TEM study of SAFARI-2000 aerosols

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The aim of our research was to obtain data on the chemical and physical properties of individual aerosol particles from biomass smoke plumes in southern Africa and from air masses in the region that are affected by the smoke. We used analytical transmission electron microscopy (ATEM), including energy-dispersive X-ray spectrometry (EDS) and electron energy-loss spectroscopy (EELS), and field-emission electron microscopy (FESEM) to study aerosol particles from several smoke and haze samples and from a set of cloud samples.

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1. Publications, presentations, and abstracts of papers

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Pósfai, M., Simonics, R., Li, J., Hobbs, P.V., and Buseck, P.R. (2003) Individual aerosol particles from biomass burning in southern Africa: 1. Compositions and size distributions of carbonaceous particles, SAFARI-2000 special issue of ***J. Geophys. Res.*** **108 (D13)**, 8483, doi: 10.1029/2002JD002291.

Li, J., Pósfai, M., Hobbs, P.V., and Buseck, P.R. (2003) Individual aerosol particles from biomass burning in southern Africa: 2. Compositions and aging of inorganic particles, SAFARI-2000 special issue of ***J. Geophys. Res.*** **108(D13)**, 8484, doi: 10.1029/2002JD002310.

Abel, S.J., Haywood, J.M., Highwood, E.J., Li, J., and Buseck, P.R. (2003) Evolution of biomass burning aerosol properties from an agricultural fire in southern Africa, ***Geophys. Res. Lett.*** **30(15)**, 1783, doi:10.1029/2003GL017342.

Li, J. (2002) Characterization of individual aerosol particles from the North Atlantic Ocean and southern Africa. Ph.D. diss., Arizona State University, Tempe, AZ.

Presentations

Li, J., Pósfai, M., Hobbs, P.V., and Buseck, P.R. (2003) Analysis of individual aerosol particles from biomass burning in southern Africa, 2003 Symp. on "Recent Developments and Applications of Atomic Resolution Electron Microscopy and Spectroscopy – a Silver Jubilee," Tempe, AZ, ASU, ***Prog. & Abstr.*** (January, 2003).

Buseck, P.R. (2002) Electron microscopy of individual aerosol particles (Invited), GAC-MAC Joint Ann. Mtg., Saskatoon, Saskatchewan (May, 2002).

Pósfai, M., Simonics, R., Li, J., Hobbs, P.V., and Buseck, P.R. (2001) Individual aerosol particle types produced by savanna burning. Am. Geophys. Union Fall Mtg., San Francisco, CA, ***Eos Transactions, AGU*** **82**, Fall Meeting Suppl,. Abstract A42B-07 (December, 2001).

Li, J., Pósfai, M., Hobbs, P.V., and Buseck, P.R. (2001) Individual-particle analysis of aerosols from southern Africa. ***Eos Transactions, AGU*** **82**, Fall Meeting Suppl,. Abstract A51A-0027 (December, 2001).

Buseck, P.R., Garvie, L.A., Li, J., and Pósfai, M. (2001) Chemical analysis of individual aerosol particles by electron energy-loss spectroscopy (EELS). ***Eos Transactions, AGU*** **82**, Fall Meeting Suppl,. Abstract A11B-04 (December, 2001).

Pósfai, M., Simonics, R., Li, J., Hobbs, P.V., and Buseck, P.R. (2001) Individual aerosol particle types produced by savanna burning. SAFARI 2000 Data Workshop, Siavonga, Zambia (August, 2001).

Li, J., Pósfai, M., Hobbs, P.V., and Buseck, P.R.(2001) An electron microscopy study of individual aerosol particles from biomass burning in southern Africa during the SAFARI 2000 Experiment, SAFARI 2000 Data Workshop, Siavonga, Zambia (August , 2001).

Abstracts of Papers

Pósfai, M., Gelencsér, A., Simonics, R., Arató, K., Li, J., Hobbs, P.V., and Buseck, P.R (2004) Atmospheric tar balls: particles from biomass and biofuel burning, ***J. Geophys. Res.*** **109**, D06213, doi: 10.1029/2003JD004169.

