

J Atmos Chem (2007) 56:259–273
DOI 10.1007/s10874-006-9055-5

Hygroscopic behavior of aerosol particles from biomass fires using environmental transmission electron microscopy

Trudi A. Semeniuk · Matthew E. Wise · Scot T. Martin ·
Lynn M. Russell · Peter R. Buseck

Received: 25 June 2006 / Accepted: 8 November 2006 /
Published online: 21 December 2006
© Springer Science + Business Media B.V. 2006

Abstract We used both a conventional transmission electron microscope and an environmental transmission electron microscope (ETEM) to determine morphology, composition, and water uptake of 80 individual aerosol particles collected from the young smoke of flaming and smoldering fires during SAFARI-2000, a comprehensive air quality campaign in southern Africa. Six representative carbonaceous particle types are described, including soot, tar balls, and heterogeneously internally mixed particles containing C with S-, K-, Mg- or Na-rich inorganic phases. The hygroscopic behavior of these particles over the range 0–100% relative humidity (RH) was studied in detail. Soot and tar balls did not take up water, whereas the mixed organic–inorganic particles took up water between 55 and 100% RH, the exact value depending on the composition of their water-soluble phases. The inorganic phase appeared to determine the hygroscopic properties of all mixed organic–inorganic particles. Thus, incorporation of inorganic plant material or reactions with inorganic atmospheric components can dramatically alter the hygroscopic properties of carbonaceous particles in smoke plumes. The fraction of these mixed organic–inorganic particles plausibly increases with time, which will modulate the effects of smoke on radiative budgets.

Key words biomass burning · deliquescence · efflorescence · ETEM · soot

1 Introduction

Aerosol particles from biomass burning significantly alter regional and global radiative forcing and atmospheric chemistry (Andreae et al. 1998). Most particles emitted during

T. A. Semeniuk · M. E. Wise · P. R. Buseck (✉)
School of Earth and Space Exploration and Department of Chemistry & Biochemistry,
Arizona State University, Tempe, AZ 85287, USA
e-mail: pbuseck@asu.edu

S. T. Martin
Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA

L. M. Russell
Scripps Institute of Oceanography, University of California, San Diego, La Jolla, CA 92093, USA

biomass burning events consist of organic carbon and soot (black carbon), some of which are heterogeneously mixed with inorganic phases (Andreae et al. 1998; Pósfai et al. 2003; Reid et al. 2005). The effects of these different types of carbonaceous aerosol particles, especially on radiative, chemical, and cloud formation processes, are important for global climate models (Jacobson 2001).

Recent studies document reduced cloud formation in smoky regions because of strong radiative effects of smoke particles on surface heating, evaporation, and convection (Andreae et al. 2004; Koren et al. 2004). However, the microphysical effects of smoke particles on clouds and precipitation are not well understood and are largely inferred from satellite observations and modeling (Andreae et al. 2004; Roberts et al. 2003). It has been hypothesized that biomass-burning particles can be cloud-nucleating constituents (Novakov and Corrigan 1996; Pósfai et al. 2004b; Reid et al. 2005). The ability of a smoke particle to act as a cloud condensation nucleus (CCN) depends, in part, on its hygroscopic properties, which in turn determine its phase (solid or liquid, see Martin 2000) in the atmosphere. Therefore, a fundamental understanding of the relationship between particle chemistry and atmospheric conditions such as relative humidity (RH) is critical in the evaluation of the role of carbonaceous aerosol particles in cloud formation processes as well as their effects on radiation and atmospheric chemistry.

Both laboratory and field studies have probed the hygroscopic characteristics of carbonaceous particles. Combustion-generated soot particles are a major component of anthropogenic emissions; therefore, the majority of the studies have focused on soot particles (e.g., Chughtai et al. 1999). Laboratory studies on the hygroscopic properties of soot with and without chemical modification find that pure soot is hydrophobic (Seisel et al. 2005), but that its nucleation ability is significantly enhanced by the presence of soluble compounds, e.g., sulfur-bearing compounds or hygroscopic organic molecules (Lammel and Novakov 1995; Lee et al. 2006; Rose et al. 2006). In contrast, non-volatile organic coatings inhibit hygroscopic growth of combustion particles (Petzold et al. 2005).

Semi-volatile organics present in biomass smoke show increased hygroscopic growth with increasing RH as well as with increasing oxidation (Cocker et al. 2001; Maria et al. 2004). The hygroscopic properties of partially soluble organic molecules also appear to be enhanced by the presence of trace soluble compounds, especially inorganic substances (Broekhuizen et al. 2004; Lohmann et al. 2004). Water-soluble organic molecules, including volatile organic acids, are well documented to be active CCN (Corrigan and Novakov 1999; Facchini et al. 1999; Yu 2000).

Few studies have looked at hygroscopic properties of ambient carbonaceous particles in detail. Ebert et al. (2002) showed that ambient soot agglomerates can be activated, and water films on these particles were observed at slight water vapor supersaturations ($RH > 100\%$) using an environmental scanning electron microscope. Malm et al. (2005) studied the hygroscopic properties of aerosol particles containing organic material using nephelometry during an aerosol characterization study at Yosemite National Park. They found that the ambient organic aerosol particles were weakly hygroscopic. Growth factors for this ambient particulate organic material were determined using a humidified tandem differential mobility analyzer (Carrico et al. 2005). Measurements of particles around 200 nm in size showed that water uptake began in the range 40–70%, and continued weakly at $RH > 80\%$. Both monomodal and bimodal hygroscopic growth profiles were observed, suggesting that some particles were internally mixed.

Additional work is necessary to fully understand the interactions of carbonaceous aerosol particles with water vapor. In particular, an evaluation of the effects of

heterogeneous mixing on the hygroscopic properties of natural organic and soot particles is needed. Thus, using an environmental transmission electron microscope (ETEM), we investigated the hygroscopic behavior of natural smoke particles, with emphasis on internally mixed particles, over a range of RH values. Changes in size and phase of different types of carbonaceous particles were documented from 0 to 100% RH, yielding information on the behavior of these particles under conditions they encounter in the atmosphere and their potential to act as CCN.

2 Methods

2.1 Sampling

We investigated natural aerosol particles from three TEM samples collected during the SAFARI-2000 dry season field campaign. A total of nine fires, five prescribed and four non-prescribed burns, were investigated by the Cloud and Aerosol Research Group (CARG) of the University of Washington with their Convair-580 aircraft (Hobbs 2001). We chose to look at samples that represent young smoke from smoldering and flaming fires. Samples 15-SS and 15-SF, respectively, were from non-prescribed smoldering and flaming grass fires in Kruger National Park (SA) on 17 August 2000. Sample 26-S was from a flaming prescribed woodland burn of Miombo near Kaoma (Zambia) on 1 September 2000. Sampling conditions are summarized in Table 1.

