

# Soot and sulfate aerosol particles in the remote marine troposphere

Mihály Pósfai,<sup>1</sup> James R. Anderson, and Peter R. Buseck

Departments of Geology and Chemistry, Arizona State University, Tempe

Herman Sievering

Global Change and Environmental Quality Program and Center for Environmental Sciences, University of Colorado at Denver

**Abstract.** Sulfate aerosol particles containing soot aggregates were observed in the marine troposphere in both hemispheres under conditions that ranged from extremely clean to heavily polluted. Even in clean air above the remote Southern Ocean during the First Aerosol Characterization Experiment (ACE 1), depending on the sample, between 10 and 45% of sulfate particles contained soot inclusions. We identified aircraft emissions and biomass burning as the most likely major sources of soot. Internally mixed soot and sulfate appear to comprise a globally significant fraction of aerosols in the troposphere. Anthropogenic combustion aerosols can thus potentially change the radiative climate effects of sulfate aerosols and may have an impact on cloud properties even in the remote troposphere.

## 1. Introduction

Sulfate and carbonaceous particles are the two most important anthropogenic aerosol constituents influencing climate [Charlson *et al.*, 1992; Chuang *et al.*, 1997; Haywood and Ramaswamy, 1998; Schult *et al.*, 1997]. Biomass burning [Crutzen and Andreae, 1990; Hobbs *et al.*, 1997] and fossil fuel combustion [Penner, 1995] produce both aerosol types. Sulfates are also formed from gases emitted by marine sources [Charlson *et al.*, 1987] and occur across the globe. The concentration of black carbon (BC) is variable: 800 ng/m<sup>3</sup> in continental rural regions [Penner *et al.*, 1993], 40 ng/m<sup>3</sup> in the Arctic [Bodhaine, 1995], and 20 ng/m<sup>3</sup> in remote oceanic regions [Clarke, 1989; Rau and Khalil, 1993]; however, it seems to be ubiquitous in atmospheric aerosols [Cooke *et al.*, 1997; Lioussé *et al.*, 1993].

The terms "BC" and "soot" are often used interchangeably. As discussed by Penner and Novakov [1996], soot refers to primary combustion-generated carbonaceous aerosol, whereas BC is used to emphasize the light-absorbing property of carbonaceous particles. Since in this study we use microscope methods, and the observed carbonaceous particles have morphological features characteristic of combustion aerosol, we use the term soot instead of BC.

Whereas sulfates and their climate-cooling effects have been studied extensively during the past decade, the global importance of soot aerosols is just being recognized [Cooke and Wilson, 1996; Lioussé *et al.*, 1996; Haywood and Ramaswamy, 1998; Schult *et al.*, 1997]. Soot is generally the major light-absorbing aerosol species [Chýlek *et al.*, 1995]. It can also contribute to cloud condensation nuclei (CCN), thereby changing the radiative

properties and microphysics of clouds [Hudson *et al.*, 1991; Kaufman and Fraser, 1997].

The combined climate effects of soot and sulfate aerosols are difficult to estimate. There are insufficient data on the concentrations and vertical distribution of soot in the atmosphere [Haywood and Ramaswamy, 1998]; little is also known about what fraction, if any, of the soot and sulfate particles are aggregated with one another (internally mixed) in remote regions. Sulfate/soot aggregates have been observed in urban and polluted continental and marine atmospheres [Katrinak *et al.*, 1992; Okada, 1985; Mészáros and Mészáros, 1989; Parungo *et al.*, 1992, 1994] and some investigations have shown a correlation between sulfate and BC concentrations in remote marine regions [O'Dowd *et al.*, 1993; Van Dingenen *et al.*, 1995; Clarke *et al.*, 1996].

Knowledge of the extent of internal mixing is important for understanding the mechanisms of sulfate formation and soot removal and for assessing the climate effects of both types of particles. For example, if the sulfates contain strongly absorbing inclusions such as soot, then their direct climate cooling effect is moderated [Chýlek *et al.*, 1995]; on the other hand, the originally hydrophobic soot particles can become active CCN if they are coated with hygroscopic sulfates.

We used transmission electron microscopy (TEM) to study soot aerosol particles in order to identify their possible sources and to determine whether individual sulfate particles contain soot inclusions in (1) the polluted marine boundary layer (MBL), (2) the relatively clean free troposphere (FT) above the Atlantic Ocean, and (3) the remote, undisturbed MBL and FT above the Southern Ocean. Our study provides the first direct evidence that a significant fraction of sulfate particles occurs internally mixed with soot even in the essentially unpolluted troposphere.

<sup>1</sup>Now at Department of Earth and Environmental Sciences, University of Veszprém, Veszprém, Hungary.

