Minerals in the Air: An Environmental Perspective

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Abstract

The troposphere comprises roughly the lowest 10 km of the atmosphere, the part we inhabit, that envelops us, and that we inhale and look through every day of our lives. Clouds, rain, all manner of storms, and other aspects of weather originate within it, and it contains 85% of the mass of the atmosphere, including aerosol particles. These particles, like greenhouse gases, can influence climate. Mineral particles are major constituents of this aerosol. Their sizes, shapes, compositions, and degrees of agglomeration can all be determined using transmission electron microscopy. These variables have, to a considerable extent, been overlooked in studies of atmospheric chemistry and provide an important potential area of research for geoscientists.

Introduction

There is broad agreement that airborne particles have important consequences for health, visibility, climate, and human welfare in general. Globally, the most abundant group of aerosol particles by mass (~50%) consists of minerals (because of their relatively large sizes, their number concentration is far lower). Yet their study and environmental impacts have been relatively overlooked. Atmospheric scientists, if they even consider them, tend to group all airborne minerals into categories such as crustal, soil, or mineral dust, whereas most mineralogists and geochemists ignore them entirely. A major question we address is whether geoscientists, with their unique skills, are neglecting an important area of science where their talents and expertise are needed. For completeness, in our discussion we also include the range of common inorganic aerosol particles.

Anthropogenic emission of the "greenhouse gases" (e.g., CO_2, CH_4, N_2O, and halocarbons) is widely recognized as producing a warming effect through their absorption of radiation emitted from the Earth. Airborne particles, many of which are minerals, also have important effects on the Earth's energy balance, and thereby on global warming. For example, there is a strong correlation between the quantity of aerosol dust and recent periods of glaciation, with deposition rates between 2 and 20 times current values (Thompson and Mosley-Thompson, 1981; Hammer et al., 1985; Petit et al., 1990; Rea, 1994; Steffensen,1997; Reader et al. 1999). It seems likely that the airborne minerals affected global climate by their interactions with solar and terrestrial radiation (Andreae, 1995, 1996; Duce, 1995; Li et al., 1996; Sokolik and Toon, 1996; Tegen and Lacis, 1996; Mahowald et al., 1999) and also by the amounts of nutrients supplied to the oceans, thereby affecting biological productivity and amounts of CO_2 released into the atmosphere (Martin and Gordon, 1988; Watson, 1997). Additionally, the large surface areas provided by airborne minerals result in abundant crystallographic sites for heterogeneous condensation and subsequent reaction of gaseous species (Dentener et al., 1996; Zhang and Carmichael, 1999). Although not the focus of

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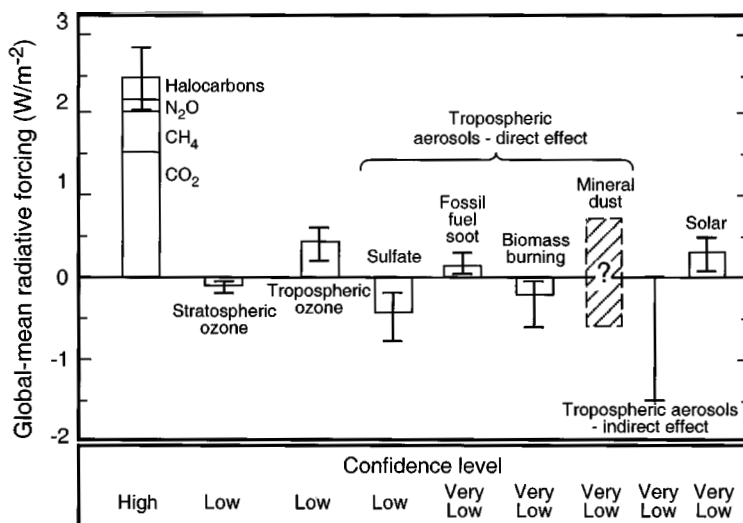
FIG. 1. Globally averaged radiative forcing at the tropopause as a result of increases in greenhouse gases aerosols, and solar activity from pre-industrial times to the present. After IPCC (1996); the bar indicating uncertainty for mineral dust was added by the authors).

the current paper, at local and regional scales mineral aerosols also have major impacts on visibility and human health.

