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Individual aerosol particles from biomass burning in southern Africa: 2, Compositions and aging of inorganic particles

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[1] 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 K_2SO_4 and KNO_3 particles were present in aged smoke. This change indicates that with the aging of the smoke, KCl particles from the fires were converted to K_2SO_4 and KNO_3 through reactions with sulfur- and nitrogen-bearing 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. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; *KEYWORDS:* individual particle analysis, SAFARI 2000, biomass burning, potassium salt, aging of smoke, tar balls

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1. Introduction

[2] Emissions from biomass burning are a significant source of aerosol particles and trace gases to the atmosphere [*Crutzen and Andreae*, 1990; *IPCC*, 1996; *Kuhlbusch et al.*, 1996; *Kuhlbusch and Crutzen*, 1996]. Savanna burning is the single largest source of biomass burning worldwide, with the biomass burnt and carbon released being three times those from forest fires [*Andreae*, 1991]. Since Africa has more than 60% of the savanna on Earth, extensive savanna burning in this region causes important perturbations to Earth's atmosphere, especially during the winter dry season.

[3] The vast amount of particulate emissions from biomass burning can influence regional and global climate through scattering and absorbing solar radiation [*Andreae*, 1991; *Kuhlbusch et al.*, 1996; *Kuhlbusch and Crutzen*, 1996]. Moreover, smoke particles can serve as cloud condensation nuclei (CCN) [*Hobbs and Radke*, 1969; *Hallet et al.*, 1989; *Rogers et al.*, 1991; *Kuhlbusch and Crutzen*, 1996] and may affect the formation, coverage, and lifetime of clouds. The combined direct radiative effects of pyrogenic particles and their indirect effects through clouds have been estimated to cause a global reflection of solar radiation that is comparable to that from sulfate aerosol [*Penner et al.*, 1992; *Dickinson*, 1993]. In addition, because of the long-range transport of biomass burning emissions, essential nutrient elements can be lost from the source region, thus altering the biogeochemical cycles of trace elements in the tropics [*Goldammer and Crutzen*, 1993; *Menaut et al.*, 1993; *Kaufman et al.*, 1994].

[4] Individual-particle analysis using electron microscopy has been used to characterize aerosol particles [*Sheridan et al.*, 1993; *Pósfai et al.*, 1994, 1995; *Buseck et al.*, 2000; *Li et al.*, 2003]. Because of their resolution down to fractions of a nanometer, electron microscopes can provide information on the morphologies, sizes, structures, and mixing states of even the finest atmospheric aerosols. Some studies at the individual-particle level have been made on aerosols emitted from biomass burning [*Cachier et al.*, 1991; *Woods et al.*, 1991; *Gaudichet et al.*, 1995; *Martins et al.*, 1996, 1998; *Reid and Hobbs*, 1998; *Liu et al.*, 2000; *Okada et al.*, 2001].

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Table 1. Samples Studied

UW Flight Number	Date and Time, UTC	Light Scattering Coefficient, m^{-1}	Sampling Conditions	Location
1819	20 August 2000, 1325:00–1355:00	1.5×10^{-3}	Smoke from prescribed fire	Madikwe Game Reserve on South Africa/Botswana border
1820	22 August 2000, 0936:50–1019:30	7.85×10^{-5}	Haze at variable altitudes, 335–1219 m	Skukusa, Kruger National Park, South Africa
1821	23 August 2000, 1255–13:55	1×10^{-8}–1×10^{-6}	Free troposphere, at 4572 m	Near Pietersburg, South Africa
1831	5 September 2000, 1233:45–1243:45	2.65×10^{-4}	Smoke from flaming dambo grass fire	Near Kaoma, Zambia
1834	7 September 2000, 0904:00–0908:30	1×10^{-3}	Young smoke from fire	Timbavati Game Reserve, South Africa
	7 September 2000, 0939:00–0940:00	1×10^{-3}	Smoke 16 km downwind of fire	Timbavati Game Reserve, South Africa
	7 September 2000, 0952:00–1005:00		Smoke 8–37 km downwind of fire	Timbavati Game Reserve, South Africa

However, more detailed investigations of the chemical and physical characteristics of smoke particles is needed to better understand their environmental and climatic impacts.

[5] The objective of this study is to characterize in detail the major aerosol types from biomass burning in southern Africa, their speciation, aggregation, coating, and relative abundances. As a result of coagulation, outgassing, and gas-to-particle conversion, particles from biomass burning evolve rapidly after emission, and their physical, chemical, and optical properties can change dramatically as the smoke ages [*Reid and Hobbs*, 1998; *Hobbs et al.*, 2003]. Therefore, we investigate the aging of the smoke, with emphasis on reactions and evolution of inorganic aerosol particles. We also compare particulate emissions from the burning of different vegetation types. While providing information on all particles sampled, the focus of this study is on the inorganic constituents of the aerosol; carbonaceous particle types are described in more detail in a companion paper [*Pósfai et al.*, 2003], by *Kirchstetter et al.* [2003], and by *Eatough et al.* [2003].

2. Experimental

2.1. Sampling

[6] Aerosol samples were collected on the University of Washington's Convair-580 research aircraft in August–September 2000 during the Southern Africa Regional Science Initiative (SAFARI 2000) field study in southern Africa (see Appendix A by P. V. Hobbs in the work of *Sinha et al.* [2003]). To study aerosols from different sources over southern Africa, samples were obtained from smoke plumes from biomass burning, boundary layer hazes, and the free troposphere (Table 1).

[7] Aerosol particles were sampled using two 3-stage impactors (Model MPS-3, California Measurements, Inc.). The nominal diameter ranges for the three stages were: >2, 2–0.3, and <0.3 μm. Sampling durations ranged from several minutes to an hour, depending on the specific sampling conditions (Table 1). Particles were deposited directly onto transmission electron microscope grids with Formvar or lacey carbon supporting films.

2.2. Analytical Techniques

[8] We used a JEOL 2000FX transmission electron microscope (TEM) and a HITACHI S-4700 field-emission scanning electron microscope (FESEM) to analyze the aerosol samples. The high resolution of the TEM and FESEM enables observation of particles down to tens of nanometers in diameter. TEM and SEM imaging, chemical data, and selected-area electron diffraction (SAED) patterns were correlated to identify the phases of the particles. Both microscopes have energy-dispersive X-ray spectrometer (EDS) systems with ultrathin-window detectors that allow analysis of elements with atomic number >5. However, elements lighter than sodium were not quantified because of high absorption within the samples. Small spot sizes and low beam currents were used to avoid beam damage to particles during EDS analysis. A JEOL 4000FX high-resolution TEM was used to obtain structural information about soot spheres at high magnifications.

3. Results and Discussion

3.1. Major Aerosol Types in the Smoke

[9] The samples collected from biomass-burning smoke consist mainly of potassium salts, "tar balls" (defined below), organic particles, soot, and calcium-bearing particles. Minor amounts of mineral dust, sea salt, and ammonium sulfate were also present. Most of the aerosol particles in the smoke from biomass burning were in the submicrometer size range. The particles we examined were dry; any water and volatile species that might have been present were presumably lost in the vacuum of the TEM. The potassium salts and $(NH_4)_2SO_4$ particles may have crystallized on the TEM grids. Therefore, their morphologies observed in the TEM may have differed from their shapes prior to collection. However, since the relative humidities in southern Africa during the dry season are generally low (20–40%), desiccation in the TEM may not have made much difference to the morphologies of the particles.

3.1.1. Potassium-Salt Particles

[10] Potassium-salt particles were the most abundant inorganic aerosol constituents in the smoke from biomass burning. They included KCl (Figure 1), K_2SO_4, KNO_3, and minor potassium- and calcium-bearing sulfate with variable K/Ca ratios. Most had amorphous organic coatings or formed small inclusions in organic particles (Figure 2). These potassium salts were very beam-sensitive. They ranged in diameter from 20 nm to 1.5 μm, with most from 100 to 600 nm. Most of the KCl particles had euhedral morphologies, and some were rounded. Some rounded