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## 2. Experiment

Results obtained from three sets of aerosol samples are discussed in this paper. We collected aerosol particles during the

1992 Atlantic Stratocumulus Transition Experiment/Marine Aerosol and Gas Exchange (ASTEX/MAGE) experiment above the North Atlantic Ocean near the Azores Islands on June 19 and 20, days on which a polluted air mass of European origin arrived at the sampling site [Huebert *et al.*, 1996]. The results from the ASTEX/MAGE experiment are used here as a reference to which other TEM observations can be compared. Also included are results from two samples that were collected in the North Atlantic FT during the Second Aerosol Characterization Experiment (ACE 2). Much of our discussion focuses on data obtained from a set of samples that was collected during the December 1995 ACE 1 campaign, conducted above the Southern Ocean, near Tasmania [Bates *et al.*, 1998].

The ASTEX/MAGE samples were collected on the bow tower of the research vessel *Malcolm Baldrige*, 18-m above sea level. Particles were collected directly on TEM grids with carbon-coated Formvar films. The grids were placed on the fourth stage of a Casella cascade impactor; the fourth stage of the impactor collects particles with nominal diameters in the 0.2- to 0.7- $\mu\text{m}$  range. Sampling conditions and the analyses of third-stage impactor samples are given by Pósfai *et al.* [1995].

Our ACE 2 samples were collected at a 2360-m altitude on Izaña, Tenerife, Canary Islands. Cu TEM grids with holey carbon films were placed on the lower stage of a two-stage filter stack. The upper cut size is 1.5  $\mu\text{m}$ , and particles down to 0.05  $\mu\text{m}$  were collected. Results from two samples are discussed here; one was collected from clean marine air (on July 20, 1997), whereas the other was from an air mass that contained mineral dust from Africa (on July 25, 1997).

During the ACE 1 experiment we sampled aerosols with a one-stage impactor on the National Center for Atmospheric Research (NCAR) C-130 aircraft and obtained TEM samples in clear air at altitudes ranging from 30 to 5400 m during Lagrangian experiment "B" on December 7, 8, and 9 (flights 24, 25, and 26). The community aerosol inlet (CAI) was used; it is described by Bates *et al.* [1998]. According to Huebert *et al.* [1998], the CAI allowed the efficient sampling of aerosol particles smaller than 3.5  $\mu\text{m}$ . The impactor had a nominal lower cut size of 0.2  $\mu\text{m}$ ; however, we also observed soot particles smaller than 0.1  $\mu\text{m}$ .

In this Lagrangian experiment, an air mass was tagged by balloons and tracked so that the same air mass could be sampled repeatedly during each of three research flights. Because the aircraft flew circles with diameters of 60 km relative to one of the balloons, the chance of our actually sampling the exhaust of our own airplane was negligible. Contamination was detectable by spike-like increases in NO and aerosol concentrations when we intentionally crossed the exhaust plume.

Most of the ACE 1 samples are representative of a clean marine aerosol; the particular air parcel for the Lagrangian experiment was chosen because it had not passed over land for several days prior to arriving at the sampling site. Median concentrations of Rn, a passive tracer of continental air, were slightly lower in the baseline sector at Cape Grim in December 1995 than during the preceding 4 years (1990 to 1994), whereas elemental carbon concentrations were slightly greater (9.3 ng m<sup>-3</sup> compared with 7.3 ng m<sup>-3</sup> during the reference period) [Hainsworth *et al.*, 1998]. Concentrations of fine aerosol (<2  $\mu\text{m}$  diameter) non-sea-salt sulfate were lower than normal throughout December, with average values around 1 nmol m<sup>-3</sup> [Hainsworth *et al.*, 1998].

For TEM analysis, we used a JEOL 2000FX electron microscope operated at a 200-kV accelerating voltage.

Compositions were determined by energy-dispersive X-ray spectrometry (EDS) using an attached ultrathin-window detector that allowed the detection of C and heavier elements. For X rays emitted by elements lighter than Na, the absorption within the specimen is large, and the overlapping peaks make intensity measurements difficult. Since the particles discussed in this study contained mainly S, N, O, and C, we obtained qualitative results from EDS spectra. The crystal structures of ammonium sulfate particles were confirmed using selected-area electron diffraction (SAED). High-resolution images were obtained using a 400-kV, JEOL 4000EX electron microscope.