Although most geoscientists would have no problem agreeing that NaCl (halite) and other salts derived from the sea are minerals, atmospheric scientists tend to reserve the term for silicates. In such cases, "mineral" is commonly modified by "crustal" or used as an adjective to describe "dust" (e.g., Tegen et al. 1997; Liao and Seinfeld, 1998; Chiapello et al. 1999; Reader et al. 1999), which seems to mean what geoscientists refer to as rock-forming minerals, i.e., mainly aluminosilicates.

Despite their mass abundance among aerosol particles, little attention has been given to specific, individual rock-forming minerals. For example, the definitive reference on the effect of aerosols on climate is the report of the Intergovernmental Panel on Climate Change (IPCC, 1996). That influential publication emphasized the importance of aerosols and stimulated much of the current interest in the study of aerosols and their effects on climate. Nevertheless, the IPCC summary of radiative forcing, reproduced here as Figure 1, contains no reference to minerals; the bar for mineral dust was added by us. Moreover, none of the general circulation models (GCMs) used by the IPCC for global studies of climate change have a mineral dust feedback, implying that minerals are either inconsequential or

optically inert. An interesting and, as yet, unresolved question is whether we are simply at an early stage in the recognition and evaluation of the impact of airborne minerals, or whether they are relatively unimportant. We believe the former alternative is correct. However, minerals do present special problems connected with their variety and complexity, the associated difficulties with identification, and the fact that the radiative properties of most minerals are not well known.

Although geoscientists and atmospheric scientists may use the term mineral differently, the more important point is that the tools and knowledge of mineralogy provide important information and novel perspectives for the study of airborne particles and their effects on the environment. The goals of this paper are to introduce the topic to geoscientists, to review some of the relevant literature, and to detail current issues and ways they are being addressed.

Radiative Forcing and Climate

The global energy budget of the Earth reflects a balance between absorption of solar radiation and blackbody emission of terrestrial radiation by the Earth and its atmosphere. Solar radiation (often called "short-wave") strongly peaks in the visible wavelength range, whereas terrestrial radiation (often called "long-wave") is in the near-infrared 5
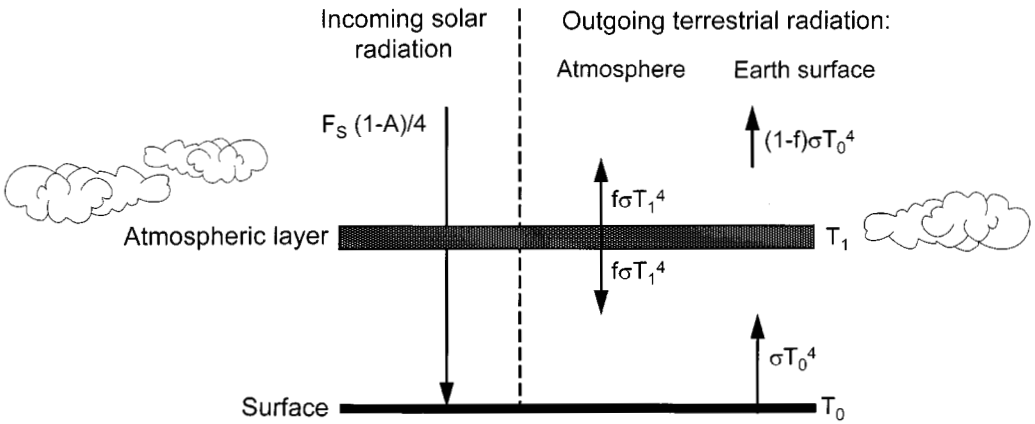
FIG. 2. Radiation balance for the atmosphere. See text for details (after Jacob, 1999).

to 50 μm wavelength range. Gases in the atmosphere are largely transparent to visible solar radiation, but many trace gases (called greenhouse gases) efficiently absorb the long-wave terrestrial radiation emitted by the surface and re-emit it toward the Earth. The resulting warming of the Earth's surface is called the greenhouse effect.