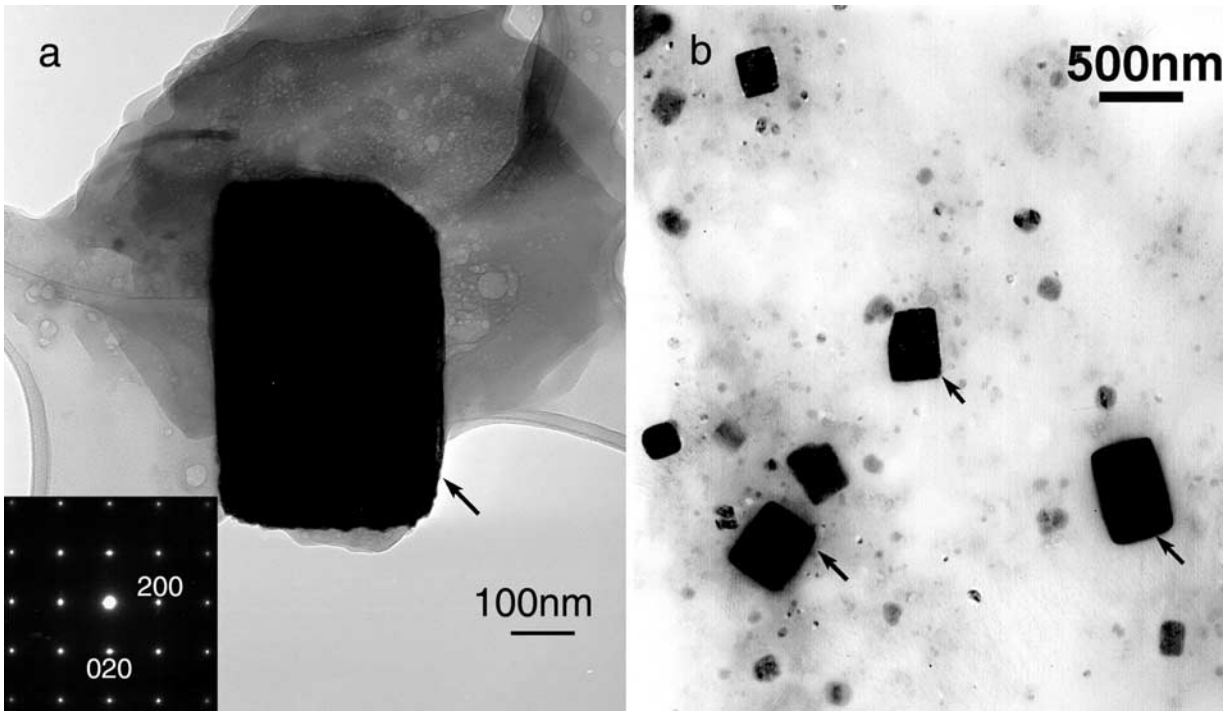

Figure 1. Transmission electron microscope images of euhedral KCl crystals (arrowed) in young smoke from flaming fires. The crystals are internally mixed with organic materials. (a) Particles in smoke from the Madikwe Game Reserve fire, South Africa, on 20 August 2000; (b) Particles in smoke from the Timbavati fire on 7 September 2000. The inset in (a) is the SAED pattern of the large KCl crystal, showing its [001] orientation.

particles contained potassium and chlorine, and they were more beam-sensitive than the pure KCl particles. These particles were likely mixtures of KCl and NH_4Cl [*Liu et al.*, 2000], which formed through reactions of chlorine and NH_3 species emitted from the fire. Some of the potassium sulfate and nitrate crystals were rectangular or rounded, but most were irregularly shaped. Selected-area diffraction patterns of KCl and K_2SO_4 particles were obtained to confirm their crystallinity. The occurrence of KNO_3 was inferred from the elements present in the EDS analyses.

[11] Excess fine potassium not attributable to mineral dust or sea salt is an indicator of biomass burning [*Andreae*, 1983]. The occurrence of KCl, K_2SO_4, and KNO_3 as fine particles in the individual-particle analyses is consistent with bulk analyses of biomass-burning aerosol from other locations using PIXE and ion chromatography [*Allen and Miguel*, 1995; *Yamasoe et al.*, 2000]. The high abundance of potassium salts was observed in vegetation fires in the Amazon Basin by *Yamasoe et al.* [2000], who reported that K^+, Cl^-, and SO_4^{2-} were the dominant species in the aerosol particles in the plumes from such fires. Potassium and chlorine are organically bound or present in the fluids of the vegetation [*Liu et al.*, 2000]. Volatilization and reactions of the elemental constituents in the vegetation during burning leads to the nucleation and condensation of the potassium-salt particles [*Gaudichet et al.*, 1995].

3.1.2. "Tar Balls" and Organic Particles

[12] We define "tar balls" as spherical, amorphous carbonaceous particles (Figure 3). Under high magnification they do not show the fine graphitic structure that is characteristic of soot. Besides the major component of carbon, they may also contain variable, minor amounts of potassium, oxygen, sulfur, and silicon [*Pósfai et al.*, 2003]. Other organic particles in the smoke did not have a spherical morphology but were mostly subrounded or irregularly shaped (Figure 2). They may have had similar chemical compositions to the tar balls, but most contained potassium-salt inclusions and so their EDS analyses show variable concentrations of potassium, chlorine, and sulfur. The tar balls and organic particles had similar diameter ranges from 50 to 500 nm, with a few particles larger than 1 μm.

[13] Organic particles with and without potassium-salt inclusions were the most abundant particle type in the smoke from the biomass-burning fires we examined. They accounted for 70 to 83% of the total particle number in the smoke. The relative abundance of tar balls ranges from 0 to 20% of the total particles. More detailed observations on carbonaceous particles including tar balls, organic particles, and soot are described in a companion paper [*Pósfai et al.*, 2003].

3.1.3. Soot

[14] The soot content varied greatly in different smoke samples. Soot forms branching aggregates containing from less than ten to thousands of spheres, each of which is 20 to 60 nm in diameter (Figure 4). Most of the soot aggregates contained potassium, and some had minor amounts of silicon. The potassium enrichment in soot has been used as a fingerprint of its biomass-burning origin [*Andreae*, 1983]. High-spatial-resolution electron energy-loss spectroscopy (EELS) results showed chemical heterogeneity even within one aggregate, with varied potassium contents in different soot spheres [*Buseck et al.*, 2001]. High-resolution

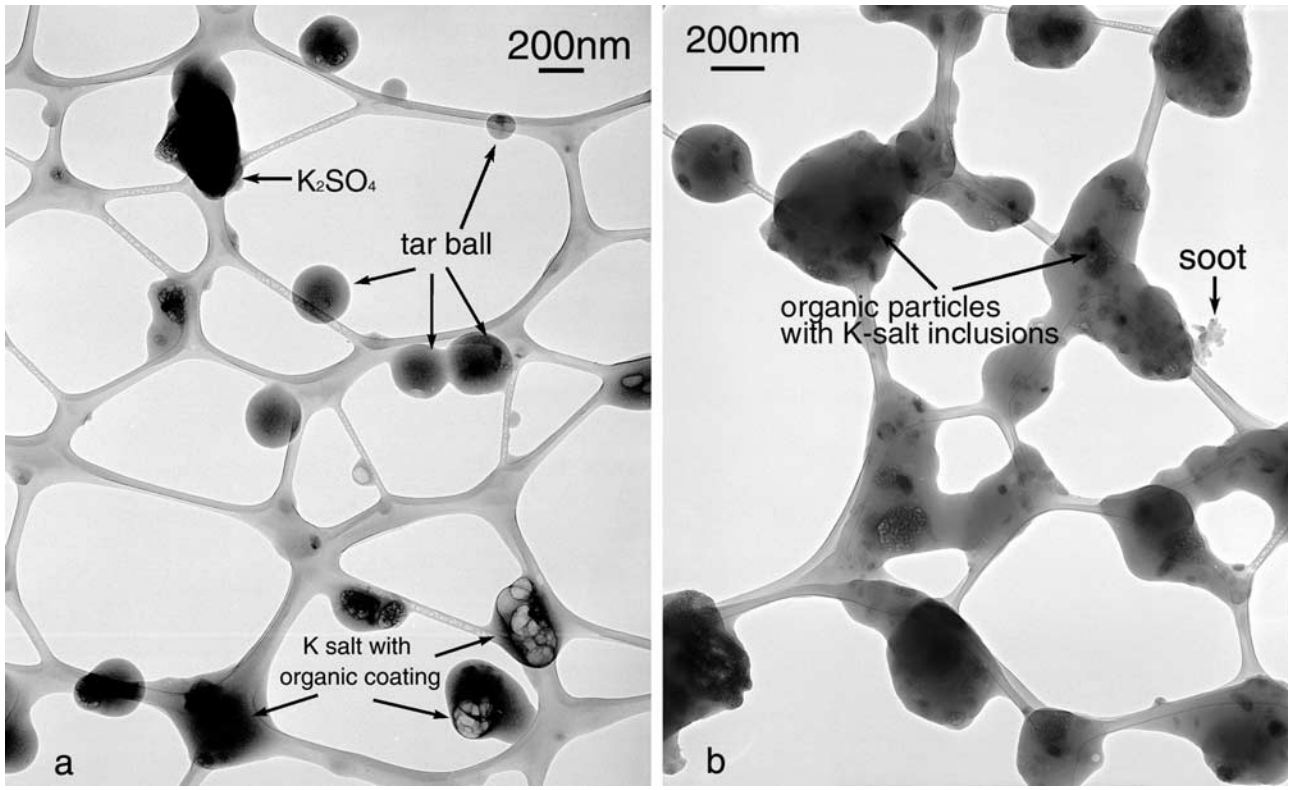

Figure 2. Transmission electron microscope images of particles from aged smoke collected between 8 and 37 km downwind from the Timbavati fire, South Africa, on 7 September 2000. Particles were deposited on lacey carbon substrate. (a) The relative number concentration of tar balls increased in the aged smoke compared to the young smoke. The potassium-salt particles have organic coatings. Some are damaged by the electron beam. Most of the KCl crystals in the young smoke have transformed into potassium sulfate and nitrate with the aging of the smoke. (b) Potassium salts form inclusions within organic particles.