Smoke was sampled using a bag-house system onboard the Convair-580 aircraft. Plume air containing biomass-burning aerosols was collected in a 2.6 m³ Velostat bag. The aerosol particles were then impacted directly onto TEM grids using an MPS-3 microanalysis particle sampler (California Instruments, Inc.) attached to the grab-bag system. Size fractionated samples consisted of three TEM grids with particle sizes >2, 2–0.3, and <0.3 μm. Cu-mesh grids with a lacey carbon (LC) substrate were used for sampling. We selected both intermediate (2–0.3 μm) and fine (<0.3 μm) fractionated samples to study using the ETM.

Further details regarding the grab-bag sampling procedure used to collect smoke particles are given in Hobbs et al. (2003), and a more detailed description of the TEM sampling procedure is given in Pósfai et al. (2003) and Li et al. (2003).

2.2 Conventional TEM analyses

Detailed chemical, morphological, and microstructural characterization of carbonaceous particles for the SAFARI-2000 TEM samples was performed in vacuum (i.e., 0% RH) by Pósfai et al. (2003) using a Philips CM20 TEM. Semi-quantitative energy-dispersive X-ray spectrometry (EDS) measurements identified three chemically distinct types of C-rich particles with variable K, S, Cl, and Si content. These particles included organic particles with inorganic phases, tar balls, and soot. Detailed descriptions of these particle types are

Table 1 Sampling conditions for our SAFARI-2000 samples (Hobbs 2001, 2004)

Sample:	15-SS	15-SF	26-S
Altitude (m)	800	1,060	1,200
Temperature (°C)	17	14	23
Relative humidity (%)	45	35	20

Table 2 Numbers of different types of carbonaceous particles analyzed in our intermediate- and fine-sample fractions of SAFARI-2000 samples

Sample/grid fraction:	15-SS (int.)	15-SF(fine)	26-S (int.)	26-S fine)
Soot/aggregated soot	13	8	43	29
Tar balls	3	5	0	12
Organic (+S, K)	65	48	81	70
Organic (+KCl)	0	39	0	1
Organic (+other species)	3	0	2	1

given in Pósfai et al. (2003). We used these particle types as a basis for particle selection in our ETEM study at elevated RH.

Initial selections of individual particles for the ETEM study, and detailed morphological and chemical analysis of 80 particles, was carried out using a Philips CM200 TEM. These particles comprised a subset of the ca. 400 particles inventoried during our study. We chose to study dominantly organic particles having inorganic inclusions, coatings, or attached grains (Table 2). LC grids provided an ideal substrate for chemical analysis of particles because C-rich particles could be measured independently of the carbon substrate. EDS measurements were limited to 10-s exposure times to reduce particle damage under the electron beam prior to ETEM experiments. Despite these precautions, it is likely that only relatively refractory organic material was observed in TEM samples (Pósfai et al. 2004b, 2003). Comparison of our TEM results with those from the original analyses by Pósfai et al. (2003) suggests that there were no noticeable chemical or physical effects of extended storage on these particles.

2.3 ETEM analyses

To study the hygroscopic properties of the particles we used a 200-kV FEI Tecnai F20 TEM outfitted with a differentially pumped environmental cell identical to that described in Wise et al. (2005). The cell was kept at constant temperature through liquid nitrogen cooling and resistive heating. At 18°C, 100% RH was attained with ~15.5 torr of water vapor present in the cell. The accuracy of RH measured using the ETEM was verified by measuring the deliquescence relative humidity (DRH) of laboratory-generated NaCl particles prior to each experiment. The DRH measured using the ETEM for NaCl was accurate to at least 2% for the duration of our experiments.

ETEM experiments on the selected 80 biomass-burning particles were carried out using the same procedure as was outlined in Wise et al. (2006), with more RH steps at >75% RH. Initial images and particle positions were recorded at 0% RH before we introduced water vapor into the column. At each selected RH step, we allowed the sample to equilibrate for ~1 min before the electron beam was turned on and each particle was imaged. The process of recording images of all particles at the selected RH took ~5 min. RH was increased incrementally during the water uptake experiments, with images recorded at ~15, 40, 50, 55, 60, 65, 70, 75, 82, 85, and 90% RH. Images were also taken at 100% RH, and at ~80, 70, 60, 50, 40, 30 and 0% RH for the efflorescence experiment. The combined deliquescence and efflorescence experiment took ca. 3 h to complete. The images for each particle were compared using analysis tools in Digital Micrograph software (Gatan, Inc.).

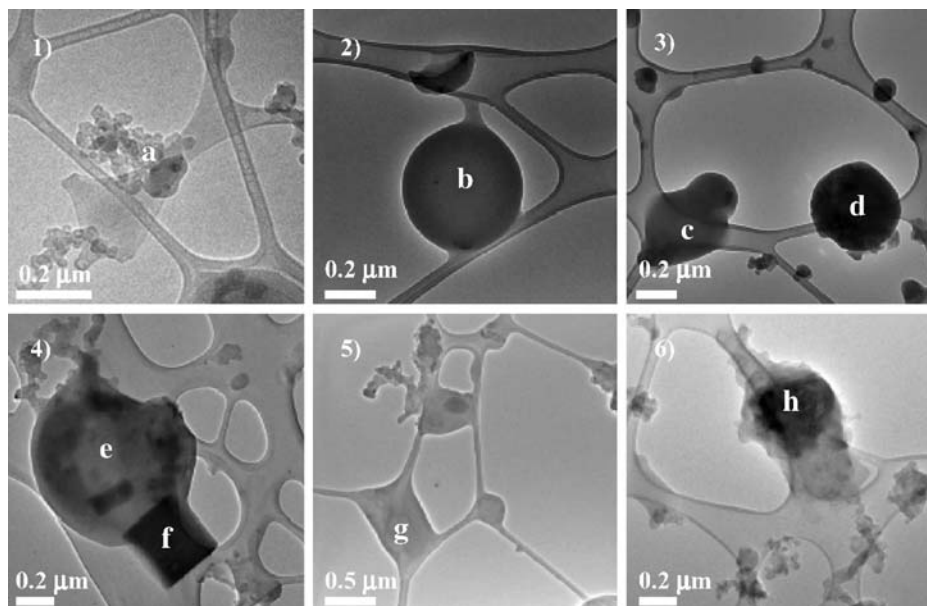


Fig. 1 Bright-field TEM images (Philips CM200 TEM) on lacey carbon substrates of six particle types collected in smoke plumes during the SAFARI-2000 field campaign: (1) soot particle, (2) tar ball, (3) organic particles with K and S compounds, (4) organic particle with attached KCl grain, (5) Mg-rich organic particle, and (6) Na-rich organic particle. The letters in the figure indicate the areas at which EDS measurements were obtained

3 Results and discussion

3.1 General sample description

Pósfai et al. (2003) and Li et al. (2003) reported differences in type and concentration of particles in smoke samples from SAFARI-2000, reflecting fire intensity and smoke age. High concentrations of organic particles having incorporated inorganic phases (e.g., KCl) were found in young smoke samples, whereas high concentrations of internally mixed organic/sulfate or soot/sulfate particles were found in aged smoke. Both particle types are heterogeneous mixtures. The intensity of the fire also influenced the different smoke compositions. For example, flaming fires emitted more soot particles, and smoldering fires more tar balls (Pósfai et al. 2004b).

