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## Airborne minerals and related aerosol particles: Effects on climate and the environment

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**ABSTRACT** Aerosol particles are ubiquitous in the troposphere and exert an important influence on global climate and the environment. They affect climate through scattering, transmission, and absorption of radiation as well as by acting as nuclei for cloud formation. A significant fraction of the aerosol particle burden consists of minerals, and most of the remainder—whether natural or anthropogenic—consists of materials that can be studied by the same methods as are used for fine-grained minerals. Our emphasis is on the study and character of the individual particles. Sulfate particles are the main cooling agents among aerosols; we found that in the remote oceanic atmosphere a significant fraction is aggregated with soot, a material that can diminish the cooling effect of sulfate. Our results suggest oxidation of SO<sub>2</sub> may have occurred on soot surfaces, implying that even in the remote marine troposphere soot provided nuclei for heterogeneous sulfate formation. Sea salt is the dominant aerosol species (by mass) above the oceans. In addition to being important light scatterers and contributors to cloud condensation nuclei, sea-salt particles also provide large surface areas for heterogeneous atmospheric reactions. Minerals comprise the dominant mass fraction of the atmospheric aerosol burden. As all geologists know, they are a highly heterogeneous mixture. However, among atmospheric scientists they are commonly treated as a fairly uniform group, and one whose interaction with radiation is widely assumed to be unpredictable. Given their abundances, large total surface areas, and reactivities, their role in influencing climate will require increased attention as climate models are refined.

There is widespread concern over the enhanced global warming that might result from the buildup of “greenhouse gases” in the atmosphere. The effects of aerosols (suspensions of solid or liquid particles in air) on Earth’s radiation balance is less widely realized, and recognition of the role of airborne minerals has occurred only relatively recently.

Climate is fundamentally influenced by Earth’s energy budget, which depends on radiation received from the sun and energy radiated back to space. Incoming radiation is primarily in the visible range, whereas exiting radiation is largely in the IR. Greenhouse gases (H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, etc.) absorb IR radiation and radiate it back to Earth’s surface. Anthropogenic emissions of greenhouse gases cause increases in surface temperature (the “greenhouse effect”) and can have profound effects on climate and thus on societal welfare (1, 2).

Aerosol particles also have a major influence on global climate and climate change; they can locally either intensify or moderate the effects of the greenhouse gases through the scattering or absorption of both incoming solar radiation and thermal radiation emitted from Earth’s surface. Aerosols also act as cloud condensation nuclei (CCN) and thereby modify the radiative properties of clouds. The profound effects of atmospheric aero-

sols are surprising in view of their exceedingly low concentrations: the volumetric ratio of aerosol particles to atmospheric gases is between roughly 10<sup>-10</sup> and 10<sup>-14</sup> (3). The focus of this paper is on those particles, their compositions and structures and their effects on climate and, to a lesser extent, on the environment.‡

A growing awareness of the impact of particulate aerosols on climate, and the incompletely recognized but serious effects of anthropogenic aerosols, is summarized in several recent reviews (4–6). One reason for the relatively slow recognition of the role of particulate aerosols is that their study has fallen to disparate groups of scientists. Radiative transfer and other physical properties tend to be handled by one group (largely meteorologists and physicists), whereas chemical effects such as acid rain are emphasized by different scientists (mainly chemists). Perhaps the least attention to date has been on the geochemistry and mineralogy of aerosol particles and the effects of speciation.

Efforts to control greenhouse gases have been formalized by international treaty, e.g., the 1997 Kyoto Protocol on Climate Change. A comparable international effort to understand and control anthropogenic aerosol emissions has not (yet) occurred, at least in part because the extent to which they affect climate is not satisfactorily known. The incremental effects of anthropogenic increases in greenhouse gases are long lived (decades to centuries), whereas those of aerosols are shorter (weeks) (7). However, the sizes, compositions, and atmospheric lifetimes of particulate aerosols can vary spatially and temporally, and their strongest effects tend to be near their sources. If aerosols indeed offset climate responses to greenhouse gases, then the climate effects of greenhouse gases are even more substantial than has been recognized.

What role do mineralogists and geochemists have in addressing these and related issues of fundamental importance for human society and welfare? The main difference between most aerosol particles and the materials that are routinely studied by mineralogists is that most terrestrial minerals are not as fine grained. There are major problems with studying fine-grained materials, and therefore atmospheric chemists have traditionally emphasized bulk analyses to determine aerosol types. However, it is the individual chemical species that affect the radiative balance and

Abbreviations: CCN, cloud condensation nuclei; TEM, transmission electron microscope; SEM, scanning electron microscope; MBL, marine boundary layer; FT, free troposphere; NSS, non-sea salt; AFM, atomic force microscopy; ACE, Aerosol Characterization Experiments; FeLINE, experiments in the equatorial Pacific; ASTEX/IMAGE, experiments in the North Atlantic.

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‡Aerosol particles, to the extent they consist of nonanthropogenic homogeneous inorganic solids of more or less uniform composition and have ordered structures, fit generally accepted definitions of minerals. However, except for the title, in this manuscript we follow the usage common among atmospheric scientists and use “minerals” to refer to materials that once resided on Earth’s land surface.

climate as well as visibility and health. Paraphrasing a recent statement (8) and allowing for slight exaggeration, interpreting environmental and health effects of aerosols from bulk rather than individual-particle analyses is like interpreting mortality reports in a war zone from bulk airborne lead concentrations rather than from bullets.

Our group has focused on the painstaking but necessary analysis of individual particles. High-spatial-resolution methods, using electron beams as the primary probes of both chemistry and structure, have been developed to study increasingly fine-grained minerals. We examine the inorganic and, in special cases, the organic fraction of aerosol particles with electron microprobe analyzers and scanning electron microscopes (SEMs) and transmission electron microscopes (TEMs). In this paper we provide a background to the above issues and indicate ways in which mineralogical experience and experimental techniques can provide uniquely useful information. We first review the broad problems and briefly describe the analytical techniques, then discuss some of our recent transmission electron microscopy results regarding sulfate, soot, sea salt, and mineral aerosols.

