, slowing or even shutting down gas-particle partitioning, heterogeneous and multiphase chemistry and increasing lifetime of condensed-phase reactive compounds [2]. Thus, mixing state together with viscosity strongly influences aerosol processing. Indeed, recent modeling studies show that aerosol mixing state, particle morphology, and viscosity of the organic-dominated phase strongly influence heterogeneous and multiphase chemistry and gas-particle partitioning, pointing out the need to better constrain the parameters that govern phase state and morphology of aerosol particles [10].

¹Institute for Atmospheric and Climate Science, ETH Zurich, Switzerland

*Correspondence:
Claudia.marcolli@env.ethz.ch

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