A simple model of the greenhouse effect is shown in Figure 2 (after Jacob, 1999). In this model, we view the atmosphere as a single isothermal layer detached from the Earth's surface. The incoming solar radiation flux, $F_s = 1370$ W m^{-2}, at the top of the Earth's atmosphere is either reflected back to space (by clouds, aerosol, snow, and ice) or absorbed by the Earth's surface. We neglect the small fraction of solar radiation absorbed by the atmosphere. The fraction of incoming solar radiation reflected back to space is called the planetary albedo A; it has a global mean value of 0.28. The global mean solar radiation flux absorbed by the Earth's surface is thus $F_s(1 - A)/4 = 250$ W m^{-2}, where the geometric factor 4 is the ratio of th = e cross-sectional to total area of the Earth.

The long-wave radiation spectrum emitted by the Earth's surface can be closely approximated as that of a blackbody. The resulting flux integrated over all wavelengths is σT_o^4, where σ is the Stefan-Boltzmann constant ($= 5.67 \times 10^{-8}$ W M^{-2} K^{-4}), and T_o is the global mean surface temperature of the Earth. Gases, aerosols, and clouds in the atmosphere absorb a fraction (f) of this emitted terrestrial radiation, whereas the rest is transmitted to space. The Kirchhoff law for blackbody radiation states that absorptivity equals emissivity; if the atmosphere in our simple model of Figure 2 absorbs a fraction f of the long-wave radiation, then its long-wave emission flux is $f \sigma T_1^4$, where T_1 is the temperature of the atmospheric layer. This emission flux from the atmospheric layer is directed both downward and upward.

As shown in Figure 2, the energy balance for the Earth system (Earth + atmosphere) is

$$\frac{F_s(1 - A)}{4} = (1 - f)\sigma T_o^4 + f\sigma T_1^4, \qquad (1)$$

where the left-hand side is the incoming solar radiation (F_{in}) and the right-hand side is the outgoing radiation exported to space (F_{out}). The energy balance for the atmospheric layer is

$$f\sigma T_o^4 = 2\sigma T_1^4, \qquad (2)$$

since the atmospheric layer emits both upward and downward. From these two equations, we obtain as a solution for the surface temperature T_o of the Earth:

$$T_o = \left[\frac{F_s(1 - A)}{4\sigma\left(1 - \dfrac{f}{2}\right)} \right]^{\frac{1}{4}}. \qquad (3)$$

The observed surface temperature $T_o = 288$ K corresponds to $f = 0.72$; we reproduce the Earth's surface temperature in our model if 72% of the long-wave radiation emitted by the Earth's surface is absorbed by the atmosphere.

We see from equation (3) that T_o increases if f increases (as from increases in greenhouse gases) or if A decreases. The potential climatic effect of a perturbation to the radiative budget of Earth is generally measured in terms of its radiative forcing, defined as the instantaneous disequilibrium ΔF between incoming and outgoing radiation in equation (1) as a result of a change in either A or f:

$$\Delta F = F_{in} - F_{out}. \qquad (4)$$

In our model, the disequilibrium is calculated at the top of the atmosphere; in research models, it is calculated at the tropopause since the stratosphere above is only weakly coupled to the Earth's surface.