### Aerosols, Climate, and the Environment

**Nature of Airborne Minerals and Other Inorganic Aerosols.** Andreae (9) estimated that the largest components of the global atmospheric aerosol are, in decreasing mass abundances: mineral aerosols—primarily from soil deflation but also with a minor component (<1%) from volcanoes (16.8 Tg), sea salt (3.6 Tg), natural and anthropogenic sulfates (3.3 Tg), products of biomass burning excluding soot (1.8 Tg) and of industrial sources including soot (1.4 Tg), natural and anthropogenic nonmethane hydrocarbons (1.3 Tg), natural and anthropogenic nitrates—largely from NO<sub>x</sub> (0.6 Tg), and biological debris (0.5 Tg).

In general, a distinction is made between *primary* particles, which are injected into the troposphere, and *secondary* particles, which form within the troposphere. Sea salt from spray, desert dust, volcanic mineral emissions, and re-entrained road dust are examples of primary aerosols. In contrast, particles produced by condensation of gases result in secondary aerosols. Primary aerosol particles tend to be larger, dominating the “coarse” fraction, which is >1 μm in diameter and mostly mechanical in origin. The fine fraction is enriched in secondary particles, largely between 0.1 and 1 μm in diameter and mainly chemical in origin. The smaller size range is also called the “accumulation mode,” in distinction to the “coarse mode.” In addition, there is a “nucleation mode,” with particles smaller than 0.1 μm. Recently “nanoparticles” in the 3- to 10-nm range have also been distinguished (10).

Human activities affect the amounts, types, and distributions of aerosols that enter the atmosphere. Anthropogenic particles are especially abundant in the submicrometer portion of the aerosol, and they provide a major uncertainty in estimating climatic effects (11, 12).

Different particle types (mineral dust, sulfates, carbonaceous materials, sea salt, organic compounds) can occur in the same air mass. An important question that we commonly address in our individual-particle work is, to use the terminology of atmospheric chemistry, whether the particles are *internally* or *externally* mixed. Phases that are externally mixed occur within the same aerosol but in discrete separate particles. If they are internally mixed, then they occur within the same particles; *inhomogeneous* internal mixtures are much like minerals in a rock, whereas *homogeneous* internal mixtures are solutions. Changes from predominantly external to internal mixtures can occur when particles grow by coagulation with different species, a process that is especially common during entrainment into clouds.

The differences between internal and external mixtures can significantly affect the optical properties and radiative efficiency of the aerosol and its ability to act as CCN. The nature and magnitude of these effects have received considerable attention (13, 14), but there are differences of opinion. For example, some

authors (15, 16) indicate that scattering calculations for mixed aerosols are not significantly affected by assumptions regarding internal or external mixing, whereas others (17, 18) reach the opposite conclusion for mixtures of sulfate and soot. Clearly, the problems have not been resolved, and most current models do not yet consider the subtleties of internal mixtures.

Atmospheric aerosol particles can also profoundly influence the environment. Dust, smoke, and haze locally impair visibility and health in both urban and rural regions. The harmful respiratory health effects of certain mineral and anthropogenic particles are well documented and have led to a plethora of federal rules and regulations (19, 20). Knowledge of the compositions and microphysical properties of aerosols is critical first for understanding and then for ameliorating some of these pernicious environmental and health effects.

**Effects of Airborne Minerals and Other Particles on Climate — Radiative Forcing.** Forcing is the term used to describe changes imposed on the planetary energy balance. It is measured in watts per square meter (Wm<sup>-2</sup>). Aerosol radiative forcing, which refers to the effects of aerosols, is termed *direct* if it results from backscattering and absorption of radiation by the aerosol particles themselves, and *indirect* if it results from the influence of the particles on the optical properties, amounts, and lifetimes of clouds. Positive forcing results in a net warming at Earth's surface, and negative forcing results in a net cooling.

The magnitude of the radiative effects of aerosol particles depends on their compositions, sizes and size distributions, abundances, hygroscopicities, surface properties, densities, and refractive indices (15, 21–23). Some of these parameters are interdependent, and they can vary with locality, sources, and environmental variables such as intensity of sunlight and relative humidity. Also, inventories of concentrations of particle types, especially those with a broad range of spatial and temporal distributions such as from industrial, arid urban, and particular geological sources (deserts, volcanoes) need to be well known for specific particulate assemblages. Their vertical distributions and underlying surface albedos are also important (24). The composite effect is complex and will require extensive measurement before it is well understood.

Sulfates are thought to be the most important scatterers of solar radiation on a global scale, producing a net cooling at Earth's surface, whereas soot tends to be a major absorber of the solar radiation and so has a net warming effect (4). The role of mineral dust is more ambiguous (9, 25). Particles tend to be most efficient in scattering radiation having wavelengths comparable to their physical sizes; submicron dust particles are efficient scatterers of the incoming sunlight and thus can have a cooling effect, especially near Earth's surface. On the other hand, mineral particles also absorb light and thus have a heating effect at the altitude at which they occur (cf. *Mineral Dust*). Because the outgoing radiation is in the IR, and silicate minerals have bands in which they absorb in the IR, they can act as “greenhouse particles.” The larger mineral aerosol particles tend to have shorter atmospheric lifetimes and to be most concentrated in the lower troposphere, near their source areas, and so produce localized effects.