The preliminary compositional analyses of the TEM samples in our study showed high numbers of organic particles with incorporated inorganic grains (Table 2), consistent with observations of young smoke in Pósfai et al. (2003). Mixed organic–inorganic particles dominated all samples, comprising between 60 and 90% of the particles in each sample. Soot fractions were highest in intermediate-stage fractions from flaming fires, with percentage composition ranging from 10 to 30% in our samples. Tar balls were most common in fine-stage sample fractions, comprising typically between 5 and 10% of fine-mode particles.

For the purpose of our study, organic particles were subdivided into three types on the basis of composition and morphology: (1) organic particles with K and S compounds, (2)

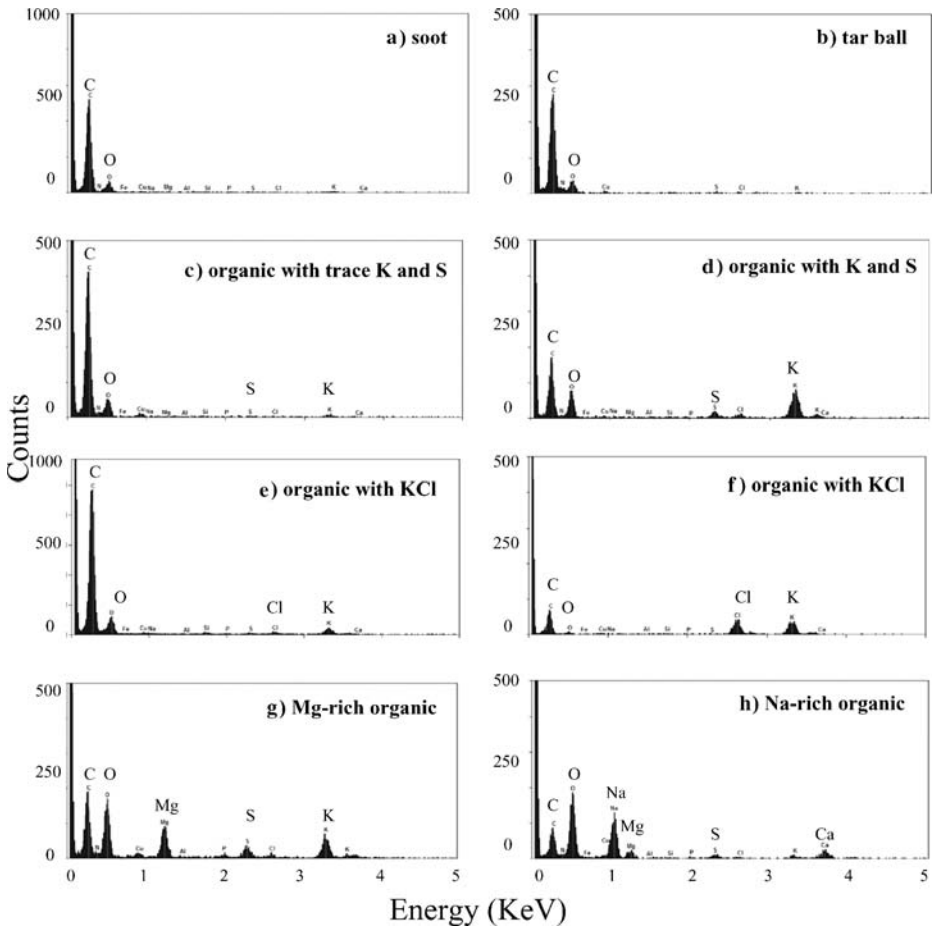


Fig. 2 EDS spectra for particles shown in Fig. 1 (locations a to g). Spectra were collected using ES Vision software on the Philips CM200 TEM at magnifications around 40,000 times with beam size 5 (6 nm) for intervals of 10–20 s

organic particles with KCl grains, and (3) organic particles with Na-, Mg- or Ca-rich components. Organic particles with K and S compounds were most common, dominating the sample from the smoldering fire. Organic particles with KCl grains occurred only in samples from flaming fires. Na-rich organic particles were found in samples from flaming and smoldering fires. Organic particles mixed with other inorganic components were rare and only present in samples from flaming fires. The numbers of each carbonaceous particle type analyzed in each sample are given in Table 2.

Six carbonaceous particle types were selected for ETEM study: (1) soot, (2) tar balls, (3) organic particles with K and S compounds, (4) organic particles with KCl attached grains or inclusions, (5) Na-rich organic particles, and (6) Mg-rich organic particles. From our multiple data sets for each type, a single representative of each particle type is presented in this paper. The particle containing KCl was from sample 15-SF, and the remaining particles illustrated were from sample 26-S. Bright-field TEM images and X-ray spectra from EDS

measurements, obtained using the Philips CM200 TEM, are shown for these representative particles in Figs. 1 and 2 respectively.

Soot particles typically had strong C peaks, and some had smaller O or S peaks associated with surface coatings. They had complex chain-like structures consisting of linked spherules (van Poppel et al. 2005). In contrast, tar balls had characteristic C and O peaks with no other elements present, were spherical, and were considerably larger than individual soot spherules (Pósfai et al. 2004a, 2003). Organic particles contained C and O, with variable amounts of K, Na, Mg, Ca, P, Cl and S. Organic particles were globular and tended to ‘wet’ the lacy carbon support. Inorganic grains attached to or included within these particles commonly had square shapes (e.g., KCl).

Organic particles with K and S compounds had a range of compositions; some particles had S and/or K peaks equal to the O peak in their spectra, while others had S and/or K in trace amounts only. In some instances we identified K_2SO_4 as an included phase. In other particles the K- and S-bearing species were too small to be imaged or, more likely, they were small enough to be obscured by the organic material in which they were embedded. KNO_3 may occur in some particles (Li et al. 2003); however N is hard to detect using EDS, especially if the N-bearing species is in low concentrations or small grains. Some of the S may be part of the organic material or residue from sulfates volatilized under the electron beam. Organic particles with KCl grains contained C, O, K, and Cl. Mixtures of inorganic phases were classified according to the strongest cation peak. Na-rich organic particles typically also had Mg, Ca, K, and S peaks. Mg-rich organic particles also contained K, S, trace Cl, and P. Ca-rich organic particles also contained Mg, K, Cl, and P.

Although point measurements on inorganic phases within organic particles identified KCl and K_2SO_4 as distinct phases, the stoichiometry of other inorganic phases was not readily determinable.