### 3. Results

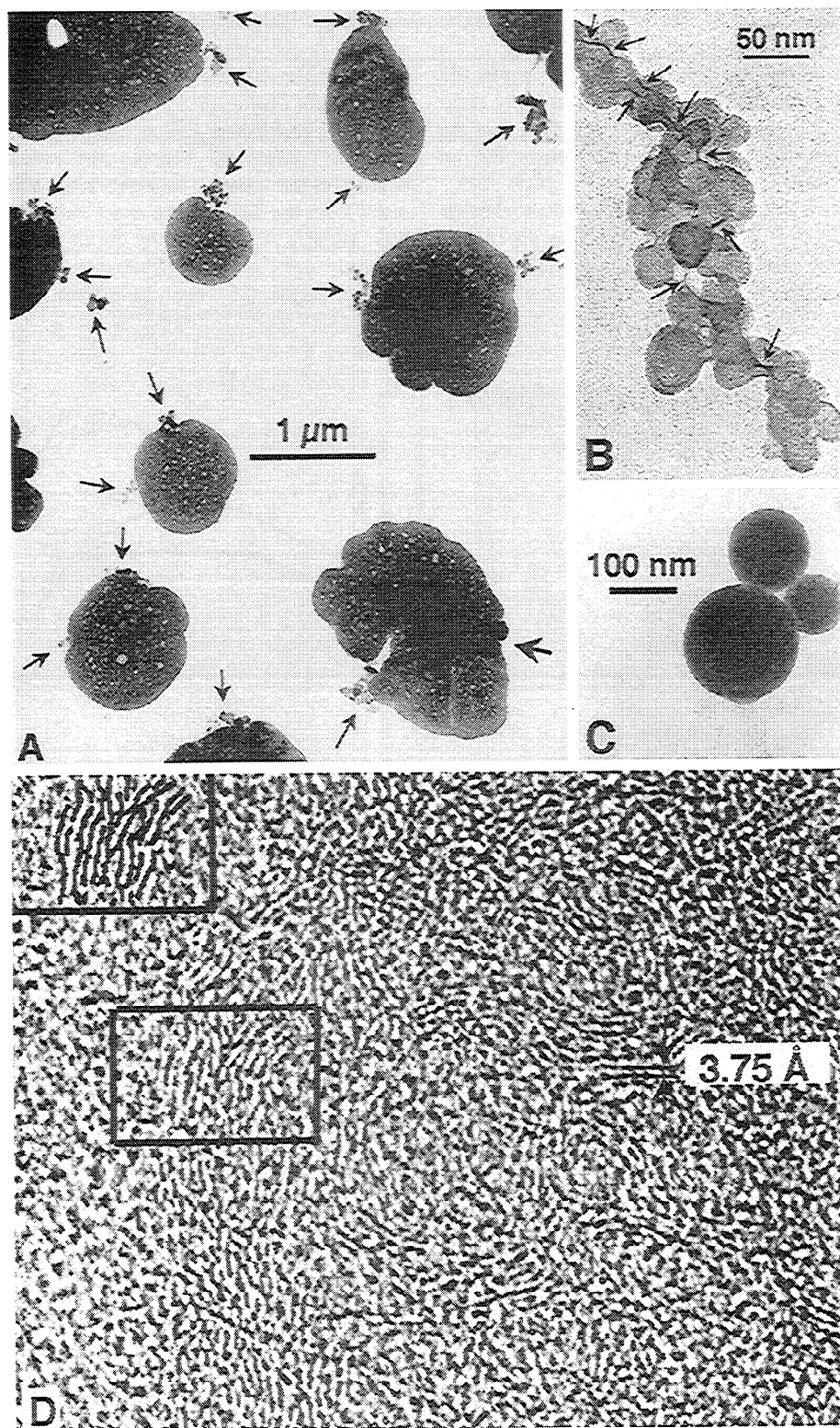
#### 3.1. Sulfate/Soot in the Polluted North Atlantic MBL (ASTEX/MAGE)

In the North Atlantic MBL samples from ASTEX/MAGE, the submicron fraction consists almost entirely of ammonium sulfate particles. A combined TEM-atomic force microscopy (AFM) study [Pósfai *et al.*, 1998] showed that the particles become flattened on the collection surface and their apparent diameters (as seen on the TEM grids; Figure 1a) are about double those of the original spherical, airborne particles. These sulfates typically contain soot (Figure 1a). Soot aggregates are either compact or chain-like associations of spherules (Figure 1b) with diameters of 10 to 50 nm. The spherules within the aggregates are typically attached to one another and coated by a carbon film (Figure 1b); their structures are revealed by high-resolution TEM (HRTEM) images that show curved, disordered graphitic layers, as is common for combustion soot [Lahaye and Prado, 1981]. Where spacings can be measured between the rather chaotically arranged layers, larger values are obtained than the layer spacing (0.335 nm) in graphite (Figure 1d). In addition to C, the soot aggregates typically contain S; some also contain minor Na, K, Si, or Ca. Spherules of fly ash are present (Figure 1c) and are amorphous, mainly consisting of SiO<sub>2</sub>, with variable Na, Mg, K, Ca, Fe, Mn, and Zn. The association of soot with silica fly ash is consistent with a coal-combustion origin [Ramsden and Shibaoka, 1982; Sheridan, 1989].