TEM images of the soot spheres showed onion-like structures of curved, disordered graphitic layers (Figure 5). Some soot particles form aggregates with organic particles and potassium salts.

3.1.4. Ca-Bearing Particles

[15] Large aggregates of calcium-bearing particles were present in the smoke samples, and the lengths of the aggregates range from 2 to 15 μm. The calcium-bearing particles were very fine grained, with diameters ranging from 50 to 300 nm, although some were up to 500 nm (Figure 6). Most were crystalline, and some contained magnesium and potassium. Based on compositions and SAED patterns, the calcium-bearing particles included the carbonates aragonite and calcite, sulfate (gypsum), and phosphate in the form of apatite. Energy-dispersive x-ray spectrometer analyses of some aggregates showed chemical heterogeneity, so different parts of the aggregates likely contained varied mixtures of CO_3^{2-}, PO_4^{3-}, and SO_4^{2-}. Some aggregates were internally mixed with organic particles.

[16] Since calcium carbonate, sulfate, and phosphate do not readily deliquesce, their morphologies as observed in the TEM should not differ from those in the atmosphere. Agglomeration of fine Ca-bearing particles was observed in both heavily and lightly loaded areas on the grids and did not change during the TEM analysis. Therefore, we believe the aggregation of Ca-bearing particles was not the result of collection on the grids or an artifact of the TEM analysis.

[17] Large aggregates of calcium carbonate, sulfate, and phosphate have not been reported in previous studies of aerosols from biomass burning. Calcium sulfate and sulfate containing both potassium and calcium have been observed in smoke from African savanna and wetlands fires and were reported to originate from biomass burning [*Woods et al.*, 1991; *Echalar et al.*, 1995; *Gaudichet et al.*, 1995]. However, they were described as less than 1-μm crystals, rather than forming large aggregates as we observed. The morphology and fine grain size of the calcium-bearing particles in our smoke samples suggest that they are not mineral dust. We infer that they condensed during the burning process from elements in the burnt vegetation. However, further work is needed to confirm the vegetative source.

[18] The calcium-bearing particles were common in the smoke samples, but rarely occurred in the hazes. This scarcity may be because of the large sizes of the aggregates and thus their short residence time in the atmosphere.

3.1.5. Mineral Dust and Sea Salt

[19] The majority of the coarse aerosol particles that were collected over southern Africa consisted of mineral dust and sea salt, most with diameters larger than 2 μm. Compared to the high abundances of carbonaceous particles and potassium salts, only minor amounts of mineral dust and sea salt occurred in the smoke plumes. The main minerals were quartz, muscovite, smectite, illite, and rutile (Figure 7).

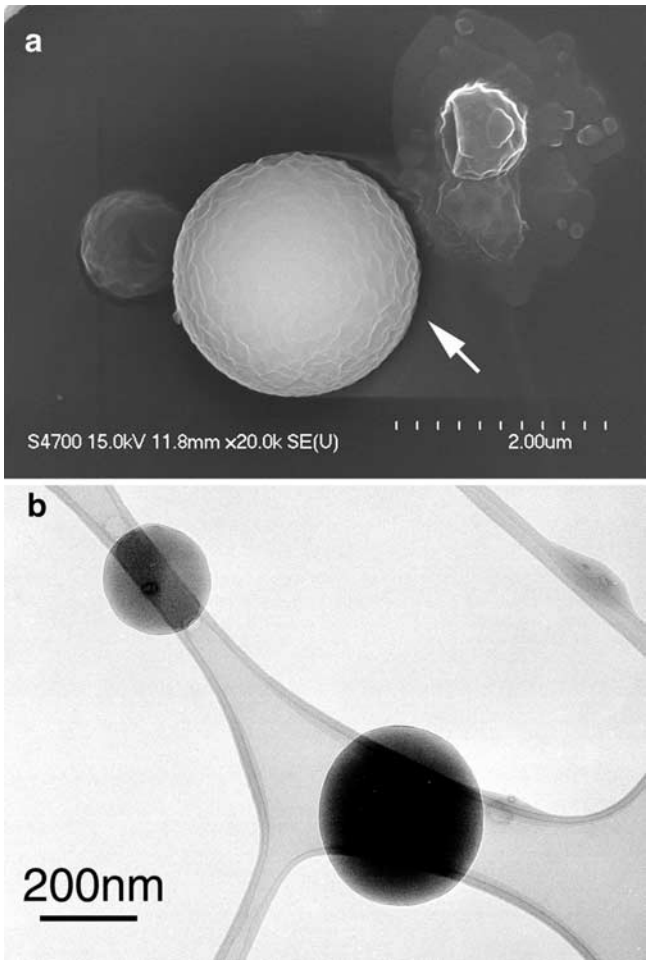

Figure 3. (a) Scanning electron microscope image of a tar ball (arrowed) in young smoke from the Madikwe Game Reserve fire, South Africa, on 20 August 2000; (b) TEM image of tar balls in aged smoke 16 km downwind from the Timbavati fire on 7 September 2000.

Some were aggregated with sea salt, organic particles, and tar balls. Based on compositions and SAED patterns, most of the NaCl in the sea-salt particles was deduced to have partly or completely reacted to Na_2SO_4 and $NaNO_3$, probably as a result of reactions with sulfuric acid, nitric acid, and/or NO_x during transport.

[20] The minerals in the smoke plumes may have deposited on the vegetation before the fire and then have been resuspended into the plume during burning [*Hegg et al.*, 1990]. Intensive fires can mobilize soil dust from the ground [*Gaudichet et al.*, 1995]. The occurrence of sea salt in our samples suggests the incursion of marine air.

3.1.6. Ammonium Sulfate

[21] Ammonium sulfate is a minor species in the smoke samples we examined. Most particles were less than 500 nm across. Less than 5% of the ammonium sulfate particles contain soot inclusions.

3.2. Aging of the Smoke From Biomass Burning

[22] Three sets of smoke samples were collected on 7 September 2000 in the plume from a prescribed fire near the Timbavati Game Reserve in South Africa. These samples were obtained from close to the fire, 16 km downwind, and 8 to 37 km along the length of the plume. This kind of sampling enables us to study the reactions and evolution of the smoke aerosols during short-term aging in the atmosphere. A detailed description of the evolution of gases and particles in the Timbavati smoke plume is given by *Hobbs*

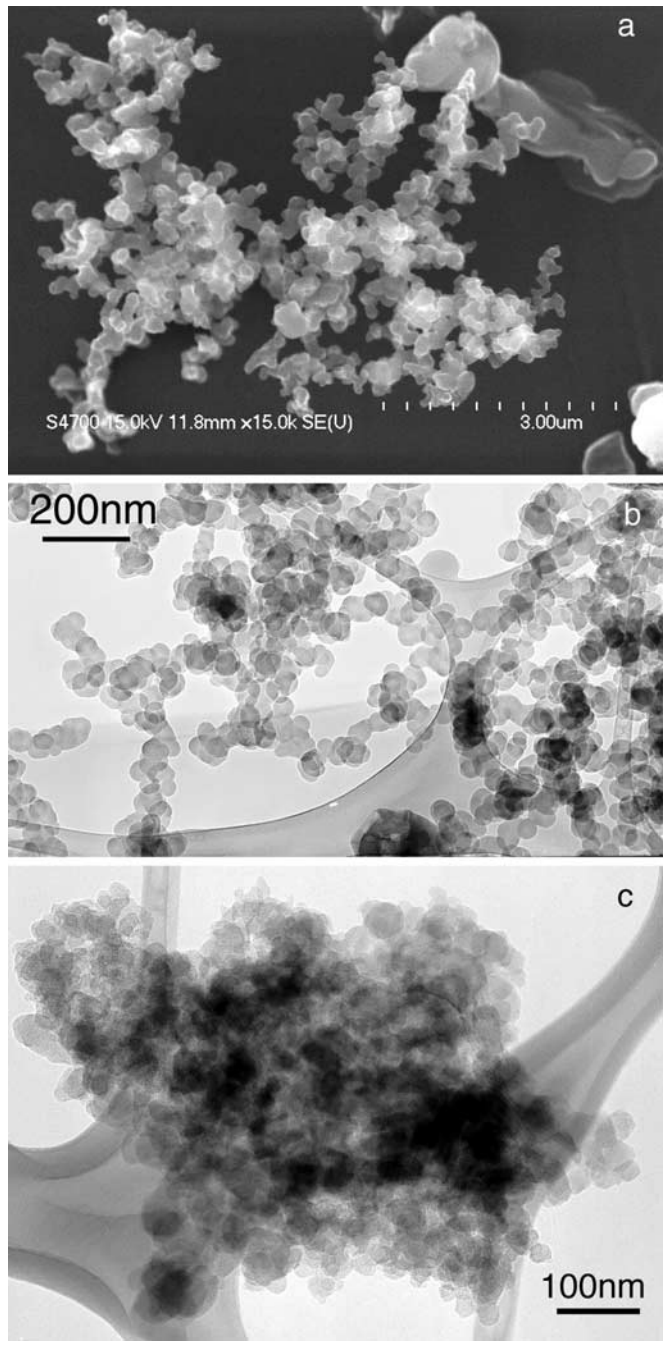

Figure 4. (a) Scanning electron microscope image of soot aggregates in young smoke from the Madikwe Game Reserve fire, South Africa, on 20 August 2000; (b) TEM image of chain-like soot aggregates in flaming smoke from the dambo fire near Kaoma, Zambia, on 5 September 2000; (c) TEM image of a compact soot aggregate in regional haze near Skukusa, South Africa, on 22 August 2000.