3.2 Hygroscopic properties of the particle types

Water uptake by atmospheric organic particles containing thousands of different organic molecules typically occurs over a wide range of RH values (Marcolli et al. 2004). We observed water uptake by C-rich particles within the range of 55–100% RH in the SAFARI-2000 samples. The hygroscopic properties of each of the six particle types are described and illustrated in Figs. 3 through 8. Table 3 summarizes the number of ETEM experiments carried out for each particle type.

For soot from our SAFARI-2000 samples (labeled A, Fig. 3), small changes in particle morphology, measured using Digital Micrograph, occurred from 0 to 100% RH. These morphological changes persisted as the RH was dropped to 0% in the ETEM and appeared to be non-reversible. We believe these soot particles were hydrophobic up to 100% RH. Furthermore, other types of particles in the field of view did not appear to take up water. Although we do not have composition data for these particles, we speculate that both inorganic compounds and organic molecules were present. We observed this type of behavior during repeated TEM sessions.

Table 3 Number of ETEM experiments performed on each type of carbonaceous particle

Soot/aggregated soot	11
Tar balls	5
Organic (+S, K)	41
Organic (+KCl)	16
Organic (+other species)	7

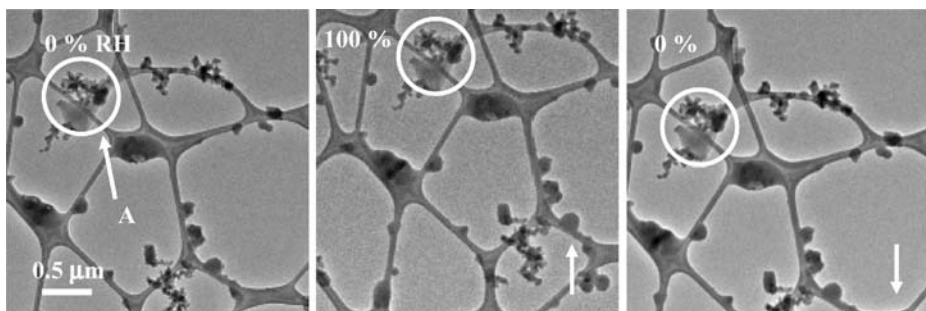


Fig. 3 Images of a soot particle (labeled *A* and circled for clarity) as RH was raised from 0 to 100% RH (denoted by the *up arrow*). The final image (denoted by the *down arrow*) shows the soot particle after the RH was decreased from 100 to 0% RH. Images of the soot particle taken between 0 and 100% RH are not included because negligible changes in particle morphology occurred

Tar balls (labeled *B*, Fig. 4) also exhibited small changes in particle morphology at >60% RH. A slight increase in size, measured on images with Digital Micrograph, appears to be non-reversible. Hand et al. (2005) noted uptake of water at >83% RH in aged tar balls from samples from the Yosemite Aerosol Characterization Study.

Particles *C* and *D* (Fig. 5) contained organic material with different amounts of *K* and *S* (particle *D* contains more of both elements). The morphology of particle *C* did not change appreciably as RH was increased from 0 to 100% and subsequently decreased from 100 to 0% in the ETEM. Particle *D* contained a greater fraction of *S* and *K*, which affected its hygroscopic properties. At RH values below 60%, no changes in morphology occurred, but above 60% there was water uptake, and a deliquescence sphere grew, presumably to maintain equilibrium with the water vapor surrounding it. It appears as if particles with only trace *K* do not typically take up water whereas if both *K* and *S* are present the particles pick up water at approximately 60% RH. This behavioral difference suggests that *K* is present within the carbonaceous material in particle *C*, but within *K*-salts in particle *D* (Pósfai et al. 2003).

As RH was increased from 0% RH for an organic particle having a *KCl* grain attached (Fig. 6), no changes in particle morphology were evident until 85% RH, when a small amount of water uptake occurred on the right side of the *KCl* grain. As RH was increased to 90%, further water uptake occurred, and the organic particle was nearly engulfed by the deliquescence sphere. The organic particle and the *KCl* grain did not appear to deliquesce,

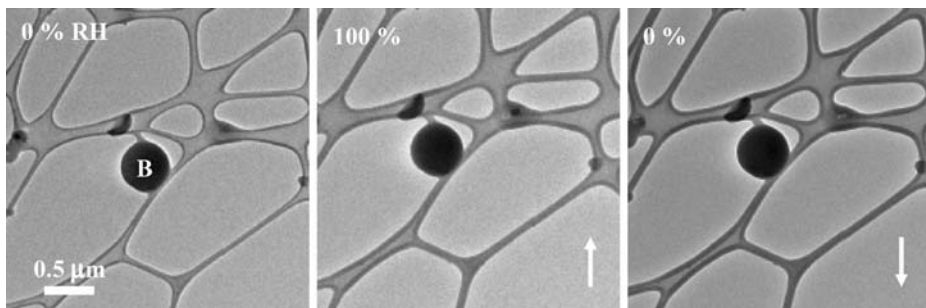


Fig. 4 Images of a tar ball (labeled *B*) as RH was increased from 0 to 100% RH. The final image shows the tar ball after RH was decreased from 100 to 0%. Images of the tar ball taken between 0 and 100% RH are not included because negligible changes in morphology occurred