"Tar balls" are amorphous, carbonaceous spherules that occur in the tropospheric aerosol as a result of biomass and biofuel burning. They form a distinct group of particles with diameters typically between 30 and 500 nm and readily identifiable with electron microscopy. Their lack of a turbostratic microstructure distinguishes them from soot, and their morphology and composition (_90 mol % carbon) renders them distinct from other carbonaceous particles. Tar balls are particularly abundant in slightly aged (minutes to hours old) biomass smoke,

indicating that they likely form by gas-to-particle conversion within smoke plumes. The material of tar balls is initially hygroscopic; however, the particles become largely insoluble as a result of free radical polymerization of their organic molecules. Consequently, tar balls are primarily externally mixed with other particle types, and they do not appreciably increase in size during aging. When tar balls coagulate with water-bearing particles, their material may partly dissolve and no longer be recognizable as distinct particles. Tar balls may contain organic compounds that absorb sunlight. They are an important, previously unrecognized type of carbonaceous (organic) atmospheric particle.

Pósfai, M., Simonics, R., Li, J., Hobbs, P.V., and Buseck, P.R. (2003) Individual aerosol particles from biomass burning in southern Africa: 1. Compositions and size distributions of carbonaceous particles, SAFARI-2000 special issue of ***J. Geophys. Res.*** **108 (D13)**, 8483, doi: 10.1029/2002JD002291.

Individual aerosol particles in smoke plumes from biomass fires and in regional hazes in southern Africa were studied using analytical transmission electron microscopy (TEM), which allowed detailed characterization of carbonaceous particle types in smoke and determination of changes in particle properties and concentrations during smoke aging. Based on composition, morphology, and microstructure, three distinct types of carbonaceous particles were present in the smoke: organic particles with inorganic (K-salt) inclusions, "tar ball" particles, and soot. The relative number concentrations of organic particles were largest in young smoke, whereas tar balls were dominant in a slightly aged (_1 hour) smoke from a smoldering fire. Flaming fires emitted relatively more soot particles than smoldering fires, but soot was a minor constituent of all studied plumes. Further aging caused the accumulation of sulfate on organic and soot particles, as indicated by the large number of internally mixed organic/sulfate and soot/sulfate particles in the regional haze. Externally mixed ammonium sulfate particles dominated in the boundary layer hazes, whereas organic/sulfate particles were the most abundant type in the upper hazes. Apparently, elevated haze layers were more strongly affected by biomass smoke than those within the boundary layer. Based on size distributions and the observed patterns of internal mixing, we hypothesize that organic and soot particles are the cloudnucleating constituents of biomass smoke aerosols. Sea-salt particles dominated in the samples taken in stratus clouds over the Atlantic Ocean, off the coast of Namibia, whereas a distinct haze layer above the clouds consisted of aged biomass smoke particles.

Li, J., Pósfai, M., Hobbs, P.V., and Buseck, P.R. (2003) Individual aerosol particles from biomass burning in southern Africa: 2. Compositions and aging of inorganic particles, SAFARI-2000 special issue of ***J. Geophys. Res.*** **108(D13)**, 8484, doi: 10.1029/2002JD002310.

Individual aerosol particles collected over southern Africa during the SAFARI 2000 field study were studied using transmission electron microscopy and field-emission scanning electron microscopy. The sizes, shapes, compositions,

mixing states, surface coatings, and relative abundances of aerosol particles from biomass burning, in boundary layer hazes, and in the free troposphere were compared, with emphasis on aging and reactions of inorganic smoke particles. Potassium salts and organic particles were the predominant species in the smoke, and most were internally mixed. More KCl particles occur in young smoke, whereas more K2SO4 and KNO3 particles were present in aged smoke. This change indicates that with the aging of the smoke, KCl particles from the fires were converted to K2SO4 and KNO3 through reactions with sulfur- and nitrogenbearing species from biomass burning as well as other sources. More soot was present in smoke from flaming grass fires than bush and wood fires, probably due to the predominance of flaming combustion in grass fires. The high abundance of organic particles and soluble salts can affect the hygroscopic properties of biomass-burning aerosols and therefore influence their role as cloud condensation nuclei. Particles from biomass burning were important constituents of the regional hazes.