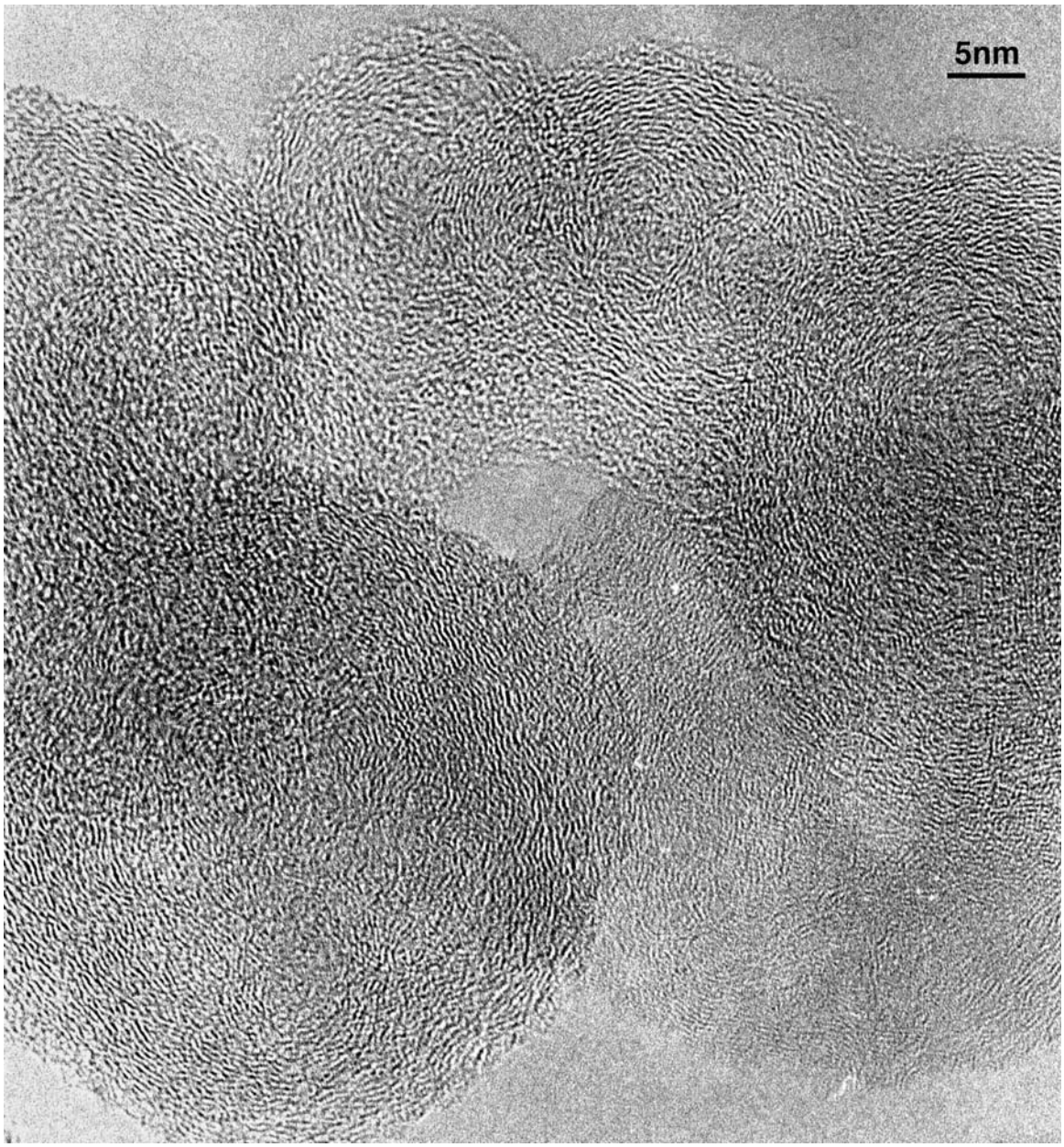

Figure 5. High-resolution TEM image of a soot aggregate in smoke from the Madikwe Game Reserve fire, South Africa, on 20 August 2000. The soot spheres show structures with onion-like curved, disordered graphitic (graphene) layers.

et al. [2003]. Here we are concerned with the changes of individual smoke particles as the smoke aged.

[23] Euhedral KCl crystals were the most abundant inorganic particle type in the young smoke from the Timbavati fire. Some tar balls were present, and partly or completely reacted sea-salt particles also occurred including Na_2SO_4, $NaNO_3$, and their mixtures with NaCl. Large aggregates of small calcium-bearing particles were also present in the smoke; these included calcium carbonate, sulfate, and phosphate. There were only small amounts of chain-like soot aggregates. In the smoke sample collected 16 km downwind of the fire, most of the KCl particles had been converted to K_2SO_4 and KNO_3, with only minor KCl left. The particles collected from 8 to 37 km downwind from the fire contained mixtures of potassium sulfate, nitrate, and lesser amounts of chloride in potassium salts. The atomic percentages of the major elements potassium, chlorine, and sulfur (nitrogen was not quantified) in the potassium salts of the three sets of samples are plotted in the triangle diagrams in Figure 8. The diagrams show the relative abundances of different potassium salts in the young and older smoke, and the conversion of KCl particles to sulfate and nitrate with aging of the smoke.

[24] The trend of the transformation in the potassium salts is consistent with previous analyses of particles from biomass burning in Africa [*Gaudichet et al.*, 1995; *Ruellan et al.*, 1999; *Liu et al.*, 2000]. However, using TEM, we were able to see the morphologies, structures, and compositions

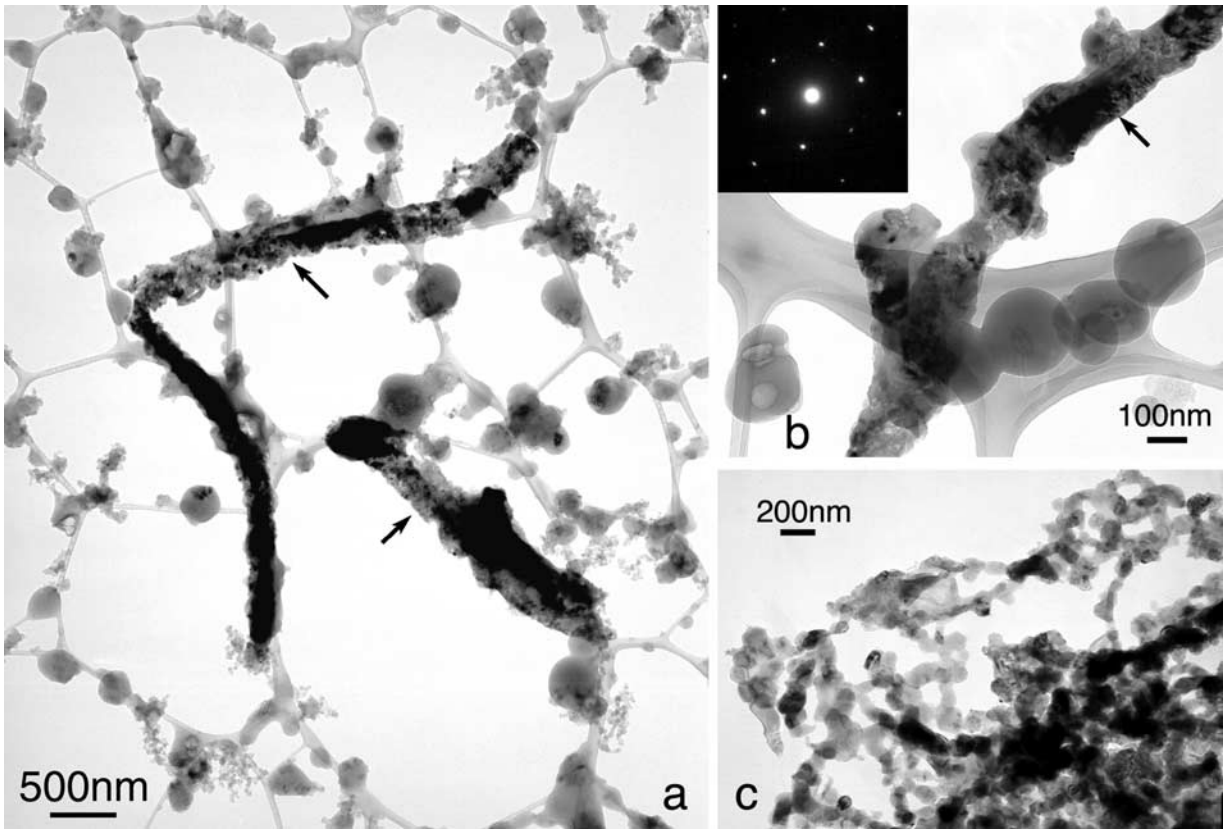

Figure 6. Transmission electron microscope images of aggregates of calcium-rich particles. (a) Large aggregates (arrowed) of fine calcium sulfate and phosphate particles in smoke from the dambo fire near Kaoma, Zambia, on 5 September 2000. Most particles also contain variable amounts of potassium and magnesium, and are internally or externally mixed with soot and organic particles with potassium-salt inclusions; (b) Calcium carbonate particles (arrowed) aggregated with tar balls in aged smoke 8 to 37 km downwind of the Timbavati fire, South Africa, on 7 September 2000. Most of the $CaCO_3$ is calcite, as confirmed by the inset SAED pattern; (c) Aggregates of $CaCO_3$ particles in smoke collected close to the Timbavati fire, South Africa, on 7 September 2000. Most particles in (c) are aragonite crystals.

of individual potassium-salt particles to confirm their transformation.