Cloud droplets form on aerosol particles as nuclei. The number, sizes, and compositions of such CCN have major influences on cloud formation. Hygroscopic materials such as sulfates and sea salts are especially efficient as nuclei; mineral dust and combustion products can also be effective, especially if they are wettable or acquire hygroscopic coatings (26). Increased numbers of CCN lead to more cloud droplets and concurrent decreases in droplet sizes (for given cloud water contents) (27–29). Because of multiple scattering within the cloud, cloud albedo tends to increase with numbers and small sizes of hygroscopic aerosol particles, which results in increased cooling. In addition, clouds with more and smaller droplets are less prone to rain and drizzle formation and therefore persist longer, having more time to exert their cooling effect.

### Mineralogical Techniques Applied to Single Aerosol Particles

**Electron-Beam Analyses.** The traditional method of studying the chemistry of aerosol particles is through bulk methods. By using such techniques, large numbers of particles are analyzed *en masse*. However, the results provide no information about individual aerosol species and the mixing state of the aerosol; knowing whether the aerosol particles are attached to one another or to other types of particles is critical for understanding processes that involve or modify the particles during atmospheric transport.

Our approach has been to emphasize the individual particles because the radiative, environmental, and health effects of particles depend on their speciation rather than their averaged bulk compositions. Our primary instruments are the analytical SEM, electron microprobe analyzer (EMPA), and TEMs. The SEM and EMPA can operate in automated mode, running unattended around the clock and producing large numbers of analyses (30–35).

Particle analysis using TEMs, which are the main instruments used for the results reported here, cannot be automated because of the complexity of the method (sample tilting in diffraction mode to obtain critical crystal orientation, combined with changes to imaging and analysis modes to obtain size, shape, and chemical information). Thus, the TEM does not readily provide the statistical depth produced by the SEM or EMPA, but it can be used to analyze far smaller particles (down to  $<1$  nm vs.  $\geq 0.1$   $\mu\text{m}$ ) and, perhaps more importantly, it can provide crystallographic, morphologic, size, and chemical information for individual particles. Many of the aerosol particles of greatest interest for influencing climate fall within a size range that is accessible only by using the TEM (36–44). A general background for mineralogical transmission electron microscopy is given by ref. 45.

**Aerosol Time-of-Flight Mass Spectrometry.** A recent instrumental development of considerable interest is the aerosol time-of-flight mass spectrometer (ATOFMS), which can be used for rapid measurements of both sizes and compositions of individual particles (46–48). Particles pass through a laser beam, which blasts each particle into positively and negatively charged ions. These are then analyzed in the ATOFMS to determine the atomic or molecular weight of each ion, from which fragment compositions can be determined. Particle sizes are calculated from their velocities as they move through the ATOFMS. A result is that chemical and size information is obtained from individual particles in real time, although back calculations are required to infer parent species from their ion fragments.

**Samples.** Because the oceans cover  $\approx 70\%$  of the globe, much attention has been given to the profound effects of the oceans on climate. A recent area of interest is the role of aerosol particles in the marine troposphere and the effects they have on climate. Marine aerosols are important because there is generally enough humidity to form clouds, but there can be a shortage of CCN; thus, the indirect climate effect of aerosols is far more pronounced over sea than land. Aerosols in such areas are also the most likely to represent unpolluted, “global background” conditions, and the contributions of natural and anthropogenic sources are easier to identify than in continental or polluted oceanic atmospheres.

Two recent international research programs are shedding important new insights onto the role of aerosols in the troposphere. The Aerosol Characterization Experiments (ACE) took place in late 1995 in the Southern Ocean near Tasmania (ACE-1) and in 1997 in the North Atlantic (ACE-2). They produced integrated measurements from ships, airplanes, and ground stations; ACE-1 involved researchers from 45 institutions in North America, Europe, Australia, and Asia (49).

In the ACE-1 campaign we used two platforms. At Cape Grim, Tasmania, we collected aerosol particles onto filters in a two-stage impactor (for SEM analysis) and directly onto TEM grids.

We also used a one-stage impactor that was mounted on a C-130 aircraft. In this paper we use results from a Lagrangian experiment in which a tagged air mass was followed and the aerosol evolution within it studied over time. The airplane flew “stacked circles,” with each circle at a different altitude.

From the ACE-2 experiment we use data obtained from particles collected onto TEM grids that were placed on filters. The sampling station was on a mountain top (at 2,600 m altitude) on Izaña, Canary Islands. We also include results from earlier experiments in the equatorial Pacific (FeLINE; ref. 41) and the North Atlantic (ASTEX/MAGE; refs. 42, 50).

### Open Problems, Issues, and Results

**Sulfates<sup>§</sup> and Associated Soot and Organic Species.** Sulfates are probably the main climate-cooling aerosols (51–53). They scatter solar radiation and are effective as CCN; the result is negative forcing and thus cooling at Earth’s surface. The radiative forcing of sulfate aerosol particles, especially in the Northern Hemisphere, is roughly equivalent in magnitude but opposite in sign to the combined forcing by the greenhouse gases (12, 51, 53–55).

If sulfates are internally mixed with other aerosol species, their hygroscopic behavior and optical properties can change dramatically (14, 17, 18) and result in diminished cooling. It is therefore important to determine the state of mixing of these particles. We studied sulfate particles in sample sets obtained from (i) the polluted marine boundary layer (MBL) near the Azores Islands (ASTEX/MAGE), (ii) the remote unpolluted Southern Ocean MBL and free troposphere (FT) (ACE-1), and (iii) the essentially clean North Atlantic FT at Izaña, Canary Islands (ACE-2). In distinction to the relatively small amount of primary sulfate that is in sea water and thus occurs in every sea-salt aerosol particle, the secondary sulfate aerosol, which is what interests us here, is called non-sea salt (NSS) sulfate.