Soot-free sulfate particles from ASTEX/MAGE tend to be smaller than soot-bearing ones; about 50% of the smallest (0.1- to 0.2- $\mu\text{m}$  diameter) and as much as 90% of the larger (~1  $\mu\text{m}$ ) sulfate particles contain soot. There is almost no "free soot" in the samples; all soot aggregates are internally mixed with sulfates. These results are in agreement with aerosol volatility studies [Clarke *et al.*, 1996, 1997] that indicate an internal mixture of sulfate with a nonvolatile species within the pollution plume that was sampled during ASTEX/MAGE. The soot/sulfate particles were probably advected from the continental atmosphere and aged in the MBL; the number concentration of sulfate aerosol could have been determined by the soot and fly-ash particles that provided condensation sites for sulfate. The good agreement between our results and those of Clarke *et al.* [1996, 1997] serves as independent proof that the aggregation of soot with sulfate, as seen by TEM, is not an artifact but represents true atmospheric distributions of the two species relative to each other.

#### 3.2. Sulfate/Soot Above the Southern Ocean (ACE 1)

Soot/sulfate aggregates occur in all samples from ACE 1 that were collected from the C-130 during Lagrangian experiment "B"; collections were at altitudes from 30 to 5400 m above the Southern Ocean. Depending on the sample, 11 to 46% of sulfate