If the radiative forcing is applied as a constant perturbation, then the Earth system will eventually evolve to a new radiative equilibrium. The resulting change ΔT_o in the Earth's surface temperature can be readily calculated in our model (Jacob, 1999):

$$\Delta T = M \Delta F, \qquad (5)$$

where M is the climate sensitivity parameter:

$$\lambda = \left\{ \frac{1}{4\sigma\left(1 - \dfrac{f}{2}\right)T_o^3} \right\}. \qquad (6)$$

Substituting the previously given values for f, λ, and T_o, we obtain M = 0.3 K m² W⁻¹.

This model has obvious weaknesses, notably in the lack of vertical resolution of the atmosphere, the lack of wavelength dependence, and the lack of climate feedbacks. Nevertheless, calculations with global three-dimensional models of the atmosphere and ocean system (general circulation models or GCMs) confirm that OT and OF are linearly related, with k ranging from 0.3 to 1.4 K m² W⁻¹, depending on the GCM (IPCC, 1996). The value calculated in our model is at the low end of the GCM values, mostly because we did not account for the feedback from water vapor, a major greenhouse gas (as Earth warms, increasing evaporation of water from the oceans reinforces the greenhouse effect and provides a positive feedback). But we see from the above discussion that the concept of radiative forcing can serve as a general indicator of the potential for climate change associated with a given radiative perturbation.

Aerosols and Radiation

Aerosol particles occur in a wide range of sizes, shapes, compositions, and degrees of agglomeration. Examples are given in Figures 3 to 5, which show particles collected from a variety of tropospheric environments. Collectively, these figures illustrate features that would be taken for granted by geochemists, but that are at odds with widely accepted assumptions used among atmospheric scientists. We discuss and explain these in sequence, following a review of aerosols and radiation.

Aerosols have complicated effects on the radiation balance of the Earth. Depending on their types and sizes, they may absorb and scatter (reflect) short-wave solar radiation, and also absorb long-wave terrestrial radiation (there is no significant scatter in the IR wavelength range). Perturbations to both f and A may result in our model, as well as a vertical displacement of solar heating, since some solar radiation is absorbed by the aerosol layer instead of by the surface. The sum of these perturbations represents the direct radiative effect of aerosols.

Aerosols also affect the radiative budget of Earth through cloud formation. They serve as condensation nuclei for clouds, so that an increase in aerosol number causes a rise in cloud albedo both by increasing the number of droplets and by increasing the lifetimes of clouds. This is called the indirect radiative effect of aerosols, and it depends on the aerosol sizes and number concentrations.