[25] The concentration of tar balls also changed as the smoke aged. In the young smoke and the smoke at 16 km downwind, the relative number concentration of tar balls was less than 5%. However, in the smoke sample from 8 to 37 km downwind, the abundance of tar balls increased to ~20%. This increase suggests condensation from organic gases or transformation from other organic particles during aging [*Pósfai et al.*, 2003].

[26] The conversion of KCl to sulfate and nitrate is similar to the transformation of sea salt observed in other field studies [*Pósfai et al.*, 1995; *Li et al.*, 2003]. Similar reaction mechanisms are probably involved in the conversions of KCl in smoke particles and NaCl in sea salt. During transport, photochemical oxidation and aqueous-phase reactions between KCl particles and SO_2 could form particulate K_2SO_4 and release gaseous HCl. In southern Africa, sulfur dioxide had various sources including biomass burning [*Andreae et al.*, 1998; *Sinha et al.*, 2003], industrial, and biogenic. The formation of KNO_3 probably resulted from the reaction of KCl with gaseous HNO_3 that formed through photochemical reaction of NO_x emitted by the fires.

[27] Based on a wind speed of 11.3 ± 0.9 m s^{-1} measured from the aircraft, it took ~24 min for the smoke to travel from the fire to 16 km downwind. During this period, more than 90% of the KCl particles were completely converted to potassium sulfate or nitrate. *Gaudichet et al.* [1995] also reported that the conversion from KCl to potassium sulfate occurred within rather short distances of fires.

[28] *Rogers et al.* [1991] reported that the majority (80 to 100%) of the submicrometer particles from biomass burning act as CCN. Our observations support the fact that smoke particles can be efficient CCN, because organic particles with water-soluble potassium salts dominated in the smoke samples from biomass-burning in southern Africa. Although the analytical methods we used cannot identify the organic species, ion chromatography analyses revealed the presence of water-soluble organic species in savanna fire emissions [*Allen and Miguel*, 1995; *Gao et al.*, 2003]. Some of these soluble organic materials were likely in the organic particles with potassium-salt inclusions [*Pósfai et al.*, 2003]. On the other hand, the transformation from KCl to potassium sulfate and nitrate with aging of the smoke could lead to changes in the hygroscopic properties of the smoke particles and thus their cloud-nucleating

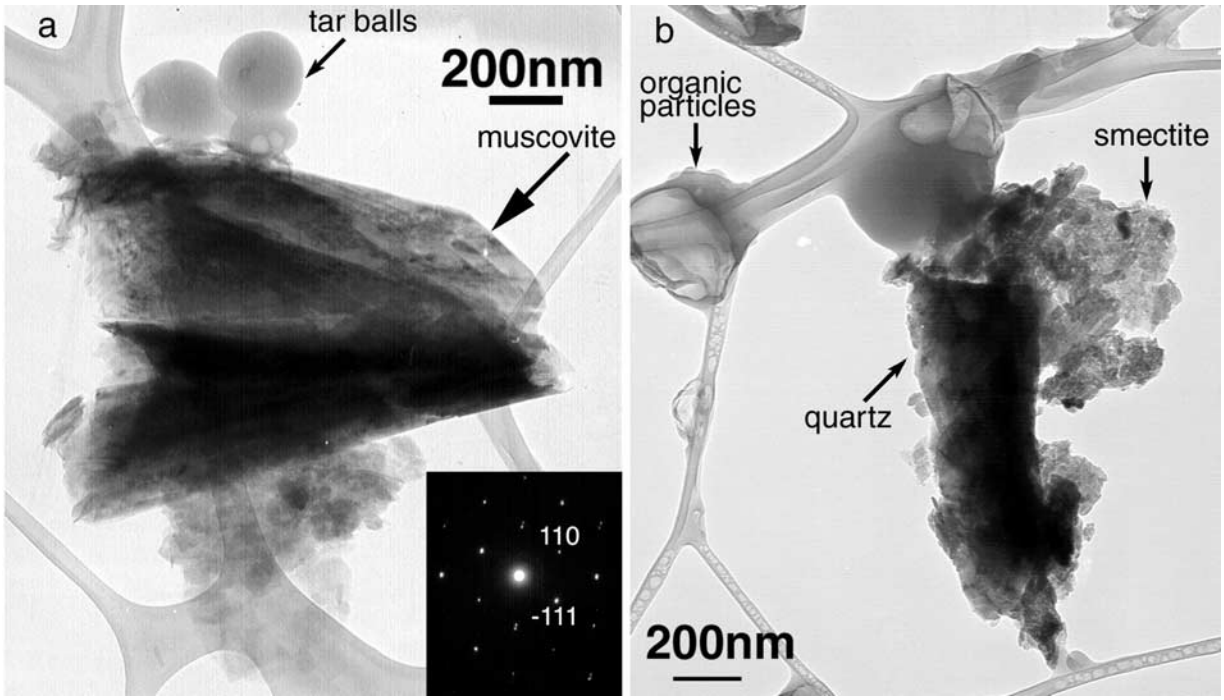

Figure 7. Transmission electron microscope images of mineral dust in regional haze over South Africa on 22 August 2000. (a) Muscovite particles with tar balls; (b) Quartz aggregated with smectite and organic particles. Most organic particles are internally mixed with K salts, which were damaged by the electron beam.

potential. Because the deliquescence relative humidities of K_2SO_4 (97.4% at 298 K) and KNO_3 (92.5% at 298K) are higher than that of KCl (84.3% at 298K) [*Dean*, 1992], some of the aged smoke particles may have been less efficient in cloud nucleation than those in the nascent smoke.

3.3. Effects of Fuel Type and Burning Phase

[29] Emissions from fires are related to the nature of the fuel and the burning processes [*Hobbs et al.*, 1996]. Smoke from a flaming dambo grass fire near Kaoma, Zambia, was sampled on 5 September 2000. Soot aggregates of varied sizes were abundant in the smoke. The number concentration of soot aggregates in this fire was 18%, compared to 3% in the plume from the Timbavati fire, which burned mostly wood and bush (Table 2). *Patterson and McMahon* [1984] also reported that smoke from flaming combustion contains considerably more soot than that from smoldering combustion. During flaming combustion, the oxygen supply is limited, and parts of the flame are quenched before the oxidation of carbon radicals is complete, thus leading to the formation of soot [*Andreae et al.*, 1998].

[30] The modified combustion efficiency (MCE) can be used to quantify the relative amounts of flaming and smoldering combustion of a fire [*Ward and Hao*, 1992]. The MCE is defined as the ratio of carbon emitted as CO_2 to the total CO_2 and CO emitted. According to laboratory studies of *Yokelson et al.* [1996], pure flaming combustion has an MCE near 0.99 and pure smoldering combustion an MCE of $\sim$0.80. Therefore, an MCE >0.9 suggests >50% flaming combustion, and an MCE <0.9 suggests >50% smoldering combustion.

[31] The fire average MCE for the dambo fire near Kaoma, Zambia (0.974) was the highest of all the fires studied in SAFARI 2000 [*Sinha et al.*, 2003; *Yokelson et al.*, 2003]; the fire-average MCE for the Timbavati fire was much lower (0.935, Table 2). The greater MCE value of the dambo fire indicates a higher percentage of flaming combustion, which produced the distinctly greater soot abundance. EDS analyses of the potassium-salt particles from the dambo grass fire showed that they were mostly potassium sulfate and nitrate, with few chloride particles.