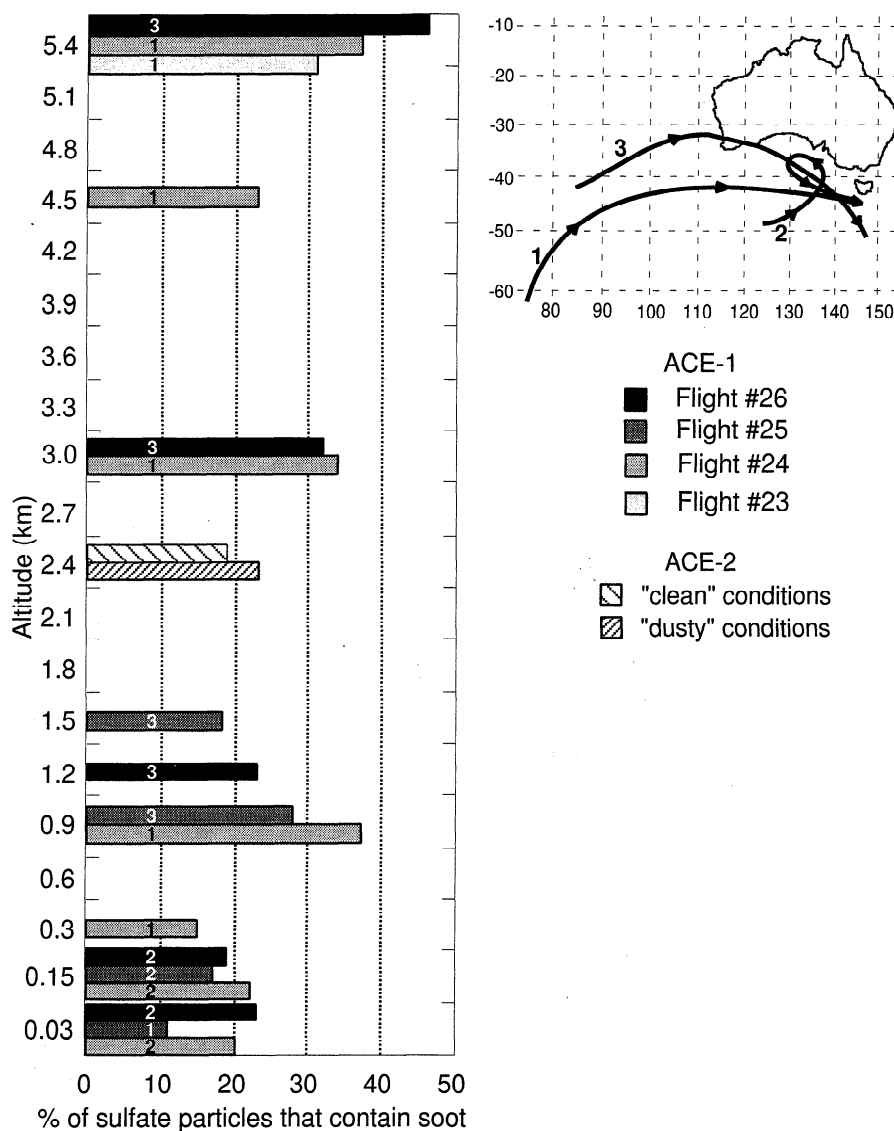


**Figure 1.** TEM images of aerosol particles collected in the polluted MBL of the North Atlantic Ocean, near the Azores Islands. (a) Ammonium sulfate particles containing soot (marked by the small arrows) and fly-ash spheres (marked by the bold arrow in the lower-right corner). (b) A typical chain-like soot aggregate; the arrows point to a carbon film that connects individual spherules within the aggregate. (c) Fly-ash spheres, consisting of amorphous silica. (d) High-resolution image showing disordered graphitic layers within a soot aggregate. The background of the image is a support film of amorphous carbon onto which the particles were collected. The inset in the upper-left corner is a copy of the boxed area; the graphitic layers are highlighted in the inset.

particles contained soot (Figure 2). The ratio of soot-bearing to soot-free sulfates seemed to increase slightly with the size of the host sulfate particles. Air mass trajectories for most samples did not pass over land for at least several days prior to arriving at the sampling site (see map insert in Figure 2), suggesting that the observed soot/sulfate aggregation is representative for an unpolluted marine aerosol.

No significant differences in aggregation exist among the sets of particles collected during the flights of Lagrangian experiment B (Figure 2), indicating that particle aging did not play a major role in forming soot/sulfate aggregates over the 33 hours of the

experiment. This observation period is long enough to monitor changes in the aerosol; the aging of sea-salt particles as they converted into sulfates was observed during the same experiment [Buseck and Pósfai, 1999]. The aggregation of soot with sulfate likely occurred before the air mass arrived at the first sampling site. The differences between the ratios of soot-containing sulfates in the samples collected at an altitude of 5.4 km may result from the fact that the exact same air mass may not have been sampled; as indicated by the air mass back-trajectories and relatively high CN counts [Hudson et al., 1998], the sample from the last flight (26) may have been slightly influenced by



**Figure 2.** Percentage of soot-containing sulfates relative to all ( $d > 0.1 \mu\text{m}$ ) sulfate particles. The samples were collected at several altitudes above the Southern Ocean, during a Lagrangian experiment of ACE 1. In this experiment, the same tagged air mass was followed and sampled in three research flights (flights 24, 25, and 26; flight 23 is a pre-Lagrangian flight) over a 33-hour period. Two North Atlantic samples (ACE 2) are also included in the diagram; these were collected at an altitude of 2.4 km on Izaña, Canary Islands. Between 100 and 200 particles were studied in each sample (for a total of over 2300 particles), randomly chosen from several regions on each TEM grid. The estimated error in the indicated percentages is +8, -3%; since some small soot particles may have escaped attention because of their low contrast in the TEM, underestimating the number of soot-containing sulfates is more likely than overestimating it. The map in the upper-right corner shows three types of generalized, 96-hour air mass back trajectories for the Southern Ocean samples; the corresponding numbers are marked on the columns that represent the ACE 1 samples in the diagram.

Australian sources. Relatively high concentrations of soot-bearing sulfates occur in the two 0.9-km samples; these samples were collected from a "buffer layer" that separated the MBL from the FT [Russell *et al.*, 1998]. In general, the fraction of soot-bearing sulfates seems to increase with altitude, at least for those sulfate particles that are larger than 0.1  $\mu\text{m}$ , those that were efficiently collected on our grids.

Typical soot-bearing ammonium sulfate particles from the Southern Ocean troposphere are shown in Figures 3a, 3c, and 3d. Some sulfates are surrounded by halos of smaller particles (Figure 3a); such halos are artifacts resulting from interactions between the hydrated particle and the collection substrate and presumably indicate the acidic nature of the original sulfate [Sheridan *et al.*, 1993; Pósfai *et al.*, 1994]. However, electron diffraction patterns confirm that the particles are crystalline ammonium sulfate when they are in the TEM; either during storage or upon exposure to the vacuum of the TEM, the assumed acidic sulfates presumably converted into ammonium sulfate.

The sulfate can be easily sublimed with the electron beam, leaving behind a S-bearing residue and the soot inclusions (Figure 3c). Some soot aggregates are only tens, whereas others are hundreds of nanometers across. In general, the soot aggregates from the Southern Ocean consist of 10- to 20-nm spherules that do not seem to be attached by a common film (Figure 3b) and are smaller and have more ordered structures than those in the ASTEX/MAGE samples (compare Figure 1b). High-magnification images (Figure 3d) show that in the typical soot particles from the Southern Ocean several wavy but roughly concentric graphitic layers are distinguishable within each spherule, forming onion-like structures (Figure 3d).