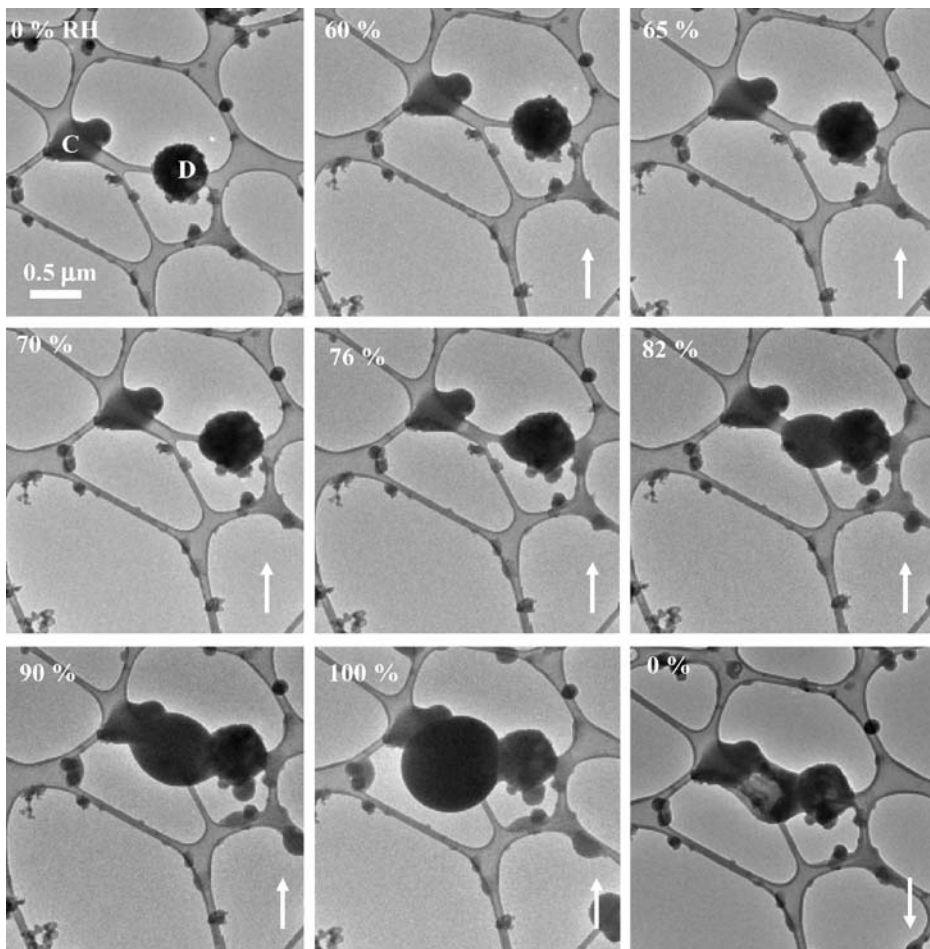


Fig. 5 Images of two organic particles (labeled *C* and *D*), containing different amounts of K and S, as RH was raised from 0 to 100% RH and then lowered from 100 to 0%. Images taken of the particles between 0 and 60% RH are not included because no changes in morphology occurred

since their original shape remained generally well defined throughout the deliquescence experiment. However, when the RH was returned to 0%, efflorescence of the KCl grain occurred, with recrystallization occurring dominantly outside the original grain boundary. The formation of the deliquescence sphere adjacent to the KCl grain and the ‘skeleton’ rim of the original grain on efflorescence are phenomena that we observed repeatedly, e.g., the second particle imaged but not labeled in Fig. 6. Therefore, we attribute this behavior to the presence of a non-deliquesced coating around the KCl grain and not to external factors such as electron beam damage. Similar hygroscopic behavior is described for other coated particles in Semeniuk et al. (2006). All the KCl grains we investigated appeared to be in the liquid state at >85% RH; however only 5 of 15 organic particles with KCl grains developed a recognizable deliquescence sphere during the experiment. KCl inclusions wholly within organic particles did not develop obvious deliquescence spheres, but had identical efflorescence behavior to the attached KCl particle in Fig. 6. We suggest that the organic

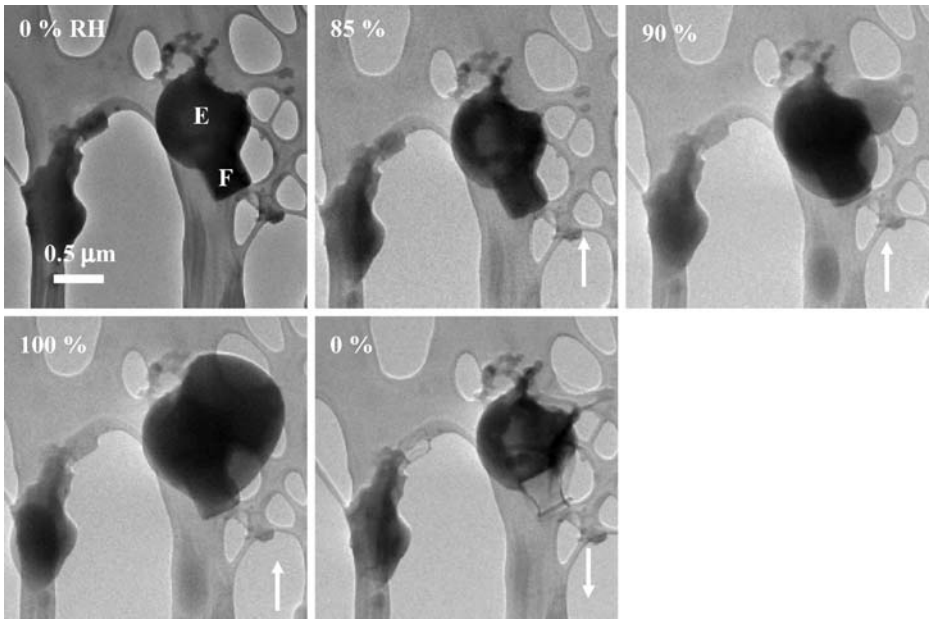


Fig. 6 Images of an organic particle (*labeled E*) with an attached KCl grain (*labeled F*) as RH was increased from 0 to 100% and then decreased to 0%. Images taken between 0 and 85% RH are not included because no changes in morphology occurred

material may inhibit or perturb the growth of the deliquescence sphere of included KCl grains, but it does not affect the change of state from solid to liquid and back to solid experienced by the KCl particle during the ETEM experiment.

The morphology of a Mg-rich organic particle (Fig. 7) did not change until >90% RH, at which point a well-defined deliquescence sphere formed. A Na-rich organic particle (Fig. 8) had somewhat different behavior. Incipient changes occurred as low as 40% RH. The main particle appeared to develop a deliquescence sphere at 60% RH, which grew significantly over the range 60–100% RH.

The observation that both soot and tar balls in this study are hydrophobic agrees with measurements of Malm et al. (2005) for ambient organic aerosol particles. However, when

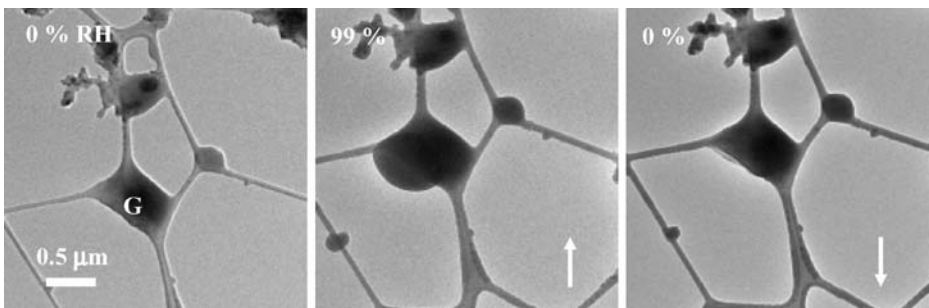


Fig. 7 Images of a Mg-rich organic particle (*labeled G*) as the RH was increased from 0 to 99% and then decreased to 0%. Images taken between 0 and 99% RH are not included because no changes in morphology occurred. Water uptake started and only occurred at 99% RH