**TEM Observations.** The compositions of hydrated sulfate particles may change during sample processing or in the vacuum of a TEM. For such samples we must rely on indirect evidence, such as morphological features, to identify the compositions of

<sup>§</sup>Here we use “sulfate” for particles that consist purely or predominantly of sulfates and are formed in the atmosphere by either homogeneous or heterogeneous reactions involving  $\text{SO}_2$  gas. They have compositions ranging from  $\text{H}_2\text{SO}_4$  to  $(\text{NH}_4)_2\text{SO}_4$ . Sea-salt sulfate and the NSS sulfate formed by conversion of the original sea-salt particles are not considered in this section.

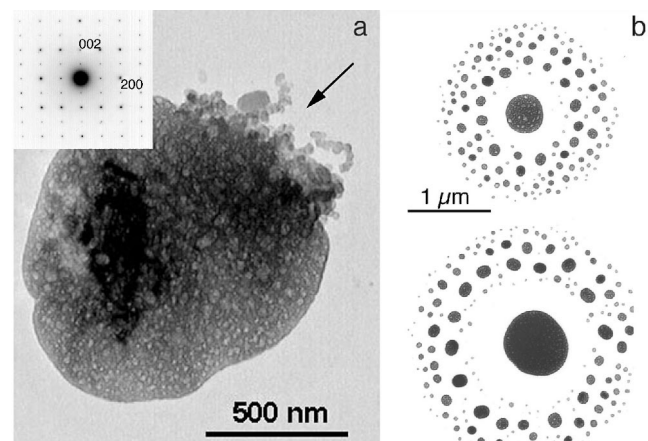


FIG. 1. TEM images of  $(\text{NH}_4)_2\text{SO}_4$ . (a) The selected-area electron-diffraction pattern (upper left) confirms the identification. The arrow points to a soot aggregate. (Azores, North Atlantic, ASTEX/MAGE); (b) Rings of small  $(\text{NH}_4)_2\text{SO}_4$  crystals that formed as the sulfate particles dehydrated. The dimensions of the halos can be used to distinguish among particles that likely had different water contents while still airborne. (Southern Ocean, ACE-1.)

the original atmospheric particles. Fig. 1*a* shows a typical particle that was collected above the North Atlantic Ocean when a polluted air mass of European origin was sampled. An energy-dispersive x-ray spectrum shows O, N, and S, and the selected-area electron-diffraction pattern was used to confirm its identity as crystalline  $(\text{NH}_4)_2\text{SO}_4$ .

Acidic particles are more hygroscopic than pure  $(\text{NH}_4)_2\text{SO}_4$  and so will contain more water and spread farther on the TEM grid than neutral species. The halos of discrete smaller particles that form (Fig. 1*b*) presumably result from the acidity of the original sulfate (37) and are likely related to the amount of adsorbed water. Different samples typically have characteristic distributions of sulfates with or without halos. For example, the images in Figs. 1*a* and *b* and 2*a* were obtained from different samples; we assume that the halo-free particle (Fig. 1*a*) was  $(\text{NH}_4)_2\text{SO}_4$  even while in the air. The sulfate with a single ring of smaller particles (Fig. 2*a*) was slightly acidic, whereas the particles with multiple rings (Fig. 1*b*) were more acidic. Other differences in appearance reflect the degree of decomposition produced by the electron beam of the TEM and contrast of the image.

**Internal Mixing of Sulfate and Soot.** There is increasing evidence that carbonaceous aerosols can have major impacts on aerosol radiative forcing (56, 57). Soot both scatters and absorbs radiation at solar wavelengths and thus produces cooling at Earth's surface while warming the atmosphere around the particle. The net effect is a slight positive forcing. The resulting warming of the atmosphere can have particularly significant effects over highly reflective areas such as those covered with snow. When soot derived from fossil fuels is entered into models, it produces a positive forcing that can offset 40% or more of the negative global radiative forcing of sulfate (17). Organic particles can be the dominant CCN aerosols above tropical rain forests (58) and densely populated areas such as the East Coast (56, 57). Internal mixtures of sea salt, sulfate, and material that is presumably organic carbon occur widely (59).

We found that many sulfate particles are internally mixed with soot in the marine troposphere (Figs. 1*a* and 2*a*). Soot/sulfate aggregates had been observed in polluted urban environments (40, 60–62), but it is surprising that even in the remote oceanic atmosphere a significant fraction of sulfates contain soot inclusions (44). Up to  $\approx 90\%$  of the submicron ammonium sulfate particles contain soot aggregates in samples collected above the North Atlantic Ocean during a pollution episode (ASTEX/MAGE). In the clean atmosphere above the Southern Ocean during the ACE-1 experiment, 11 to 46% of the sulfate particles contain soot. Soot/sulfate aggregates comprise about 20% of all sulfate particles in two samples that we studied from Izaña (ACE-2). Because we observed similar relative numbers of soot/sulfate internal mixtures in the aerosol from two essentially clean but geographically distant locations (Southern Ocean and Izaña, North Atlantic), we believe it likely that soot/sulfate internal mixing is a globally important phenomenon and must be considered when the climate effects of sulfate aerosols are modeled (44).

We observed variations in the compositions and microstructures of soot particles and in their associations with other species. (i) The polluted North Atlantic ASTEX/MAGE samples have

soot associated with silica fly ash spherules that contain various metals; the association suggests that a coal-burning power plant was the likely source of the soot. (ii) Depending on the sample, between 20% and 50% of soot particles from both the Southern Ocean and Izaña contain significant K, which is typical of biomass burning (63–66). (iii) Only C and O are detectable in most soot from the Southern Ocean; such particles typically have “compact” microstructures, as described below. Because they contain no associated fly ash, K, V, or other metals, any of which would suggest alternate sources, we conclude they were likely emitted by aircraft.

Most soot particles from the Southern Ocean atmosphere consist of only a few 10- to 50-nm globules. The  $(\text{NH}_4)_2\text{SO}_4$  particle in Fig. 2*a* contains such a typical small soot inclusion. Individual graphitic layers are wavy and subparallel, forming the poorly crystalline turbostratic structure characteristic of soot (Fig. 2*b*). Large branching soot aggregates (Fig. 2*c*) are less common than the small particles.