[32] The smoke collected from a biomass fire in the Madikwe Game Reserve on 20 August 2000 also contains large chain-like soot aggregates, although the number concentration of soot aggregates is lower than that for the dambo fire (Table 2). In addition to submicrometer, rounded or irregularly shaped potassium sulfate and nitrate, the smoke in the Madikwe fire contains abundant euhedral KCl crystals that were not observed in the dambo fire. The vegetation burnt in the Madikwe fire was mostly grass and bush, with MCEs ranging from 0.936 to 0.958 when our sample was collected [*Sinha et al.*, 2003; *Yokelson et al.*, 2003]. The Madikwe fire had an MCE and soot number concentration that were intermediate between those of the dambo and the Timbavati fires.

[33] The MCEs and soot number concentrations for the three fires are positively correlated with the BC/TC ratios measured by *Kirchstetter et al.* [2003], which indicates that the most flaming dambo grass fire produced the largest amount of soot and led to the highest black carbon-to-total carbon (BC/TC) ratios.

[34] Because of the strong light-absorption capability of soot, the large amount of soot emitted during intense

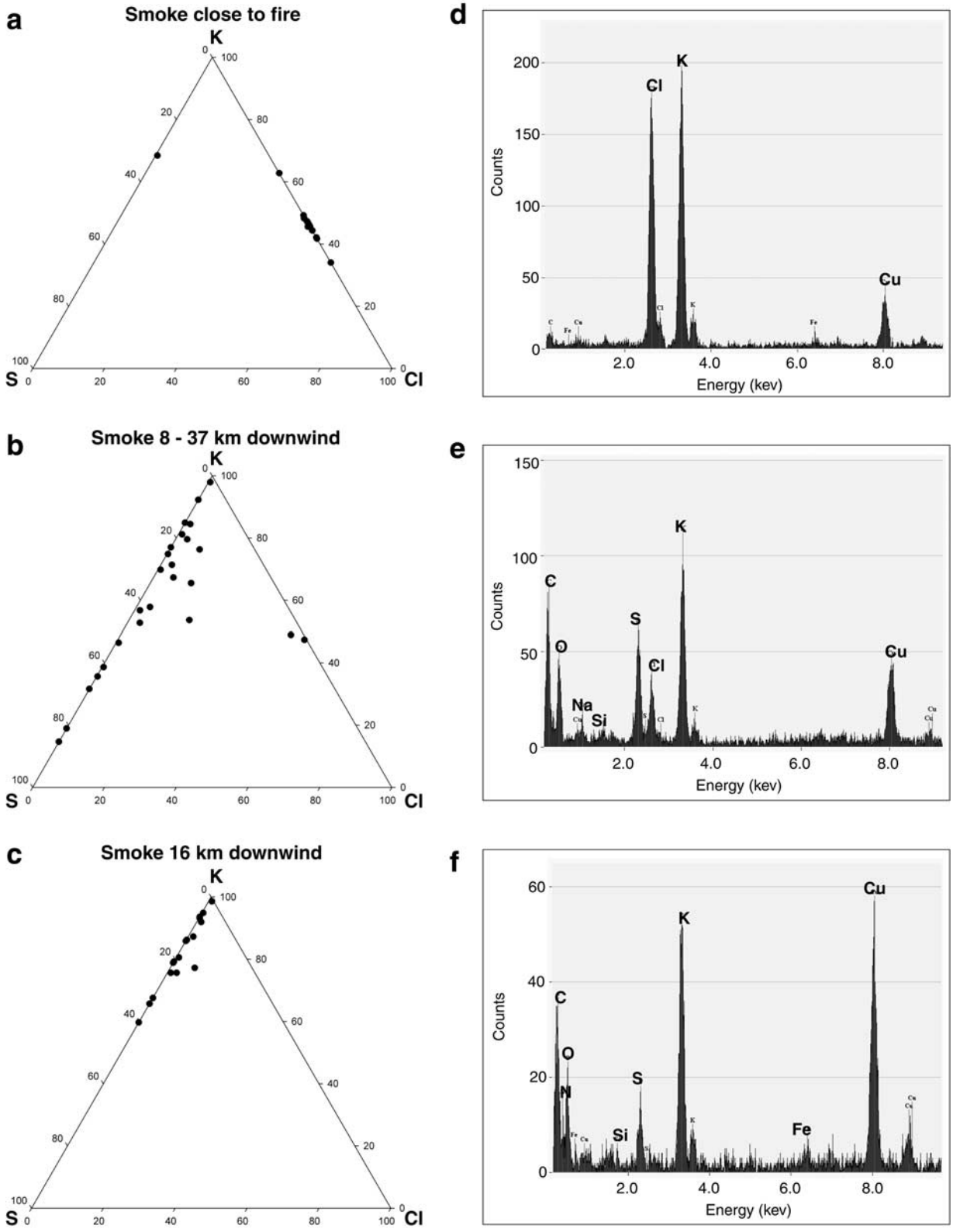

Figure 8. Compositional variations of K-salt particles with aging of smoke from the Timbavati fire, South Africa, on 7 September 2000. (a), (b), and (c) show relative atomic percentages of potassium, sulfur, chlorine in potassium salts in young smoke, smoke from 8 to 37 km downwind of the fire, and smoke 16 km downwind, respectively, indicating the transformation from KCl to K_2SO_4 and KNO_3 as the smoke aged. (d) An EDS spectrum of a KCl particle in young smoke; (e) and (f) EDS spectra of partly and completely reacted potassium-salt particles, respectively. The copper in the spectra is from the substrate.

Table 2. Comparison of Three Fires

Fire Location and Date	Vegetation Type	MCE[a]	Number Concentration of Soot Aggregates, %	BC/TC[b]
Kaoma, Zambia, 5 September 2000	Dambo grass	0.974	~18	0.26
Madikwe Game Reserve, 20 August 2000	Grass and bush	0.936–0.958	~8	0.16–0.18
Timbavati Game Reserve, 7 September 2000	Wood and bush	0.935	~3	0.12–0.15

[a]From *Yokelson et al.* [2003].
[b]From *Kirchstetter et al.* [2003].

biomass burning could perturb the regional vertical temperature profile [*Ross et al.*, 1998].

3.4. Aerosol Particles in Haze Layers and in the Free Troposphere

[35] Particles in regional hazes were collected on 22 August 2000 at altitudes from 335 to 1219 m over Skukusa, South Africa. Ammonium sulfate particles were abundant in the boundary layer haze, accounting for more than 50% of the total fine particles by number. Some ammonium sulfate particles left carbon-rich residues after evaporation under electron-beam radiation, which suggests the presence of organic coatings [*Buseck and Pósfai*, 1999; *Pósfai et al.*, 1999; *Pósfai and Molnar*, 2000]. Some particles had inclusions of soot or organic matter. *Pósfai et al.* [2003] also describe internal mixing of sulfate with soot and organic particles in hazes over southern Africa. Some of the chain-like or compact soot aggregates were externally mixed with ammonium sulfate in the Skukusa sample. Most soot aggregates contained potassium, which indicates that they originated from biomass burning. Organic particles with mostly potassium sulfate and some potassium nitrate inclusions were also present. In the coarse-particle size fraction, there were higher concentrations of reacted sea salt than mineral dust. The concentrations of sea-salt particles and minerals were higher in the haze samples than in the smoke samples. Some particles had mineral cores coated with soluble sulfate containing sodium and magnesium, which suggests possible cloud processing of mineral dust and sea salt particles. A few flyash spheres, which are amorphous spheres of silica or aluminosilicates containing minor potassium, calcium, and iron, were present as aggregates with soot, or coated with ammonium sulfate.

[36] Compact soot aggregates were also present in the haze samples (Figure 4c); such particles were rarely observed in the smoke plumes. Their presence in the