IPCC (1996) gives estimates of the cumulative radiative forcing over the past century from increasing concentrations of greenhouse gases and aerosols. The total forcing from long-lived greenhouse gases (CO_2, CH_4, N_2O, halocarbons) is 2.5 W m⁻², corresponding to ΔT_o = 1 to 3 K (equation 5) (Fig. 1). The observed warming over the past century has been less, about 0.6 K. It is now thought that anthropogenic aerosols may be a critical compensating factor. The radiative forcing from anthropogenic sulfate and carbonaceous aerosols is estimated by IPCC (1996) to be in the range from –0.3 to –1.3 W M⁻² (direct effect) and 0 to –1.5 W M⁻² (indirect effect). The negative forcing arises from the increase in planetary albedo that results from scattering of solar radiation. Sulfate and carbonaceous aerosols are in the submicrometer size range, which is too small to absorb long-wave radiation and contribute to the greenhouse effect.
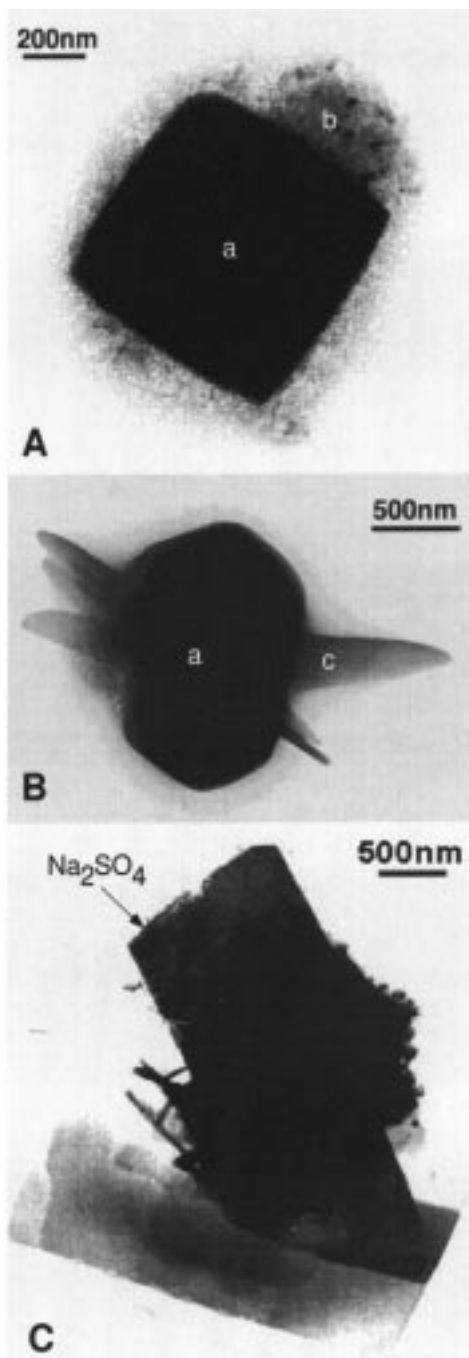
FIG. 3. Transmission electron microscope (TEM) images of reacted sea salt. A, B. Euhedral NaCl (a) with anhedral sulfate rim (b) and projecting sulfate crystals (c), Canary Islands, N. Atlantic Ocean, ACE-2. C. Tabular Na_2SO_4 particles converted from NaCl, Azores, North Atlantic Ocean, ASTER/MACE (from Pósfai et al., 1995).

As pointed out in the introduction, the IPCC report does not include radiative forcing from anthropogenic mineral dust. Yet dust accounts globally for over half of the total aerosol mass load in the atmosphere (Tegen et al., 1997), and its pervasive contribution to aerosol optical effects is evident from satellite observations (Herman et al., 1997; Husar et al., 1997). The largest sources of dust are in the northern tropics, although the amount of airborne dust varies considerably in space and time, reflecting the texture and dryness of soils as well as the wind speed. According to present estimates, 10 to 50 % of the dust in the atmosphere originates from human influences such as desertification, cultivation, and erosion (Sokolik and Toon, 1996; Tegen et al., 1996). Clearly, the anthropogenic radiative forcing from dust needs to be included in future climate change assessments.

Dust particles in the atmosphere both scatter and absorb solar radiation (Tegen and Lacis, 1996) and also are sufficiently large to absorb long-wave terrestrial radiation and thus have a greenhouse effect. The indirect radiative forcing associated with cloud formation is generally unimportant for dust because the number concentration of dust particles is small. (Because of their relatively large sizes, they make a substantial contribution to the aerosol mass concentration but not to the aerosol number concentration.) The vertically integrated short-wave optical depth of dust, including contributions from both scattering and absorption, averages about 0.03 globally; this value can be compared to a global mean estimate of 0.10 for the total optical depth of atmospheric aerosols (National Research Council, 1996). The comparison implies that dust accounts globally for 30% of the light extinction by aerosols. Over large regions of the northern tropics, the dust optical depth can exceed 0.5 (Tegen and Fung, 1994).