Our observations of soot/sulfate particles are significant for several reasons. Internally mixed soot and sulfate raise the question of whether they became attached through (i) coagulation, (ii) processing in cloud droplets, or (iii) condensation and oxidation of  $\text{SO}_2$  on the soot surfaces. If mechanism (iii) is responsible for the observed aggregates, then soot particles provided nuclei for heterogeneous sulfate formation even in the remote marine troposphere, a pathway for sulfate formation that has not been considered in climate models. Further studies are needed to unravel the processes that bring atmospheric sulfate and soot particles together.

A soot inclusion within a sulfate particle changes the optical properties of the sulfate. That particle, if soot-free, would have a cooling effect on the atmosphere; however, if it contained enough soot, it could emit IR radiation and thereby heat its immediate environment. The magnitude of the effect depends on the size of the inclusion. On the other hand, nucleation of sulfate particles on soot would result in additional CCN particles that exert increased indirect cooling. The presence of absorbing soot inclusions in clouds can have a major offset of the expected increase of cloud albedo. Clearly, the aggregation of soot with sulfate can cause changes in both the direct and indirect radiative forcing of sulfates and thus needs further study.

**Internal Mixing of Sulfate and Organic Species.** For determining climate effects, it is important to know whether inorganic particles contain organic coatings. Such coatings can influence the hygroscopic behavior of particles by retarding water evaporation (67, 68) and increasing or decreasing water adsorption by inorganic aerosols (69). Many particles of ammonium sulfate, when sublimated with the electron beam in the TEM, leave visible residues on the grid. The residues in Fig. 3 include a soot aggregate and dark films that indicate only S in their energy-dispersive x-ray spectra. The most reasonable identification of the residue films is that they consist of organic compounds that coated the original sulfate particles.

Indirect evidence for the probable presence of organic coatings on sulfates is provided by combining atomic force microscopy (AFM) and TEM images of the same sulfate particles (43). The AFM image (Fig. 4) was obtained under ambient conditions at a

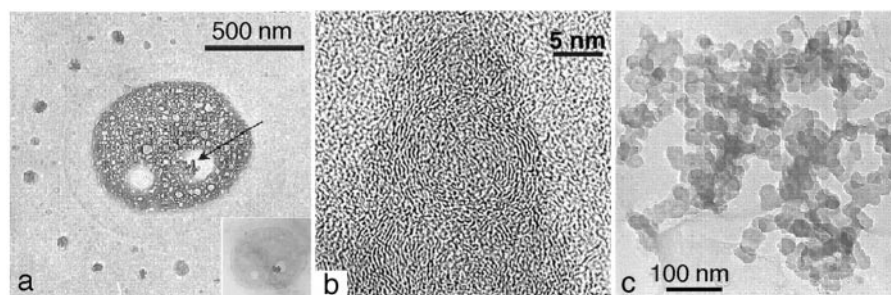


FIG. 2. TEM images of an internal mixture of  $(\text{NH}_4)_2\text{SO}_4$  and soot. (a) The halo is similar to those in Fig. 1. The arrow points to a soot aggregate. (Southern Ocean, ACE-1); (b) High-resolution image of the arrowed tip of the soot aggregate in *a*. A degree of ordering is evident in the onion-like graphitic layers, seen edge on. (c) A large branching soot aggregate; such aggregates are typical of combustion processes (95). (Southern Ocean, ACE-1.)

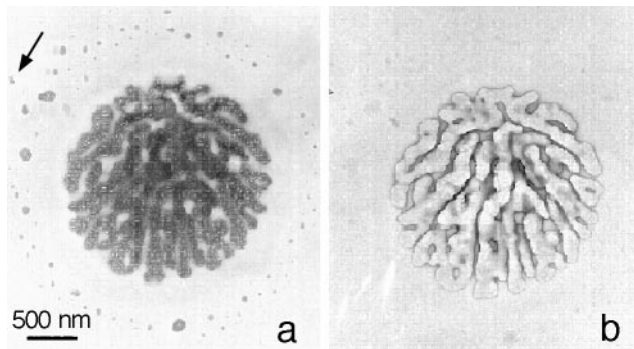


FIG. 3. TEM image of ammonium sulfate (*a*) before and (*b*) after it was sublimated by the electron beam. We believe the dark films in *b* are residues of organic material that coated the aerosol particle before sampling. The arrow marks a small soot particle. (Southern Ocean, ACE-1.)

relative humidity of 31%. The TEM image shows that the same particles are significantly smaller in the vacuum of the TEM (at 0% relative humidity) than during the AFM study. The amount of water lost when they were inserted into the TEM was calculated and was in excess of what could be expected for pure  $(\text{NH}_4)_2\text{SO}_4$ . We believe that organic coatings on the particles are responsible for the observed anomaly in the hygroscopic behavior of these sulfates.

**Sea Salt.** Sea-salt aerosol particles are generated when rising bubbles burst at the surface of the ocean and water drops are ejected into the atmosphere (Fig. 5 *a* and *b*). The droplets are typically 0.1 to 100  $\mu\text{m}$  in diameter (70). Sea-salt particles can dominate light scattering by aerosols and comprise a significant fraction of CCN above some regions of the unpolluted oceans (48). The large mass of sea-salt aerosol means that it dominates the particulate surface area in the marine troposphere and, through heterogeneous surface reactions, plays an important role in the atmospheric cycles of Cl, S, and N (Fig. 5*c*).