Abel, S.J., Haywood, J.M., Highwood, E.J., Li, J., and Buseck, P.R. (2003) Evolution of biomass burning aerosol properties from an agricultural fire in southern Africa, ***Geophys. Res. Lett.* 30(15)**, 1783, doi:10.1029/2003GL017342.

Measurements on the UK Met Office C-130 within a distinct biomass burning plume during the Southern AfricAn Regional science Initiative (SAFARI 2000) show an increase in the single scattering albedo as the aerosol ages, from 0.84 at source to 0.90 in the aged regional haze in 5 hours. Condensation of scattering material from the gas phase appears to be the dominant mechanism; the change in black carbon morphology, from a chain to clump like structure, does not significantly affect the bulk aerosol single scattering albedo.

Dissertation

Part of our Safari 2000 results are included in a Ph.D. dissertation which was defended in December, 2002.

Li, J. (2002) Characterization of individual aerosol particles from the North Atlantic Ocean and southern Africa. Ph.D. diss., Arizona State University, Tempe, AZ.

Individual aerosol particles from the North Atlantic Ocean and southern Africa were studied using transmission electron microscopy and field-emission scanning electron microscopy, with emphasis on their sizes, morphologies, compositions, species, mixing states, and relative abundances. This study provides a detailed characterization of aerosols from different sources and insight into their reactions and evolution.

Major particle types from the North Atlantic consisted of chloride, sulfate, and nitrate of sodium, ammonium sulfate, soot, flyash, silica, and iron oxide. Aerosols from two sampling sites showed dramatic differences in abundances of distinct particle types. At Sagres on the coast of Portugal, most sea salt particles were partly or completely depleted in chlorine and enriched in sulfur, nitrogen, or both. In contrast, at Punta del Hidalgo on the Canary Islands, only during polluted periods

were sea salt particles partly reacted to sulfate and nitrate. Heterogeneous oxidation of sulfur dioxide in deliquescent sea salt, reactions with nitric acid, and cloud processing may be the major mechanisms of sea salt reactions. Concentrations of other pollutants including soot, flyash, and ammonium sulfate were higher at Sagres than at Punta del Hidalgo. These differences suggested the great impact of European pollution on marine aerosols and the dilution, rapid reaction, and exhaustion of reactive pollutants as they were transported to the open ocean.

Individual aerosols from biomass burning and regional hazes in southern Africa were also characterized and the aging of smoke particles was investigated. Smoke aerosols mainly included potassium salts, tar balls, organic particles, soot, and calcium-bearing particles. Soot was most abundant in smoke from grass fires, probably owing to the predominance of flaming combustion. More potassium chloride particles occurred in young smoke, whereas more potassium sulfate and nitrate particles were in aged smoke. This change indicates the conversion of potassium salts through reactions of potassium chloride with sulfur- and nitrogen-bearing species as the smoke aged. Owing to the different hygroscopic properties of these potassium salts, the transformation suggests that the high cloud-nucleating efficiency of fresh smoke would diminish with age. Smoke particles were common in the regional hazes, suggesting that biomass burning contributed to the haze formation.

2. Discussion of work

In June 2000, we selected and purchased aerosol samplers. These were sent to the University of Washington, where they were installed into their research Convair airplane. In August 2000 we collected samples over southern Africa from the Convair.