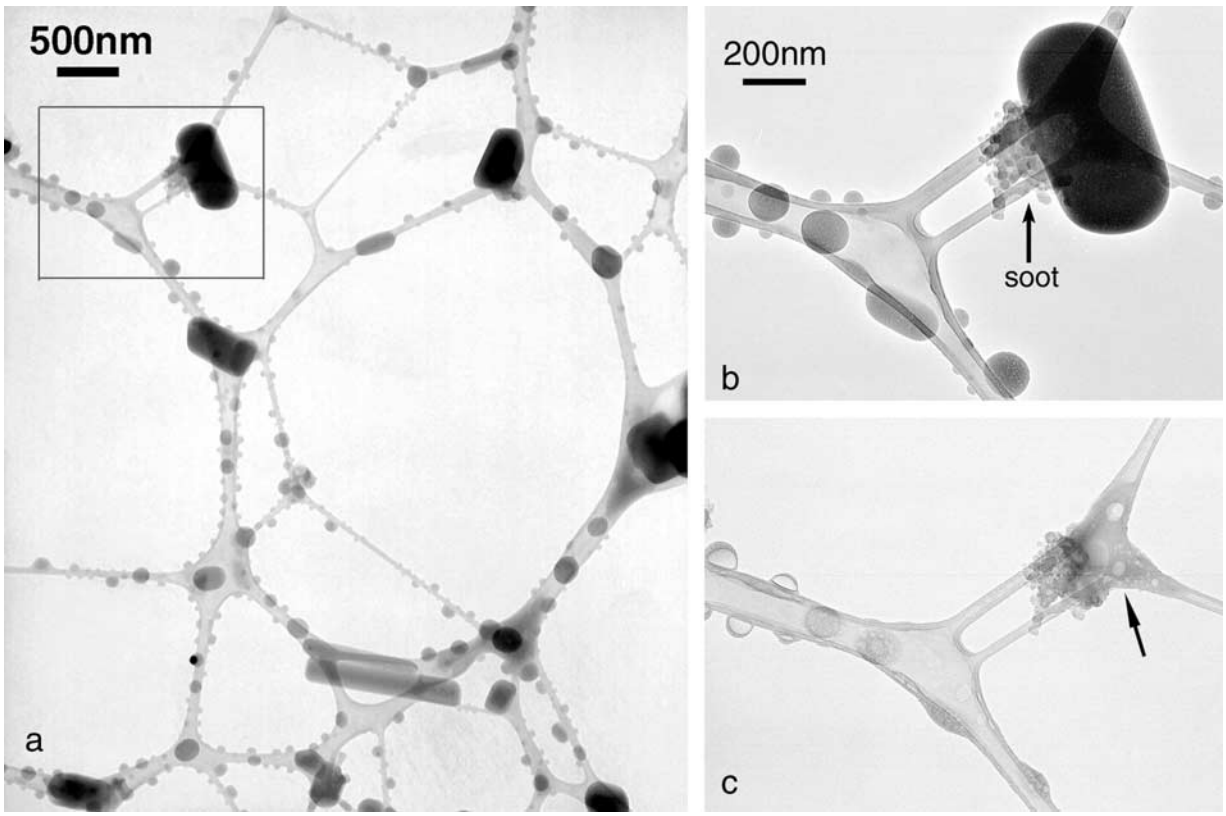

Figure 9. (a) Transmission electron microscope image of ammonium sulfate particles collected in the free troposphere near Pietersburg, South Africa, on 23 August 2000. Some particles are round and others are elongated. (b) Enlarged image of the framed area in (a), showing an $(NH_4)_2SO_4$ particle aggregated with soot; (c) Residues of the $(NH_4)_2SO_4$ particles (arrowed) after evaporation under the electron beam. The large particle contained a soot inclusion, whereas the smaller particles did not.

regional haze could be a result of the aging of the smoke. The structure, composition, and size of smoke particles can change rapidly with aging [*Hallet et al.*, 1989; *Reid and Hobbs*, 1998]. Chain-like soot aggregates (Figures 4a and 4b) in young smoke usually break down and collapse into more closely packed particles with increased sphericity [*Ruellan et al.*, 1999]. The higher abundances of potassium sulfate and nitrate than KCl in the regional hazes also indicates older smoke particles.

[37] Organic particles with potassium-salt inclusions and potassium-bearing soot were emitted during biomass burning, while ammonium sulfate could have formed from precursors from biomass burning and industrial emissions. However, the various types of aerosol particles in the haze samples suggest that different sources contributed to their formation over southern Africa. Biomass burning was an important contributor, but terrestrial, marine, and industrial emissions were also significant constituents of hazes in this region.

[38] Ammonium sulfate particles dominated in a sample collected in the free troposphere near Pietersburg, South Africa, on 23 August 2000 (Figure 9). These particles were euhedral or rounded, and their size distribution was bimodal, with most particle diameters <300 nm or from 500 nm to 2 μm. Less than 5% of the ammonium sulfate particles contained soot inclusions. After evaporation by the electron beam, some sulfate particles left similar residues as the particles in the haze layers. Only minor soot, tar balls, and organic particles were present in the sample from the free troposphere near Pietersburg; the low abundance of these particles indicate little influence from biomass burning.

4. Conclusions

[39] Major aerosol types in the smoke from biomass burning in southern Africa included KCl, K_2SO_4, and KNO_3 salts, organic particles, tar balls, soot, and calcium-bearing particles. Lesser amounts of sea salt and minerals and minor amounts of ammonium sulfate were also present. Particulate emissions varied with the vegetation types burnt and the burn intensities (flaming or smoldering). Large amounts of soot aggregates were produced by flaming grass fires.

[40] Most of the aerosol particles from biomass burning were in the submicrometer size range. Because of their small sizes and long residence times in the atmosphere, these particles have important effects on climate change and nutrient cycles. Long-range transport of fine particles can cause significant loss of nutrients such as potassium, sulfur, nitrogen, and phosphorus from their source regions.

[41] The high abundance of water-soluble salts and organic particles suggests that the smoke particles could act as efficient CCN. Through their effects on clouds, the combustion particles may contribute significantly to indirect radiative forcing. Aging of smoke can modify the properties of the pyrogenic particles. With aging, KCl particles are transformed into K_2SO_4 or KNO_3 through reactions with sulfur- and nitrogen-containing species. The different hygroscopic properties of these salt particles will also affect their cloud-nucleating ability.

[42] Particles from biomass burning are important components of regional hazes over southern Africa, although industrial, terrestrial, and marine aerosols also contribute to the hazes.

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References

Allen, A. G., and A. H. Miguel, Biomass burning in the Amazon: Characterization of the ionic component of aerosols generated from flaming and smoldering rainforest and savanna, *Environ. Sci. Technol.*, *29*, 486–493, 1995.

Andreae, M. O., Soot carbon and excess fine potassium: Long-range transport of combustion-derived aerosols, *Science*, *220*, 1148–1151, 1983.

Andreae, M. O., Biomass burning: Its history, use and distribution and its impact on environmental quality and global climate, in *Global Biomass Burning: Atmospheric, Climatic and Biospheric Implications*, edited by J. S. Levine, pp. 3–21, MIT Press, Cambridge, Mass., 1991.

Andreae, M. O., et al., Airborne studies of aerosol emissions from savanna fires in southern Africa, 2, Aerosol chemical composition, *J. Geophys. Res.*, *103*, 32,119–32,128, 1998.

Buseck, P. R., and M. Pósfai, Airborne minerals and related aerosol particles: Effects on climate and the environment, *Proc. Natl. Acad. Sci. U. S. A.*, *96*, 3372–3379, 1999.

Buseck, P. R., D. Jacob, M. Pósfai, J. Li, and J. R. Anderson, Minerals in the air: An environmental perspective, in *Frontiers in Geochemistry: Global Inorganic Chemistry*, *Konrad Krauskopf*, vol. 1, *International Book Series*, vol. 5, edited by W. G. Ernst, pp. 106–122, Bellwether, Columbia, Md., 2002.

Buseck, P. R., L. A. Garvie, J. Li, and M. Pósfai, Chemical analysis of individual aerosol particles by electron energy-loss spectroscopy (EELS), *Eos Trans. AGU, Fall Meet. Suppl.*, *82*(47), A11B-04, 2001.

Cachier, H., J. Ducret, M.-P. Bremond, V. Yoboue, J. P. Lacaux, A. Gaudichet, and J. Baudet, Biomass burning aerosols in a savanna region of the Ivory Coast, in *Global Biomass Burning*, edited by J. S. Levine, pp. 174–184, MIT Press, Cambridge, Mass., 1991.

Crutzen, P. J., and M. O. Andreae, Biomass burning in the tropics—Impact on atmospheric chemistry and biogeochemical cycles, *Science*, *250*, 1669–1678, 1990.

Dean, J. A., *Lange's Handbook of Chemistry*, McGraw-Hill, New York, 1992.

Dickinson, R. E., Effect of fires on global radiative budget through aerosol and cloud properties, in *Fire in the Environment: The Ecological, Atmospheric and Climatic Importance of Vegetation Fires*, edited by J. G. Goldammer, pp. 107–122, John Wiley, New York, 1993.

Eatough, D., N. Eatough, P. Yanbo, S. Sizemore, T. W. Kirchstetter, T. Novakov, and P. V. Hobbs, Semivolatile particulate organic material in southern Africa during SAFARI 2000, *J. Geophys. Res.*, *108*, doi:10.1029/2002JD002296, in press, 2003.

Echalar, F., A. Gaudichet, H. Cachier, and P. Artaxo, Aerosol emissions by tropical forest and savanna biomass burning: Characteristic trace elements and fluxes, *Geophys. Res. Lett.*, *22*, 223,039–223,042, 1995.

Gao, S., D. A. Heggs, P. V. Hobbs, T. W. Kirchstetter, B. Magi, and M. Sadilek, Water-soluble organic components in aerosols associated with savanna fires in southern Africa: Identification, evolution and distribution, *J. Geophys. Res.*, *108*, doi:10.1029/2002JD002324, in press, 2003.

Gaudichet, A., F. Echalar, B. Chatenet, J. P. Quisefit, G. Malingre, H. Cachier, P. Buatmenard, P. Artaxo, and W. Maenhaut, Trace-elements in tropical African savanna biomass burning aerosols, *J. Atmos. Chem.*, *22*, 19–39, 1995.

Goldammer, J. G., and P. J. Crutzen, Fire in the environment: Scientific rationale and summary of results of the Dahlem workshop, in *Fire in the Environment: The Ecological, Atmospheric and Climatic Importance of Vegetation Fires*, edited by P. J. Crutzen, pp. 1–14, John Wiley, New York, 1993.