The optical properties of atmospheric dust are largely determined by particles in the 0.2 to 2 µm size range; the resulting effect on the radiative budget is complicated and is highly dependent on the poorly known size distribution and refractive index of dust particles (Tegen and Lacis, 1996; IPCC, 2000). Dust increases planetary albedo over dark surfaces such as the oceans. In contrast, over bright surfaces such as deserts, absorption of solar radiation by dust results in a net decrease in albedo. On a global average, the short-wave radiative forcing from dust is negative—i.e., the cooling resulting from solar backscatter dominates over the heating arising from solar absorption. The greenhouse
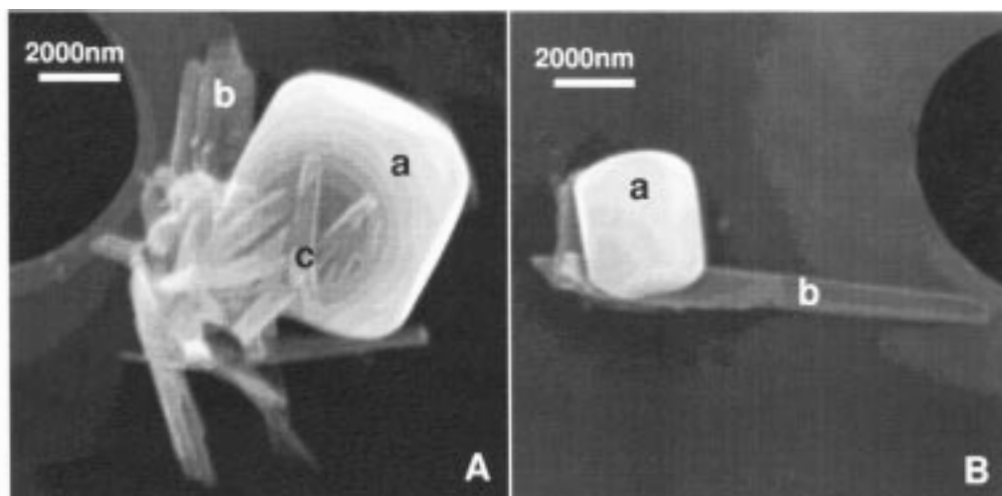
FIG. 4. Scanning electron microscope (SEM) images of partially reacted sea salt. A. Aggregation of cubic NaCl (a), tabular and rod-shaped mixed-cation sulfates (b), and Na_2SO_4 (c). Cf. Figure 2. The sulfate is a reaction product of NaCl. B. NaCl cube (a) with rod-shaped mixed-cation sulfate (b), Canary Islands, North Atlantic Ocean, ACE-2). The large black partial holes are from the SEM substrate.

warming from absorption of long-wave radiation by dust introduces further compensation in radiative forcing calculations.

Tegen et al. (1996) presented a global model study of radiative forcing at the tropopause from anthropogenic dust. They found a slight positive global forcing of 0.09 W m^{-2} at the tropopause, representing a balance between a positive long-wave forcing of 0.34 W m^{-2} and a negative short-wave forcing of –0.25 W m^{-2}. Such a calculation has large uncertainties because of our poor knowledge of the optical properties of dust particles. The latest IPCC (2000) report gives a tentative range of –0.6 W m^{-2} to +0.4 W m^{-2} for the global radiative forcing at the tropopause from anthropogenic dust. This value, while potentially large, still does not do justice to the strong regional variability of the dust radiative forcing that may have profound implications for climate; nor does it account for the climatic implications of deposition of heat in the atmospheric dust layer. Assessing the potential climatic effect of dust requires a different approach.

In a pioneering study, Miller and Tegen (1998) used a GCM to investigate the climatic consequences of the heating that results from the present-day atmospheric dust layer (as compared to an atmosphere with no dust). They found that absorption of solar radiation by the dust layer results in a net cooling of the surface of about 1 K in dusty regions of the northern tropics. The high-altitude warming resulting from the dust leads to buoyant stabilization of the lower atmospheric column, restricting convective motions and reducing precipitation. This drying effect could have a positive feedback by favoring dust generation; on the other hand, stabilization of the lower troposphere would decrease surface wind speeds and suppress dust generation (negative feedback). Considerably more work will be needed over the next decade to improve our understanding of the climatic effects of dust.