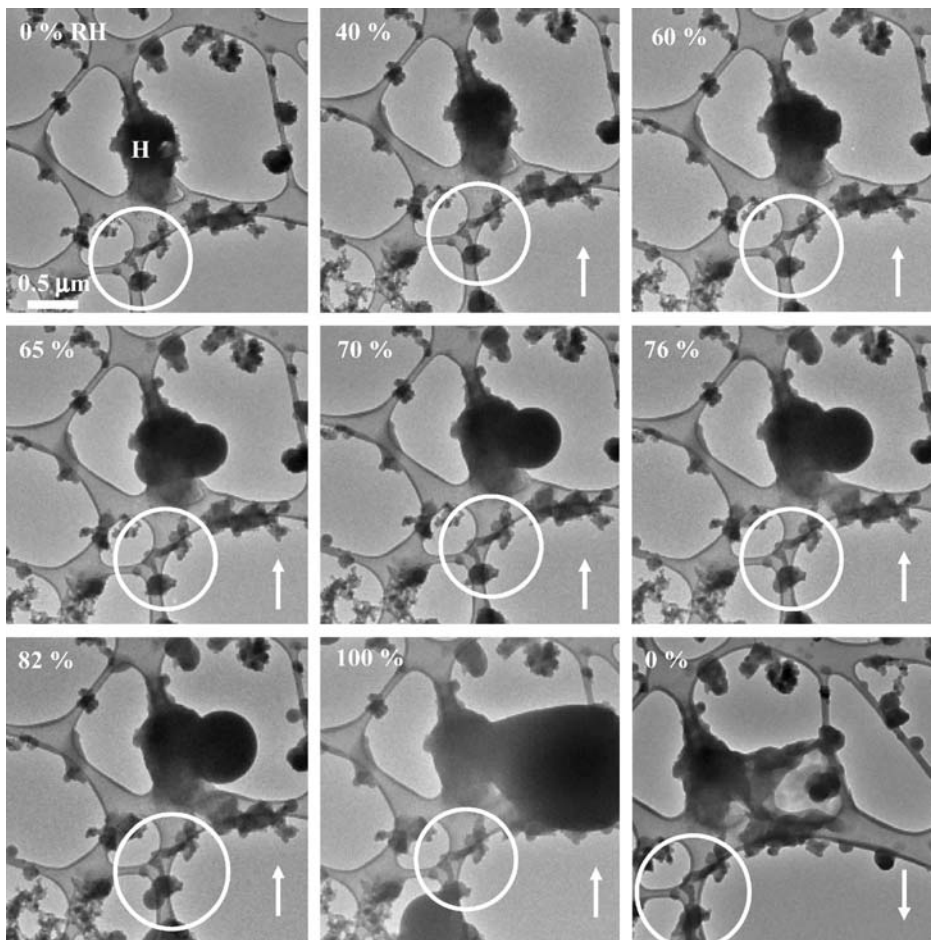


Fig. 8 Images of a Na-rich organic particle (*labeled H*) as RH was increased from 0 to 100% and then decreased to 0%. The circled region highlights changes to a soot particle having a water-soluble component. Images taken between 0 and 40% RH are not included because no changes in morphology occurred

soot is aggregated with soluble inorganic phases (i.e., KCl, H_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$), significant water uptake can occur. For example, in Fig. 8, a soot particle (circled) aggregated with soluble material began to take up water at 76% RH. More than 50% of our soot particles were aggregated or coated with such inorganic phases.

Organic coatings can also alter the hygroscopic properties of soot particles. However, it is well known that the electron beam damages organic aerosol particles (Katrib et al. 2005). Thus, we are unlikely to observe accurate hygroscopic behavior on organic-coated soot using this technique. We suspect that organic coatings may further complicate the deliquescence behavior of soot, but that the inorganic species, when present, will dominate the hygroscopic properties of these internally mixed particles because of their higher hygroscopic growth factors.

Water uptake by organic particles was significantly harder to recognize than for the inorganic particles studied using the same ETEM technique (Wise et al. 2006). This

phenomenon was partly due to the less well-defined grain boundaries and rounded morphologies of organic particles, e.g., these particles tend to cling to the LC substrate, forming “liquid-like” structures. Furthermore, not all organic molecules are expected to abruptly take up water. In our study, deliquescence spheres were only observed for particles containing inorganic phases. In general, the shape and location of the deliquescence sphere was determined by the location of the inorganic phase within the organic particle. For example, in Fig. 8, the deliquescence sphere formed and grew from a peripheral Na-rich grain.

The ambient particles from biomass smoke had a relatively high DRH compared with the other ambient particles investigated in Wise et al. (2006) and typically took up water in the range 80–100% RH. This difference reflects the nature of the inorganic components, e.g., the DRH of KCl is 84% (Cohen et al. 1987a, b) and of K_2SO_4 is 97% (Gmelin 1992). Organic coatings to included inorganic phases appeared to inhibit formation of deliquescence spheres. In cases where the inorganic phase was peripheral to the organic particle, formation of a deliquescence sphere did occur (e.g., KCl particle in Fig. 6).

Hygroscopic growth of organic particles containing inorganic phases appears to be controlled by the growth factor of the inorganic phase. Only chloride salts appeared to have significant hygroscopic growth in the particles studied in this work.

Given the detrimental effects of the electron beam on soluble organic material, we recorded changes only for organic particles with soluble inorganic components. However, such mixed organic–inorganic particles comprise up to 90% of the young smoke aerosol in our particular SAFARI-2000 samples. Hence, we were able to assess water uptake in a number of important refractory organic particle types.

4 Implications

Although soot and tar ball particles are significant components of biomass burning smoke, they appear to be hydrophobic. However, heterogeneous particles consisting of internal mixtures of organic and inorganic species are an important hygroscopic component of smoke. From our results, it appears that coatings and attached or included inorganic grains in refractory organic particles greatly enhance the hygroscopic properties of carbonaceous particles. Since our particles are mainly from young smoke generated in flaming fires, most inorganic grains are arguably primary particles from plant ash. Some particle types containing more than one phase also likely formed through in-situ atmospheric reactions, e.g., S-coated soot particles.

In-situ field measurements of humidification and light scattering effects in smoke plumes were documented during SAFARI-2000, but not necessarily in the same plumes or at the same times from which we obtained samples. These measurements showed that fresh smoke increased the light-scattering effect of ambient air by a factor of 1.4 as RH increased from 30 to 80%. In other biomass smoke studies, fresh smoke showed increased light-scattering in the range 1.15–1.3 for the same RH increase (Kotchenruther and Hobbs 1998). These measurements are consistent with our findings that internally mixed particles in fresh smoke are hygroscopic.

We observed active hygroscopic growth of smoke particles from 55 to 100% RH, with the value depending on the composition of the soluble phase. In our study, the soluble phase was inorganic and determined the hygroscopic properties of all the particles. Similar conclusions were drawn from experimental studies of CCN activation of soluble organic molecules with and without inorganic components (Bilde and Svenningsson 2004).

Experimental studies on the CCN activation of pure soot particles versus soot particles having a soluble inorganic or organic component also showed that inorganic phases significantly enhance the hygroscopic properties of carbonaceous particles (Broekhuizen et al. 2004; Dusek et al. 2006; Lammel and Novakov 1995; Rose et al. 2006). Hence, fresh soot and tar ball particles in young biomass smoke are not likely to be major contributors to CCN populations. However, aging, oxidation, and interaction with other soluble atmospheric components to form coatings will enhance the solubility of these hydrophobic particles with time (Formenti et al. 2002; Reid et al. 2005).