Soot occurs on the TEM grids either in the centers or at the edges of the sulfates (Figures 3a, 3c, and 3d). The typically light loadings of particles on the grids make it highly unlikely that soot occurs at the edges of sulfates because of scavenging of soot by hydrated sulfates as they spread on the supporting film. We believe that soot was forced to the peripheries of the particles when the sulfates crystallized from the original aerosol droplets. Thus the position of soot within the sulfate, as observed on the TEM grid, does not provide much useful information about the likely spatial relationship of the two aggregated species in the original airborne particles.

The air mass back trajectories indicate that combustion sources on the Australian landmass only could have contributed to the aerosol in a few samples. Most of the soot above the Southern Ocean could originate from either biomass burning or from ship and aircraft emissions. Soot from biomass burning invariably contains K [Andreae, 1983; Artaxo *et al.*, 1994; Turn *et al.*, 1997; Cachier *et al.*, 1991]. About a quarter of analyzed soot particles show detectable K (the detection limit for K is estimated to be about 2 at. %), but most do not contain elements heavier than O. About half of the soot particles contained significant K in the two samples collected at 0.9 km altitude, in contrast to the other Southern Ocean samples. Since these samples were collected from a "buffer layer" that served as a reservoir and mixing zone for MBL and FT air [Russell *et al.*, 1998], it is likely that a distinct aerosol layer was sampled; it may have contained particles from South African biomass burning.

Both ship [Corbett and Fischbeck, 1997] and aircraft traffic [Gardner *et al.*, 1997] could contribute to atmospheric soot in the studied region. Most ships burn low-grade residual oil that contains contaminants such as fly-ash and metals [Corbett and Fischbeck, 1997]. Since we did not observe metal peaks in the

EDS spectra or fly-ash associated with the soot particles, we conclude that most of the Southern Ocean soot originated from aircraft emissions, with a smaller fraction possibly coming from South African (and perhaps Australian) biomass burning. The morphologies and sizes of the smaller soot aggregates resemble those of aircraft-emitted particles [Blake and Kato, 1995; Poeschel *et al.*, 1992; P. J. Sheridan, personal communication, 1997], and the growing ratio of internally mixed soot/sulfate particles with altitude (Figure 2) is also consistent with aircraft as the likely source of most soot.

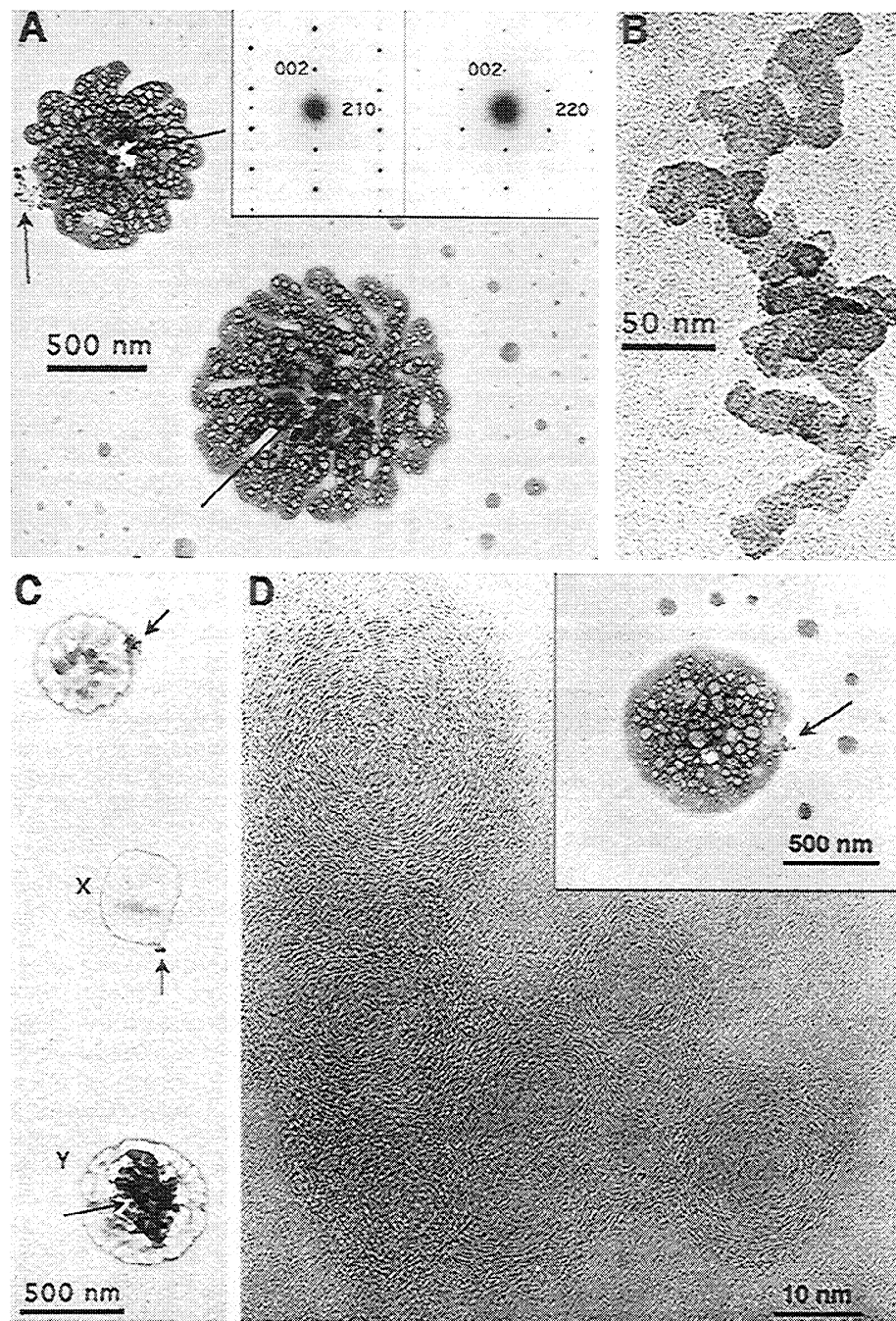
### 3.3. Sulfate/Soot in the North Atlantic FT (ACE 2)