Analysis of Aerosol Particles

Aerosol particles have, with few exception, been neglected by geoscientists. The slack has been picked up by atmospheric scientists, primarily chemists. Most emphasis has been on bulk samples. Particles are collected through the use of what amounts to sophisticated vacuum cleaners. Aerosol concentrations in the troposphere are typically in the range of 1 to 100 cm^{-3}. Collection on a filter at a typical flow rate of 10 liters per minute yields 104 to 106 particles in one minute of sampling. These bulk samples are commonly analyzed by any of several increasingly sensitive methods. The total "mineral" components are then determined by proportioning to the amounts of Al, chosen as representative of "crustal" minerals or desert dust (e.g., Chiapello et

al., 1999). The data may be processed through statistical methods, such as principal components analysis. However, no matter how the data are handled, this is clearly a crude method; it is totally unequal to the task of accurate phase identification for the range of minerals in the atmosphere.

Bulk analyses are limited in their utility. Although useful for integrating information for large numbers of particles, the effects produced by aerosol particles—whether on climate, haze, or health—depend on the characteristics of the individual particles, rather than on their averaged bulk properties. A minor or trace element might be widely dispersed, so that it is spread among all particles in tiny amounts, or it might be concentrated in a few particles in major amounts. Similarly, both speciation and whether the element(s) of interest are concentrated on particle surfaces rather than in the interiors, could have a major effect on the radiative properties.

The analysis of individual particles is much more time consuming than bulk analysis, and far fewer particles can be analyzed in given periods. However, the quality of the phase data is vastly superior. Scanning electron microscopes can be automated to produce unattended x-ray emission analyses around the clock (Germani and Buseck, 1991; De Bock et al., 1994; Katrinak et al., 1995; Anderson et al., 1996; Buseck and Anderson, 1998). Particle identifications are then based on the determined compositions. However, elements lighter than Na are not normally analyzed, and structural data are therefore not obtained. Also, as is true for all methods of chemical analysis of individual particles, the amount of water—whether structural or adsorbed—is not measured directly.

Transmission electron microscopy (TEM) has the great advantage in that it provides all the necessary information (size, shape, composition, crystallographic structure, and thus speciation) for phase identification and determination of extent of aggregation, and this information can be obtained on an individual-particle basis. TEM has been used for aerosol studies to a limited, albeit increasing, extent. When performed by atmospheric chemists, it has been common practice to group samples into broad categories such as sulfates, soot, crustal minerals, and "other." In our TEM studies, we have far greater precision for mineral identification (Pósfai et al., 1994, 1995, 1998, 1999; Buseck and Pósfai, 1999) , and we are able to detect and image particles

as small as 30 nm. However, TEM measurements are labor intensive and must be made in the laboratory. Despite significant problems and the aforementioned limitations, they can provide "ground truth" for important selected particles that can then be used as calibration for the less specific but more rapid types of measurements.

A new method of particle analysis based on aerosol time-of-flight mass spectrometry has recently attracted much interest (Prather et al., 1994; Johnston and Wexler, 1995; Noble and Prather, 1996; Gard et al., 1998; Murphy et al.,1998). Although there are various configurations and acronyms (ATOFMS—aerosol time-of-flight mass spectrometer; PALMS—particle analysis by laser mass spectrometry), they all combine a method for introducing particles into an optical path where they are sized and then ionized with a laser. The fragments are immediately inserted into and then analyzed in a time-of-flight mass spectrometer. The resulting data include size and approximate particle compositions. Major advantages are that the measurements are sensitive and made on-line using a moderately portable instrument. Limitations are that structural (crystallographic) data are lacking and speciation must be calculated or inferred from reconstructions of the complex spectra of ionized fragments. This reconstruction becomes significantly challenging if more than one phase occurs within a given particle. Calibration of these instruments for quantitative chemical analysis is notoriously difficult.