Hallet, J., J. G. Hudson, and C. F. Rogers, Characterization of combustion aerosols for haze and cloud formation, *Aerosol Sci. Technol.*, *10*, 70–83, 1989.

Hegg, D. A., L. F. Radke, P. V. Hobbs, R. A. Rasmusson, and P. J. Riggan, Emissions of some trace gases from biomass fires, *J. Geophys. Res.*, *95*, 5669–5675, 1990.

Hobbs, P. V., and L. F. Radke, Cloud condensation nuclei from a simulated forest fire, *Science*, *163*, 279–280, 1969.

Hobbs, P. V., J. S. Reid, J. A. Herring, J. D. Nance, R. E. Weiss, J. L. Ross, D. A. Hegg, R. D. Ottmar, and C. Liousse, Particle and trace-gas measurements in the smoke from prescribed burns of forest products in the Pacific Northwest, in *Biomass Burning and Global Change*, edited by J. S. Levine, pp. 697–715, MIT Press, Cambridge, Mass., 1996.

Hobbs, P. V., P. Sinha, R. J. Yokelson, T. J. Christian, D. R. Blake, S. Gao, T. W. Kirchstetter, T. Novakov, and P. Pilewkie, Evolution of gases and particles from a savanna fire in South Africa, *J. Geophys. Res.*, *108*, doi:10.1029/2002JD002392, in press, 2003.

IPCC, *Climate Change 1995*, Cambridge Univ. Press, New York, 1996.

Kaufman, J. B., D. L. Cummings, and D. E. Ward, Relationships of fire, biomass and nutrient dynamics along a vegetation gradient in the Brazilian cerrado, *J. Ecol.*, *82*, 519–531, 1994.

Kirchstetter, T. W., T. Novakov, P. V. Hobbs, and B. Magi, Airborne measurements of carbonaceous aerosols in southern Africa during the biomass burning season, *J. Geophys. Res.*, *108*, doi:10.1029/2002JD2171, in press, 2003.

Kuhlbusch, T. A. J., and P. J. Crutzen, Black carbon, the global carbon cycle, and atmospheric carbon dioxide, in *Biomass Burning and Global Change*, edited by J. S. Levine, pp. 161–169, MIT Press, Cambridge, Mass., 1996.

Kuhlbusch, T. A. J., M. O. Andreae, H. Cachier, J. G. Goldammer, J. P. Lacaux, R. Shea, and P. J. Crutzen, Black carbon formation by savanna fires: Measurements and implications for the global carbon cycle, *J. Geophys. Res.*, *101*, 23,651–23,665, 1996.

Li, J., J. R. Anderson, and P. R. Buseck, TEM study of aerosol particles from clean and polluted marine boundary layers over the North Atlantic, *J. Geophys. Res.*, *108*, doi:10.1029/2002JD002106, in press, 2003.

Liu, X. D., P. Van Espen, F. Adams, J. Cafmeyer, and W. Maenhaut, Biomass burning in southern Africa: Individual particle characterization of atmospheric aerosols and savanna fire samples, *J. Atmos. Chem.*, *36*, 135–155, 2000.

Martins, J. V., P. Artaxo, P. V. Hobbs, C. Liousse, H. Cachier, Y. J. Kaufman, and A. Plana-Fattori, Particle size distributions, elemental compositions, carbon measurements and optical properties of smoke from biomass burning in the Pacific Northwest of the United States, in *Biomass Burning and Global Change*, edited by J. S. Levine, pp. 716–732, MIT Press, Cambridge, Mass., 1996.

Martins, J. V., P. V. Hobbs, R. E. Weiss, and P. Artaxo, Sphericity and morphology of smoke particles from biomass burning in Brazil, *J. Geophys. Res.*, *103*, 32,051–32,057, 1998.

Menaut, J. C., L. Abbadie, and P. M. Vitousek, Nutrient and organic matter dynamics in tropical ecosystems, in *Fire in the environment: The Ecological, Atmospheric and Climatic Importance of Vegetation Fires*, edited by J. G. Goldammer, pp. 215–231, John Wiley, New York, 1993.

Okada, K., M. Ikegami, Y. Zaizen, Y. Makino, J. B. Jensen, and J. L. Gras, The mixture state of individual aerosol particles in the 1997 Indonesian haze episode, *J. Aerosol Sci.*, *32*, 1269–1279, 2001.

Patterson, E. M., and C. K. McMahon, Absorption characteristics of forest fire particulate matter, *Atmos. Environ.*, *18*, 182,541–182,551, 1984.

Penner, J. E., R. E. Dickinson, and C. A. O'Neill, Effects of aerosol from biomass burning on the global radiation budget, *Science*, *256*, 1432–1434, 1992.

Pósfai, M., and A. Molnar, Aerosol particles in the troposphere: A mineralogical introduction, *EMU Notes Mineral.*, *2*, 197–252, 2000.

Pósfai, M., J. R. Anderson, P. R. Buseck, T. W. Shattuck, and N. W. Tindale, Constituents of a remote Pacific marine aerosol: A TEM study, *Atmos. Environ.*, *28*, 1747–1756, 1994.

Pósfai, M., J. R. Anderson, P. R. Buseck, and H. Sievering, Compositional variations of sea-salt-mode aerosol particles from the North Atlantic, *J. Geophys. Res.*, *100*, 23,063–23,074, 1995.

Pósfai, M., J. R. Anderson, P. R. Buseck, and H. Sievering, Soot and sulfate aerosol particles in the remote marine troposphere, *J. Geophys. Res.*, *104*, 21,685–21,693, 1999.

Pósfai, M., R. Simonics, J. Li, P. V. Hobbs, and P. R. Buseck, Individual aerosol particles from biomass burning in southern Africa: 1. Compositions and size distributions of carbonaceous particles, *J. Geophys. Res.*, *108*, doi:10.1029/2002JD002291, in press, 2003.

Reid, J. S., and P. V. Hobbs, Physical and optical properties of young smoke from individual biomass fires in Brazil, *J. Geophys. Res.*, *103*, 32,013–32,030, 1998.

Rogers, C. F., J. G. Hudson, B. Zielinska, R. L. Tanner, J. Hallet, and J. G. Watson, Cloud condensation nuclei from biomass burning, in *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, edited by J. S. Levine, pp. 431–438, MIT Press, Cambridge, Mass., 1991.

Ross, J. L., P. V. Hobbs, and B. Holben, Radiative characteristics of regional hazes dominated by smoke from biomass burning in Brazil: Closure tests on direct radiative forcing, *J. Geophys. Res.*, *103*, 31,925–31,941, 1998.

Ruellan, S., H. Cachier, A. Gaudichet, P. Masclet, and J. P. Lacaux, Airborne aerosols over central Africa during the experiment for regional sources and sinks of oxidants (EXPRESSO), *J. Geophys. Res.*, *104*, 30,673–30,690, 1999.

Sheridan, P. J., R. C. Schnell, J. D. Kahl, J. F. Boatman, and D. M. Garvey, Microanalysis of the aerosol collected over south-central New Mexico during the ALIVE field experiment, May–December, 1989, *Atmos. Environ.*, *27A*, 1169–1183, 1993.

Sinha, P., P. V. Hobbs, R. J. Yokelson, I. T. Bertschi, D. R. Blake, I. J. Simpson, S. Gao, T. W. Kirchstetter, and T. Novakov, Emissions of trace gases and aerosols from biomass burning in southern Africa, *J. Geophys. Res.*, *108*, doi:10.1029/2002JD002326, in press, 2003.

Ward, D. E., and W. M. Hao, Air toxic emission from burning of biomass globally—Preliminary estimates, in *Proceedings of the 85th Annual Meeting and Exhibition*, Air and Waste Manage. Assoc., Vancouver, British Columbia, 1992.

Woods, D. C., R. L. Chuan, W. R. I. Cofer, and J. S. Levine, Aerosol characterization in smoke plumes from burning at a Florida wildlife refuge, in *Global Biomass Burning: Atmospheric, Climatic and Biospheric Implications*, edited by J. S. Levine, pp. 240–244, MIT Press, Cambridge, Mass., 1991.

Yamasoe, M. A., P. Artaxo, A. H. Miguel, and A. G. Allen, Chemical compositions of aerosol particles from direct emissions of vegetation fires in the Amazon Basin: Water-soluble species and trace elements, *Atmos. Environ.*, *34*, 1641–1653, 2000.

Yokelson, R. J., D. W. T. Griffith, and D. E. Ward, Open-path Fourier transform infrared studies of large-scale laboratory biomass fires, *J. Geophys. Res.*, *101*, 21,067–21,080, 1996.

Yokelson, R. J., I. T. Bertschi, T. J. Christian, P. V. Hobbs, D. E. Ward, and W.-M. Hao, Trace gas measurements in nascent, aged and cloud-processed smoke from African savanna fires by airborne Fourier transform infrared spectroscopy (AFTIR), *J. Geophys. Res.*, *108*, doi:10.1029/2002JD002322, in press, 2003.

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