In the ACE 2 (Izaña) samples (Figure 2, at 2.4 km altitude), the ratios of soot-bearing to soot-free sulfates are similar to those in the Southern Ocean samples, and there is no significant difference between ratios in "clean" and "dusty" samples. Whereas sulfate particles with diameters <0.1  $\mu\text{m}$  were not efficiently collected in the ACE 1 and ASTEX/MAGE samples, the ACE 2 samples contain a continuous size range of ammonium sulfate from ~0.04  $\mu\text{m}$  to ~2  $\mu\text{m}$ . As mentioned in the Experiment section, the ACE 2 particles were collected on grids coated with holey carbon. It is likely that the different collection method resulted in the deposition of <0.1  $\mu\text{m}$  particles. Even though the size distributions of sulfates are slightly different in the ACE 1 and ACE 2 samples, and the number of analyzed ACE 2 samples is limited, the relative numbers of soot-bearing sulfate particles above the Southern Ocean and North Atlantic are similar. These results suggest that soot/sulfate aggregates occur extensively in the remote FT.

## 4. Discussion and Conclusions

The hygroscopic properties of soot could be controlled by its composition [Lammel and Novakov, 1995]. Organic surface groups can enhance water adsorption [Chughtai *et al.*, 1996], and trace metals such as Fe increase the catalytic activity of soot [Grgič *et al.*, 1993]. Almost all soot particles in the ASTEX/MAGE samples occur within sulfates; the nucleating ability of soot may be enhanced by its S and the metal contents of the associated fly-ash particles. In the Southern Ocean samples, K-bearing soot particles are typically included in sulfates; on the other hand, a large number of K-free, presumably aircraft-emitted soot particles from the Southern Ocean occur without being aggregated with sulfates. The low contrast of these individual soot particles in the TEM hinders their counting, so we could not establish a reliable relationship between the numbers of free and sulfate-included soot particles in the different samples. The presence of these free soot particles indicates that they are poor nuclei, consistent with their chemical purity. These observations are supported by studies that identify most coal combustion [Grgič *et al.*, 1993] and biomass-burning soot particles as active CCN, and particles produced by jet fuel combustion as poor CCN [Hudson *et al.*, 1991].