There is controversy about the significance of sea salt for aerosol radiative effects in the MBL. It had been thought that sea-salt particles are mostly too large to be efficient scatterers of solar radiation and that the smaller NSS sulfate is the main contributor to radiative effects in the MBL. However, recent data indicate that in some regions sea salt can be a major source of CCN and can even dominate NSS sulfate (21, 70). Individual-particle analysis can be used to determine sea salt vs. sulfate number concentrations and sizes to obtain a better understanding

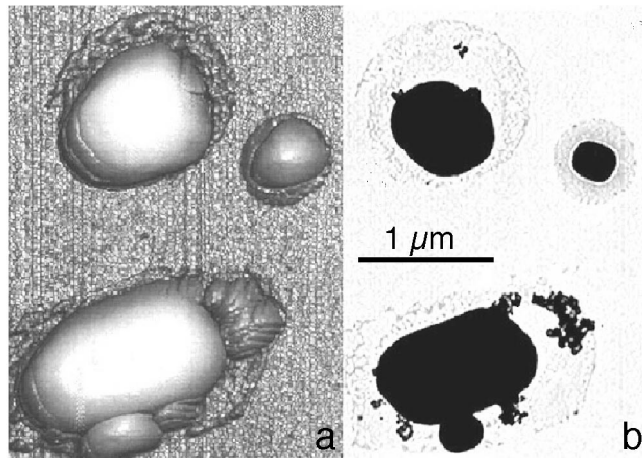


FIG. 4. (*a*) AFM and (*b*) TEM images of identical sulfate particles. Note the decrease in size caused by dehydration within the TEM. The amount of lost water is larger than expected and suggests increased hygroscopicity through organic coatings. (AFM image by Huifang Xu) (Azores, North Atlantic, ASTEX/MAGE.)

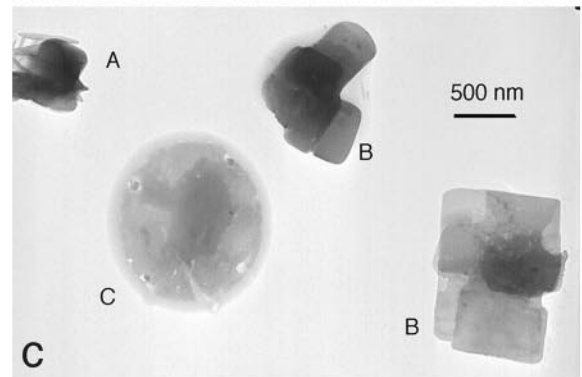
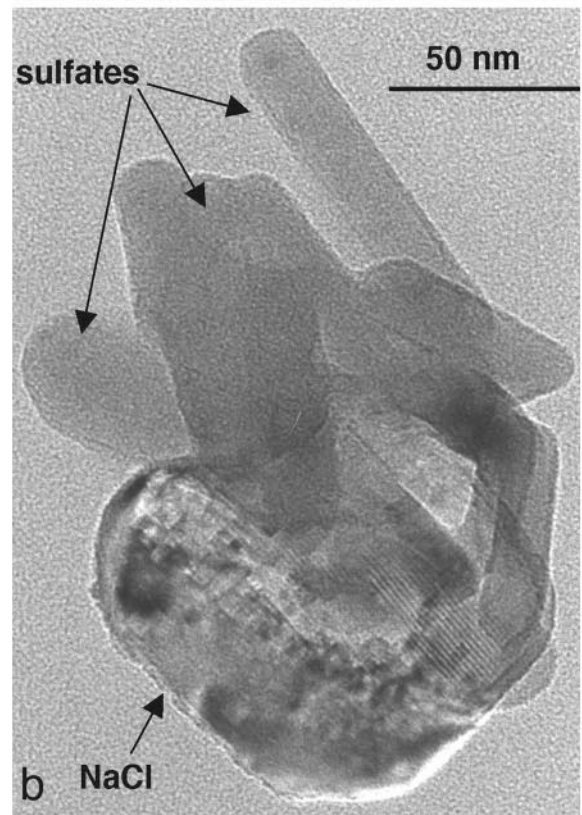
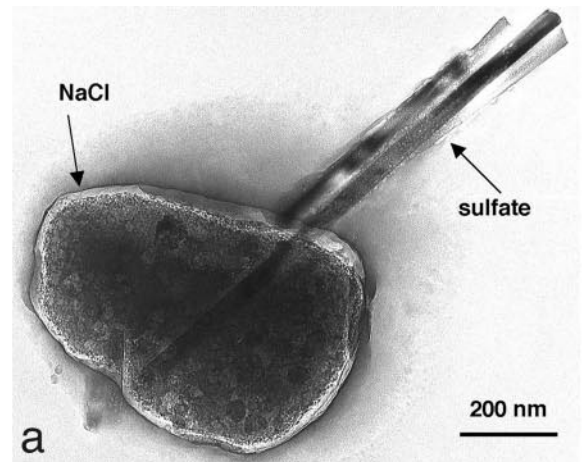


FIG. 5. TEM images of sea salt. (*a* and *b*) Subhedral halite (NaCl) and euhedral sulfate crystals. The particle in *b* belongs to the smallest sea-salt particles that occur in the ACE-1 samples. (Southern Ocean, Cape Grim, ACE-1); (*c*) Halite particles in various stages of conversion to sulfate and nitrate. Grain A is partly converted, whereas C has been completely converted to nitrate and grains B to sulfates. (Azores, North Atlantic, ASTEX/MAGE.)