Using transmission and scanning electron microscopy, we analyzed samples from the following:

- Flaming and smoldering grass fires from Kruger National Park, South Africa
- A fire near the Timbavati Game Reserve, South Africa
- A fire on the Madikwe Game Reserve on the South Africa/Botswana border
- A smoldering fire near Beria, Mozambique
- A flaming grass fire (dambo vegetation type) near Kaoma, Zambia
- Haze from flights over Skukusa and Pietersburg, South Africa
- Above the Atlantic Ocean, near Walvis Bay, Namibia

From those studies we distinguished the following major particle groups from savanna fires in southern Africa:

1. **Carbonaceous particles** (presumably organic) that contain inorganic K-salt inclusions; in general, this is the most abundant particle type. Crystalline inclusions occur within them and have variable compositions, depending on the sample. The

K-salt inclusions decompose in the electron beam, but the carbonaceous part is beam-stable. The ratio of carbonaceous/inorganic components within individual particles is variable, but C is the major element in all these particles.

2. **"Tar ball" particles.** These carbonaceous particles are grouped separately, mainly because of their distinctive spherical morphology. Tar balls are stable in the electron beam and have fairly uniform compositions. They mostly contain C, minor O and K, and S in some cases.

3. **Soot.** This is a minor component of some samples, generally with K and minor Si. Particles are assigned into this group on the basis of their characteristic, branching morphology. Compact, onion-like microstructures are typical; some particles contain crystalline islands a few nanometers across; these are likely graphitic in structure.

4. **Other particle types** include ammonium sulfate particles coated by an organic film, sea-salt particles, and mineral dust. Some sample sets contain fresh, mostly unreacted sea salt particles larger than about 1.5 μm and associated with particles that originated from the fires. However, other samples contain sea salt particles that are partly or completely reacted.

We examined smoke from both flaming and smoldering fires in order to assess the differences in the properties of individual particles from both types of emissions. Smoke particles from burning of different vegetation types were characterized to distinguish particulate emissions related to fuel types. Smoke samples immediately above biomass fires were studied from seven research flights that sampled fire emissions in the Kruger National Park and the Timbavati Game Reserve, South Africa; in the Madikwe Game Reserve, South Africa/Botswana; west of Beira, Mozambique; and near Kaoma, Zambia. Aged smoke samples were also collected from smoke plumes at different distances downwind from the fire sources in the Madikwe Game Reserve, in the Timbavati Game Reserve, and near Beira.

Persistent, stratified haze layers that seriously degrade visibility are striking features during the dry season in southern Africa. Samples collected from layers of this regional haze provided an opportunity to study the particle types that occur in the hazes and how their compositions and sizes compare with particles in young smoke. We analyzed haze samples from four of the flights listed above, from two flights over Skukusa and Pietersburg, South Africa, and from a sample collected above the Atlantic Ocean, off Walvis Bay, Namibia. In addition, haze aerosol particles associated with marine stratus clouds were analyzed.

The strategy used in this study was to identify major particle groups based on morphology, composition, and behavior in the electron beam. Selected-area electron diffraction (SAED) was used to determine the structures and species of inorganic particles. Compositions, mixing states, and relative abundances of different particle

types were characterized in detail. We termed the three most important particle types in biomass smoke plumes a) 'organic particles with K-salt inclusions,' b) 'tar balls' (carbon-rich, spherical particles) and c) 'soot.' The K-salt inclusions mainly consisted of KCl, K_2SO_4, and KNO_3. In addition, large aggregates of fine-grained Ca-bearing particles occurred in the smoke; these have not been reported in previous studies of aerosols from biomass burning. These Ca-bearing particles may have condensed during the burning process from elements in the burnt vegetation.

The relative number concentrations of organic particles were largest in young smoke, whereas tar balls were dominant in a slightly aged (~1 hr) smoke from a smoldering fire. Flaming fires emitted relatively more soot particles than smoldering fires, but soot was a minor constituent in most studied plumes. Compared to two fires in the Madikwe Game Reserve and the Timbavati Game Reserve, the dambo grass fire near Kaoma, Zambia emitted the largest amounts of soot. This high soot abundance is probably the result of the dominance of flaming combustion of the grass fire. Further aging caused the accumulation of sulfate on organic and soot particles, as indicated by the large number of internally mixed organic/sulfate and soot/sulfate particles in the regional haze. Externally mixed ammonium sulfate particles dominated in the boundary layer hazes, whereas organic/sulfate particles were the most abundant type in the upper hazes. Apparently, elevated haze layers were more strongly affected by biomass smoke than those within the boundary layer.