The effects of hygroscopic properties of fresh biomass smoke particles on atmospheric chemistry and cloud microphysics appear to be limited to the fraction of carbonaceous particles that contain water-soluble inorganic or organic compounds. The ratio of these fractions depends in part on fire intensity, with flaming fires producing more inorganic particles and smoldering fires more soluble organics (Gao et al. 2003). In fact water-soluble organics are likely oxidized in flaming fires (Gao et al. 2003).

Heterogeneous organic–inorganic particles were the dominant hygroscopic particle type in our young smoke samples from SAFARI-2000. These internally mixed particles likely formed through primary (combustion of vegetation) and secondary (atmospheric reactions and cloud processing) processes, suggesting that the fraction of these hygroscopic particles will increase with time. Thus, aging of smoke will lead to modulation of its effects on the radiative budget.

Acknowledgements This study was supported by the National Science Foundation under Grant No. 0304213 from the Division of Atmospheric Chemistry. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation. We acknowledge the use of sample material collected during the SAFARI-2000 field campaign by Tom Kirchstetter, Kristy Ross, and the crew of the University of Washington Convair-580. We thank Mihály Pósfai, Jia Li, and Peter Hobbs for their help in obtaining good samples. We gratefully acknowledge the use of the facilities within the John M. Cowley Center for High Resolution Electron Microscopy within the Center for Solid State Science at Arizona State University. We thank Karl Weiss, John Wheatley, Renu Sharma, and Peter Crozier for their assistance with microscopy. We thank Mihály Pósfai and two anonymous reviewers for helpful comments on our manuscript.

References

- Andreae, M.O., Andreae, T.W., Annegam, H., Beer, J., Cachier, H., le Canut, P., Elbert, W., Maenhaut, W., Salma, I., Wienhold, F.G., Zenker, T.: Airborne studies of aerosol emissions from savanna fires in southern Africa: 2. Aerosol chemical composition. *J. Geophys. Res.* **103**(D24), 32119–32128 (1998)
- Andreae, M.O., Rosenfeld, D., Artaxo, P., Costa, A.A., Frank, G.P., Longo, K.M., Silva-Dias, M.A.F.: Smoking rain clouds over the Amazon. *Science* **303**(5662), 1337–1342 (2004)
- Bilde, M., Svenningsson, B.: CCN activation of slightly soluble organics: the importance of small amounts of inorganic salt and particle phase. *Tellus, Ser. B Chem. Phys. Meteorol.* **56**(2), 128–134 (2004)
- Broekhuizen, K., Kumar, P.P., Abbatt, J.P.D.: Partially soluble organics as cloud condensation nuclei: role of trace soluble and surface active species. *Geophys. Res. Lett.* **31**(1), L01107 (2004)
- Carrico, C.M., Kreidenweis, S.M., Malm, W.C., Day, D.E., Lee, T., Carrillo, J., McMeeking, G.R., Collett, J.L.: Hygroscopic growth behavior of a carbon-dominated aerosol in Yosemite National Park. *Atmos. Environ.* **39**(8), 1393–1404 (2005)
- Chughtai, A.R., Miller, N.J., Smith, D.M., Pitts, J.R.: Carbonaceous particle hydration III. *J. Atmos. Chem.* **34**(2), 259–279 (1999)
- Cocker, III D.R., Mader, B.T., Kalberer, M., Flagan, R.C., Seinfeld, J.H.: The effect of water on gas-particle partitioning of secondary organic aerosol: II. *m*-xylene and 1,3,5-trimethylbenzene photooxidation systems. *Atmos. Environ.* **35**(35), 6073–6085 (2001)

- Cohen, M.D., Flagan, R.C., Seinfeld, J.H.: Studies of concentrated electrolyte-solutions using the electrodynamic balance.1. Water activities for single-electrolyte solutions. *J. Phys. Chem.* **91**(17), 4563–4574 (1987a)
- Cohen, M.D., Flagan, R.C., Seinfeld, J.H.: Studies of concentrated electrolyte-solutions using the electrodynamic balance.3. Solute nucleation. *J. Phys. Chem.* **91**(17), 4583–4590 (1987b)
- Corrigan, C.E., Novakov, T.: Cloud condensation nucleus activity of organic compounds: a laboratory study. *Atmos. Environ.* **33**(17), 2661–2668 (1999)
- Dusek, U., Reischl, G.P., Hitznerberger, R.: CCN activation of pure and coated carbon black particles. *Environ. Sci. Technol.* **40**(4), 1223–1230 (2006)
- Ebert, M., Inerle-Hof, M., Weinbruch, S.: Environmental scanning electron microscopy as a new technique to determine the hygroscopic behaviour of individual aerosol particles. *Atmos. Environ.* **36**(39–40), 5909–5916 (2002)
- Facchini, M.C., Fuzzi, S., Zappoli, S., Andracchio, A., Gelencser, A., Kiss, G., Krivacsy, Z., Meszaros, E., Hansson, H.C., Alsborg, T., Zebuhr, Y.: Partitioning of the organic aerosol component between fog droplets and interstitial air. *J. Geophys. Res.* **104**(D21), 26821–26832 (1999)
- Formenti, P., Boucher, O., Reiner, T., Sprung, D., Andreae, M.O., Wendisch, M., Wex, H., Kindred, D., Tzortziou, M., Vasaras, A., Zerefos, C.: STAAARTE-MED 1998 summer airborne measurements over the Aegean Sea – 2. Aerosol scattering and absorption, and radiative calculations. *Journal of Geophysical Research-Atmospheres* **107**(D21) (2002)
- Gao, S., Hegg, D.A., Hobbs, P.V., Kirchstetter, T.W., Magi, B.I., Sadilek, M.: Water-soluble organic components in aerosols associated with savanna fires in southern Africa: identification, evolution, and distribution. *Journal of Geophysical Research-Atmospheres* **108**(D13) (2003)
- Gmelin: *Handbook of Inorganic and Organometallic Chemistry*. Springer, Berlin Heidelberg New York (1992)
- Hand, J.L., Malm, W.C., Laskin, A., Day, D., Lee, T., Wang, C., Carrico, C., Carrillo, J., Cowin, J.P., Collett, J., Iedema, M.J.: Optical, physical, and chemical properties of tar balls observed during the Yosemite Aerosol Characterization Study. *J. Geophys. Res.* **110**(D21), doi: <http://dx.doi.org/10.1029/2004JD005728> (2005)
- Hobbs, P.V.: Summary of flights and types of data collected aboard the University of Washington's Convair-580 research aircraft in the SAFARI-2000 Field Study in southern Africa from 10 August through 18 September 2000, pp. 270, University of Washington, Seattle, WA (2001)
- Hobbs, P.V.: SAFARI 2000 CV-580 Aerosol and cloud data, dry season 2000 (CARG). Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, TN (2004)
- Hobbs, P.V., Sinha, P., Yokelson, R.J., Christian, T.J., Blake, D.R., Gao, S., Kirchstetter, T.W., Novakov, T., Pilewskie, P.: Evolution of gases and particles from a savanna fire in South Africa. *J. Geophys. Res.* **108**(D13), 8485 (2003)
- Jacobson, M.Z.: Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols. *Nature* **409**, 695–697 (2001)
- Katrib, Y., Biskos, G., Buseck, P.R., Davidovits, P., Jayne, J.T., Mochida, M., Wise, M.E., Worsnop, D.R., Martin, S.T.: Ozonolysis of mixed oleic-acid/stearic-acid particles: Reaction kinetics and chemical morphology. *J. Phys. Chem. A* **109**(48), 10910–10919 (2005)
- Koren, I., Kaufman, Y.J., Remer, L.A., Martins, J.V.: Measurement of the effect of Amazon smoke on inhibition of cloud formation. *Science* **303**, 1342–1345 (2004)
- Kotchenruther, R.A., Hobbs, P.V.: Humidification factors of aerosols from biomass burning in Brazil. *Journal of Geophysical Research-Atmospheres* **103**(D24), 32081–32089 (1998)
- Lammel, G., Novakov, T.: Water nucleation properties of carbon-black and diesel soot particles. *Atmos. Environ.* **29**(7), 813–823 (1995)
- Lee, Y.S., Collins, D.R., Li, R., Bowman, K.P., Geingold, G.: Expected impact of an aged biomass burning aerosol on cloud condensation nuclei and cloud droplet concentrations. *J. Geophys. Res.* **111**(D22), doi: <http://dx.doi.org/10.1029/2005JD006464> (2006)
- Li, J., Pósfai, M., Hobbs, P.V., Buseck, P.R.: Individual aerosol particles from biomass burning in southern Africa: 2. Compositions and aging of inorganic particles. *J. Geophys. Res.* **108**(D13), doi: <http://dx.doi.org/10.1029/2002JD002310> (2003)
- Lohmann, U., Broekhuizen, K., Leaitch, R., Shantz, N., Abbatt, J.: How efficient is cloud droplet formation of organic aerosols? *Geophys. Res. Lett.* **31**(5), L05108 (2004)
- Malm, W.C., Day, D.E., Kreidenweis, S.M., Collett, J.L., Carrico, C., McMeeking, G., Lee, T.: Hygroscopic properties of an organic-laden aerosol. *Atmos. Environ.* **39**(27), 4969–4982 (2005)
- Marcollì, C., Luo, B.P., Peter, T.: Mixing of the organic aerosol fractions: liquids as the thermodynamically stable phases. *J. Phys. Chem. A* **108**(12), 2216–2224 (2004)
- Maria, S.F., Russell, L.M., Gilles, M.K., Myneni, S.C.B.: Organic aerosol growth mechanisms and their climate-forcing implications. *Science* **306**(5703), 1921–1924 (2004)