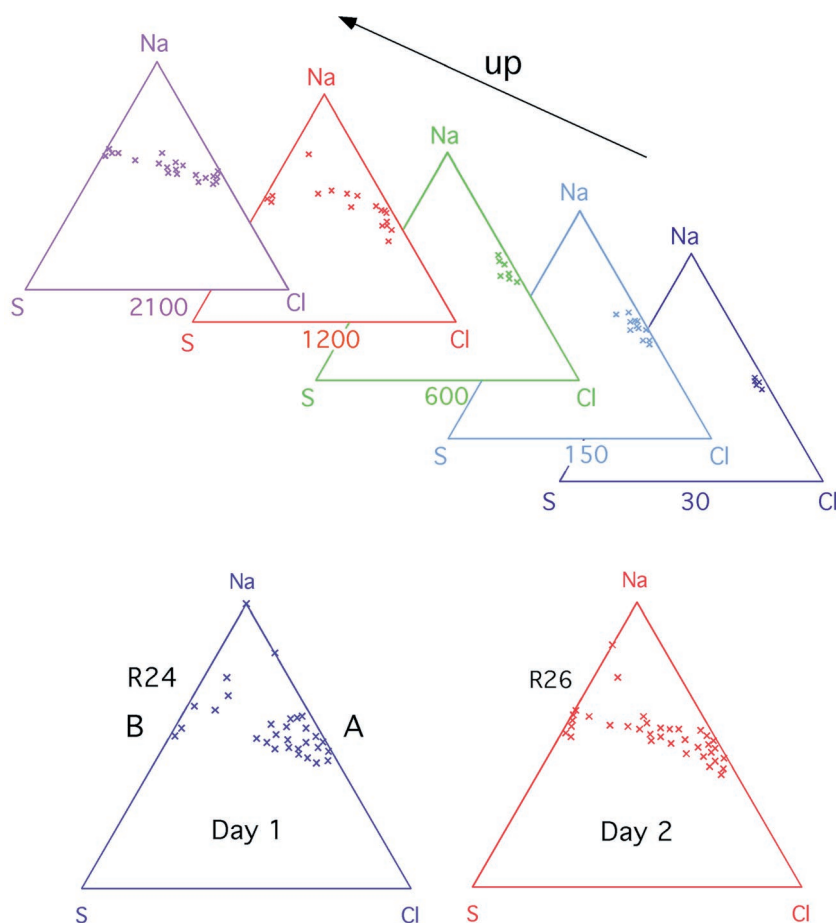


FIG. 6. Na-Cl-S plots showing changes in composition of aerosol particles with altitude (*Upper*) and time (*Lower*). Each of the upper triangles represents a sample from a single altitude (meters above sea level are indicated) and contains data from between 30 to 70 particles. The upper samples were collected during a series of flights on one day. The lower triangles contain composites of samples from several altitudes; the one on the left contains all particles indicated above, whereas the one on the right contains those collected 26 hr later. Each contains data from about 250 particles. Mg, K, and Ca are not included in the diagrams because their ratios to Na do not change (or are within our analytical error). (Southern Ocean, ACE-1.)

of the radiative importance of sea salt. During ACE-1 we found that in the windy Southern Ocean, sea salt is a constituent in almost all MBL particles; only less than 1% were pure sulfate (48), although in other areas sulfate is a major particle type (31, 71).

Changes occur with altitude in the compositions of sea-salt particles collected above the Southern Ocean (Fig. 6), and the reaction pathway from A (fresh sea salt) to B (sulfate) can be traced. Unreacted particles dominate the samples collected within the MBL (at  $\approx 30, 150,$  and  $600$  m); their S contents are consistent with the presence of sea-salt sulfate (i.e., sulfate that was in the seawater droplet when it was ejected into the atmosphere). There is more variation in particle compositions at 150 and 600 m than near the sea surface (at 30 m), but the differences are small. In addition to unreacted sea salt, S-rich particles occur at 1,200 and 2,100 m, above the thermal inversion. Several particles in the 2,100-m sample were completely converted to sulfate. More reacted particles occur in the FT, i.e., at high altitudes, presumably because they spent more time in the atmosphere and had more time to react with  $\text{SO}_2$  than the particles in the MBL. Some particles in the FT may have been transported from remote locations where  $\text{SO}_2$  concentrations could have been higher than at the ACE-1 study area.

Temporal changes in sea-salt compositions can also be observed from the ACE-1 samples. During Lagrangian experiment "B," an air mass was tagged by balloons and sampled from flights on 3 consecutive days. Sea-salt compositions from samples collected during the first (R24) and last (R26) flights are summarized in the lower part of Fig. 6. The temporal changes resemble those with increasing altitude; reacted sulfate-rich particles formed during the 26 hr between the flights. Particle aging is noticeable in the FT samples, with more sulfate particles in the second sample set than in the first. The longer the sea-salt particles reside in the air, the longer they are exposed to  $\text{SO}_2$  and the more likely they are to convert to sulfates.

**Mineral Dust.** A significant fraction of the atmospheric particulate burden consists of mineral dust; its injection rate into the atmosphere can vary temporally and spatially, e.g., as a result of dust storms, volcanic eruptions, and anthropogenic activities. The mineral-dust burden tends to be especially high near source regions. Important examples include semiarid and arid lands, areas where land use is changing, and, in general, in the tropical and subtropical belts (72, 73). Moreover, changes in climate as well as land use can profoundly affect the amount of mineral dust that enters the troposphere. Drought and increased desertification by human activities can dramatically increase the dust available for deflation, and the tropospheric dust burden will increase appreciably. The relatively short atmospheric lifetime of much such dust means its radiative forcing adjusts relatively rapidly to changes in emissions.

Mineral aerosols have a dual forcing role, producing both warming and cooling effects. The details are not well known because the scattering characteristics of mineral aerosols are hard to determine (74). Duce (75) estimates a direct forcing of  $-0.75 \text{ Wm}^{-2}$ , which is roughly equivalent to that from sulfate from biogenic gases ( $-0.68 \text{ Wm}^{-2}$ ). It has been suggested that the direct radiative forcing of mineral aerosols approaches that of anthropogenic sulfates (73) and that in the tropical and subtropical North Atlantic region mineral dust is the dominant light-scattering aerosol (72). Tegen *et al.* (76, 77) estimate that disturbed soils contribute roughly half of the total atmospheric dust, and that the negative shortwave forcing and the positive IR forcing approximately cancel at the top of the atmosphere, but that internally the energy is redistributed, leading to climate change. Because of the lack of sufficient data, all models make many assumptions about the optical and radiative properties of mineral dust and are subject to revision as improved data are acquired.