Numerous studies show that contrails behind cruising aircraft contain both sulfate and soot particles [Schumann *et al.*, 1996; Petzold *et al.*, 1997; Kärcher and Fahey, 1997; Yu and Turco, 1997]. A significant number of soot particles can be activated in plumes that form from the products of high-S fuel combustion [Andronache and Chameides, 1997; Brown *et al.*, 1997]; this activation is thought to happen primarily through the condensation of  $\text{H}_2\text{SO}_4$  on the surface of soot [Rogaski *et al.*, 1997; Yu and Turco, 1998]. Some sulfate particles in a dispersing



**Figure 3.** Aerosol particles collected above the Southern Ocean, south of Tasmania. (a) Ammonium sulfate particles with soot inclusions (marked by arrows). The inset displays two different zone-axis SAED patterns that were obtained from a similar particle; spacings are consistent with the structure of ammonium sulfate and are indexed accordingly. (b) A typical, individual soot particle that is not enclosed by sulfate. (c) Residues and soot inclusions (arrowed) that remained after three ammonium sulfate particles were intentionally sublimed with the electron beam. (d) An ammonium sulfate particle with a small soot inclusion (arrowed). Bubbles that resulted from electron-beam damage are visible in the particles in Figures 3a and 3d. The high-resolution image shows the onion-like structure of spherules within the arrowed soot inclusion.

aircraft contrail will thus contain soot inclusions. If our interpretation is correct that most soot above the Southern Ocean originated in aircraft contrails, then the concentrations of soot as well as sulfate particles in the troposphere are directly influenced by aircraft emissions at higher altitudes.

Heterogeneous processes on the surfaces of soot particles during atmospheric transport could further increase the concentration of sulfate aerosols. Even though there seems to be no consensus about the atmospheric importance of  $\text{SO}_2$  oxidation on soot [Novakov *et al.*, 1974; Chang *et al.*, 1981; Mamane and

Gottlieb, 1989], it is possible that the formation of sulfate is facilitated by soot particles that serve as heterogeneous nuclei. Since some of the soot particles can acquire a hygroscopic coating soon after emission, either by aircraft or by burning biomass, these can become CCN and provide favorable sites for SO<sub>2</sub> oxidation in the aerosol water or in cloud droplets. It remains to be determined how important this mechanism is in producing the soot-bearing sulfate particles in remote marine regions.

Regardless of the processes that form soot/sulfate aggregates, the climate effects of such particles are quite different from those of an external mixture of the same aerosol species. The direct radiative forcing (DRF) by sulfates is significantly reduced if they are internally mixed with soot [Haywood *et al.*, 1997]. Each percent increase in the soot/sulfate mass ratio is estimated to lead to a 0.034 Wm<sup>-2</sup> "top of atmosphere" positive forcing for internal mixtures [Chýlek *et al.*, 1995]. In the Southern Ocean samples, the soot/sulfate mass ratio in internally mixed particles is highly variable; we estimate that it ranges from less than 0.01 to about 0.25 (as in particles X and Y, respectively, in Figure 3c). The DRF of soot is very sensitive to the albedo of the underlying surface: the higher the surface reflectivity, the more effective is the absorption by soot [Haywood and Ramaswamy, 1998]. Therefore soot above ice or snow and above clouds has a much higher mass efficiency in terms of its DRF effect than soot above the oceans. Since high-altitude soot has a greater probability of being above clouds than low-altitude soot, aircraft-emitted soot could have a greater effect on climate than its relatively insignificant mass would suggest.

Soot particles can be effective as CCN [Chýlek and Hallett, 1992; Kaufman and Fraser, 1997], especially when they are internally mixed with hygroscopic sulfates. For example, we suggest that heterogeneous reactions forming sulfate on soot particles may be responsible for the observed larger cloud droplet concentrations in ship tracks [Radke *et al.*, 1989]. Soot aerosols have complex effects on cloud properties. Smoke particles from biomass burning can increase cloud reflectance by reducing the droplet size [Kaufman and Fraser, 1997]; on the other hand, the high absorption by soot-containing cloud droplets enhances cloud absorption [Chýlek and Hallett, 1992].

From our observations, we infer that both the indirect and direct radiative forcing by sulfate aerosols are affected by their soot inclusions in the remote marine atmosphere. However, before the effects of internal mixing can be taken into account in global climate models, it will be necessary to establish reliable numbers for the fraction of sulfates that contains soot in the global background aerosol and the average soot/sulfate mass ratio in these particles. Although TEM is an indispensable method when particle species and their mixing properties are to be determined, it is so labor intensive that it cannot provide the statistical depth that is needed for such data. In the future, we plan to combine TEM observations with other types of aerosol measurements in order to obtain more quantitative data about soot/sulfate mixing.

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J. R. Anderson and P. R. Buseck, Departments of Geology and Chemistry, Arizona State University, Tempe, AZ 85287.  
M. Pósfai, Department of Earth and Environmental Sciences,

University of Veszprém, Veszprém, POB 158, H-8201 Hungary.  
(posfaim@almos.vein.hu)

H. Sievering, Global Change and Environmental Quality Program and Center for Environmental Sciences, University of Colorado at Denver, Denver, CO 80217.

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