- Martin, S.T.: Phase transitions of aqueous atmospheric particles. *Chem. Rev.* **100**(9), 3403–3454 (2000)
- Novakov, T., Corrigan, C.E.: Cloud condensation nucleus activity of the organic component of biomass smoke particles. *Geophys. Res. Lett.* **23**(16), 2141–2144 (1996)
- Petzold, A., Gysel, M., Vancassel, X., Hitzemberger, R., Puxbaum, H., Vrochiticky, S., Weingartner, E., Baltensperger, U., Mirabel, P.: On the effects of organic matter and sulphur-containing compounds on the CCN activation of combustion particles. *Atmospheric Chemistry and Physics* **5**, 3187–3203 (2005)
- Pósfai, M., Gelencser, A., Simonics, R., Arato, K., Li, J., Hobbs, P.V., Buseck, P.R.: Atmospheric tar balls: Particles from biomass and biofuel burning. *J. Geophys. Res.* **109**(D6), D06213, doi: <http://dx.doi.org/10.1029/2003JD004169> (2004a)
- Pósfai, M., Simonics, R., Li, J., Buseck, P.R., Hobbs, P.V.: SAFARI 2000 physical and chemical properties of aerosols, dry season 2000, Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, TN (2004b)
- Pósfai, M., Simonics, R., Li, J., Hobbs, P.V., Buseck, P.R.: Individual aerosol particles from biomass burning in southern Africa: 1. Compositions and size distributions of carbonaceous particles. *J. Geophys. Res.* **108** (D13), doi: <http://dx.doi.org/10.1029/2002JD002291> (2003)
- Reid, J.S., Koppmann, R., Eck, T.F., Eleuterio, D.P.: A review of biomass burning emissions part II: intensive physical properties of biomass burning particles. *Atmospheric Chemistry and Physics* **5**, 799–825 (2005)
- Roberts, G.C., Nenes, A., Seinfeld, J.H., Andreae, M.O.: Impact of biomass burning on cloud properties in the Amazon Basin. *J. Geophys. Res.* **108**(D2), 4062 (2003)
- Rose, D., Dusek, U., Frank, G.P., Poeschl, U., Bilde, M., Hennig, T., Henning, S., Kiendler-Scharr, A., Kiselev, A., Kristensson, A., Mentel, T., Schneider, J., Snider, J.R., Stratmann, F., Tillmann, R., Walter, S., Wennrich, C., Wex, H.: CCN activation of laboratory-generated soot particles with ammonium sulphate and levoglucosan coating. *Geophys. Res. Abstr.* **8**, 08545 (2006)
- Seisel, S., Pashkova, A., Lian, Y., Zellner, R.: Water uptake on mineral dust and soot: a fundamental view of the hydrophilicity of atmospheric particles? *Faraday Discuss.* **130**, 437–451 (2005)
- Semeniuk, T.A., Wise, M.E., Martin, S.T., Russell, L., Buseck, P.R.: Water uptake characteristics of naturally-coated individual aerosol particles. *Atmos. Environ.* in preparation (2006)
- van Poppel, L.H., Friedrich, H., Spinsby, J., Chung, S.H., Seinfeld, J.H., Buseck, P.R.: Electron tomography of nanoparticle clusters: implications for atmospheric lifetimes and radiative forcing of soot. *Geophys. Res. Lett.* **32**(24), L24811 (2005)
- Wise, M.E., Biskos, G., Martin, S.T., Russell, L.M., Buseck, P.R.: Phase transitions of single salt particles studied using a transmission electron microscope with an environmental cell. *Aerosol Sci. Tech.* **39**(9), 849–856 (2005)
- Wise, M.E., Semeniuk, T.A., Brientjes, R.T., Martin, S.T., Russell, L.M., Buseck, P.R.: Deliquescence behavior of NaCl-bearing natural aerosol particles using environmental transmission electron microscopy. *J. Geophys. Res.*, in review (2006)
- Yu, S.C.: Role of organic acids (formic, acetic, pyruvic and oxalic) in the formation of cloud condensation nuclei (CCN): a review. *Atmos. Res.* **53**(4), 185–217 (2000)