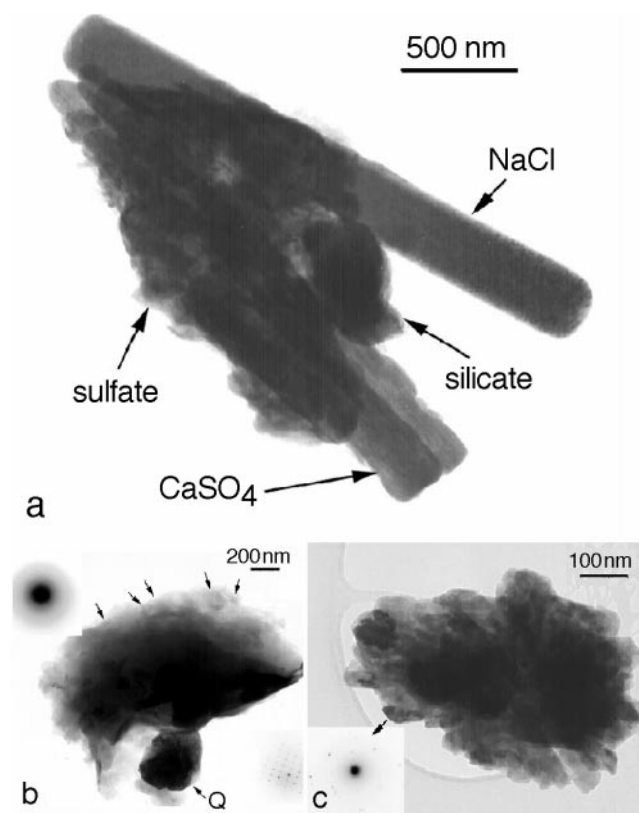


FIG. 7. TEM images of mineral dust collected from the marine troposphere. (a) Internal mixture of presumably terrestrial silicate and anhydrite with sea salt (Azores, North Atlantic, ASTEX/MAGE); (b) smectite (clay) and quartz (Q). The small grain size of the clay is visible at the thin edge (the arrows mark hexagonal platelets). Selected-area electron-diffraction patterns of clay and quartz are at the upper left and lower right, respectively. (Canary Islands, North Atlantic, ACE-2); (c) TEM image of goethite,  $\text{FeO}(\text{OH})$ , collected 2,600 m above sea level. Fe-bearing minerals like this could be important nutrient sources in remote oceans. (Canary Islands, North Atlantic, ACE-2).

Anthropogenically generated dust such as arises from transportation and industry can result in massive injections of minerals into the atmosphere. Between 30 and 50% of the soil dust burden may result from human activities (78). The resulting climatic effect can equal or even exceed that from aerosols generated by burning of fossil fuels and locally can be comparable to that from clouds (79).

Mineral-dust particles provide important reactive surfaces for atmospheric reactions. Mineral aerosols significantly affect the cycles of N, S, and atmospheric oxidants (80). An annual average of 40% (locally reaching 70%) of total sulfate is associated with mineral dust over Asia, the western United States, Australia, and North Africa, and large parts of the oceans have over 10% of the sulfate associated with mineral aerosol (81).

The association of sulfates with the larger mineral particles means that the local cooling effects of the sulfate aerosol are diminished because of a decrease in the incremental mass scattering efficiency of the sulfate. The mineral particles, being partly coated with hygroscopic sulfates—sometimes as the result of cloud processing—can also become CCN. Such processing of mineral-dust particles over the eastern Mediterranean has converted them into giant CCN that influence precipitation and the concentration of ice crystals in convective clouds (82).

Our TEM studies of individual mineral-dust particles aim at identifying major mineral species in the aerosol and determining whether they are aggregated with other aerosol species. Such information is useful for obtaining improved refractive indices and size and shape data for model calculations of the radiative

forcing of dust. The observation of internal or external mixtures is important for determining which chemical reactions take place on mineral surfaces and how the original particles change during atmospheric transport.

The compositions and aggregations of the mineral aerosols collected when a polluted air mass of European origin arrived at our sampling site near the Azores Islands reflect their transport over the ocean. An unidentified silicate is associated with euhedral anhydrite,  $\text{CaSO}_4$ , and sea salt (Fig. 7a). Smectite (Fig. 7b) is the most common mineral, and anhydrite is also widespread (42). Because the aerosol was transported in an air mass that contains high concentrations of  $\text{SO}_2$  from European pollution sources (83), it is likely that original carbonate particles reacted with  $\text{SO}_2$  to form anhydrite. Such conversions were observed in Asian (84) and Saharan (85) dust plumes. Under high-dust conditions, mineral particles provide an important pathway for  $\text{SO}_2$  removal from the atmosphere (81). Internal mixtures of sea salt, sulfate, and mineral particles were also observed by Andreae *et al.* (86), who concluded that such aggregates likely formed in clouds.

An interesting consequence of the transport of mineral aerosol particles to the oceans is that they can serve as sources of biological productivity. Large areas of the ocean, ranging from the tropical equatorial Pacific to the polar Antarctic and the Southern Ocean, contain fewer phytoplankton/zooplankton than expected from the abundance of nutrients in the sea water. A correlation exists between a relative lack of Fe and this under-productivity (87, 88). Iron in the oceans far from land is mainly provided by continental dust (89–91), which can be transported across large oceanic expanses (92–94). We have identified goethite (Fig. 7c) and other Fe minerals from the aerosol in the FT. It appears as if atmospheric transport of mineral dust is widespread and can have major effects on life at the bottom of the food chain in the large areas of the oceans that are far from the nutrients provided by river flow from the continents. Nutrients derived from mineral dust may be limiting factors on primary productivity.

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