The three main carbonaceous particle types likely have different effects on the atmosphere. Tar balls are typically not aggregated with other particle types; they show no signs of growth and seem to be typical constituents of smoke that has reached a certain age. These characteristics suggest that tar balls are not effective as cloud condensation nuclei (CCN). We plan additional studies of these particles to explain the formation of tar balls in the SAFARI 2000 biomass smoke plumes and their virtual absence in the haze samples.

Organic particles with K-salt inclusions were the dominant type in biomass smoke and in the regional hazes that were strongly affected by biomass smoke. The irregular morphologies of these particles suggest that they were hydrated on collection. At least part of their organic material may be water-soluble, and even if the carbonaceous part of organic particles were water-insoluble, the inorganic K-salt inclusions should make the mixed particle hydrophilic. Thus, organic particles with inorganic inclusions are likely responsible for the high cloud-nucleating potential of biomass smoke particles. Indirect conclusions can be drawn regarding the optical properties of organic particles: since they dominate in biomass smoke plumes, and the net direct radiative forcing by biomass smoke is negative, we assume that organic particles are not significantly absorbing in the visible range of the spectrum.

Soot particles become progressively more aggregated with organic and sulfate particles during the aging of smoke. A wide variety of soot sizes is apparent in our

samples, ranging from a few attached spherules that are smaller than 100 nm to micrometer-sized, branching aggregates. Several studies showed that internal mixing of soot with non-absorbing species such as sulfate enhances the absorption efficiency of soot because the host particle acts as a lens that focuses more sunlight onto the absorbing core. In the optically thick haze layers encountered in SAFARI 2000, the majority of the soot particles were associated with either sulfates or organic particles, and thus their absorption efficiency presumably is significantly increased relative to that in young smoke.

Organic and soot particles seem to be persistent aerosol types that survive smoke aging and transport on a regional scale. As seen in our samples, the main change that organic and soot particles experience during aging is the accumulation of ammonium sulfate on them. The smoke particles seem to provide a favorable surface for the nucleation of sulfate, and coagulation can also bring soot and sulfate together. Our results to date show that after long-range transport biomass smoke aerosol consists primarily of internally mixed organic/sulfate and soot/sulfate particles.

Smoke samples collected at different distances downwind from the fires enabled us to study the aging and reaction of the inorganic components of the smoke particles. Even though these smoke particles were still fairly young ($\leq$ 1 hr old), significant changes occurred in them compared to the particles in the smoke just above the fires. As the smoke aged, rapid conversion of K salts along the smoke plumes was detected. KCl particles, which were abundant in fresh smoke, were transformed to K_2SO_4 and KNO_3 in aged smoke through photochemical oxidation and reactions between KCl and S- and N-containing species. This alteration could affect the cloud-nucleating properties of smoke particles because of the different hygroscopic characteristics of these K salts. Because of the higher deliquescence relative humidities of K_2SO_4 and KNO_3 than that of KCl, some of the aged smoke particles may be less efficient in cloud nucleation than those in the nascent smoke. This observation corroborates CCN measurements showing the diminished effectiveness of smoke particles with aging.

The results obtained from the aerosol associated with stratus clouds over the Atlantic Ocean off the coast of Namibia provide a snapshot of aerosol-cloud interactions. The results indicate that smoke particles are not necessary for the presence of persistent stratus clouds off the coast of Namibia, since the particles in, below, and above clouds were predominantly of sea salt origin. High biological productivity, produced by strong upwelling, provides S-bearing species that convert sub-micrometer sea-salt particles to sulfate. In the cloud samples, a minority of the particles could have originated from biomass smoke, as indicated by their K contents. Whereas the cloud-nucleating particles appeared to be primarily of marine origin, the haze layers above the clouds contained aged particles from biomass smoke, creating a complicated layered system of absorbing haze and reflecting clouds.