It is clear that no one technique can provide all the information needed to completely characterize the aerosol particles in any given parcel of air. The TEM provides the most complete data per particle, but cannot be operated on-line or in automated mode. At present, no instrument or technique can provide adequate speciation of organic particles, which represent a major component of the atmospheric aerosol. Also, none of the currently available single-particle measurement methods can provide quantitative data for aerosol water.

Real versus Theoretical Aerosol Particles— Some Common Assumptions

Let us return to the figures and how they relate to several assumptions used in atmospheric studies, especially with reference to the modeling that is an essential part of predicting climate changes.
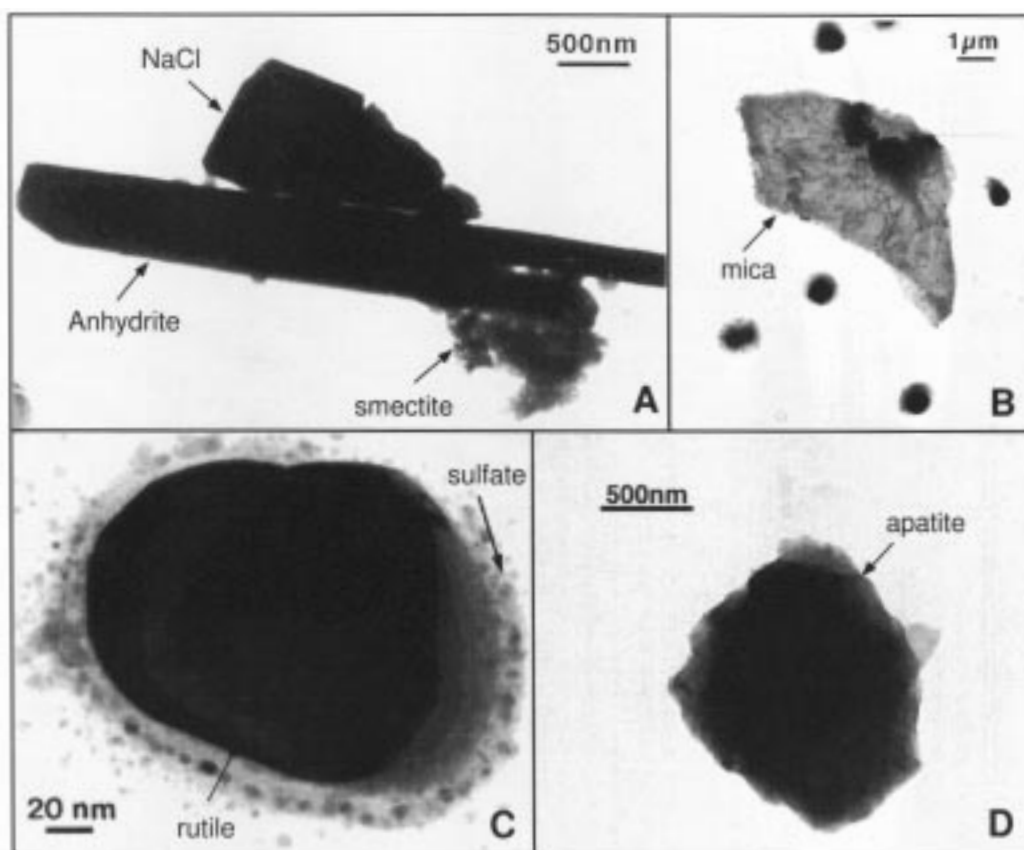
FIG. 5. TEM images of oxide and silicate mineral dust. A. Terrestrial smectite and anhydrite are internally mixed with NaCl (Azores, North Atlantic Ocean, ASTER/MACE; from Pósfai et al.,1995). B and D. Mica and apatite collected in the marine boundary layer (Canary Islands, North Atlantic Ocean, ACE-2). C. Twinned submicron rutile particle with sulfate coating (Equatorial Pacific, FeLINE-I cruise; from Pósfai et al.,1994).

Particle shapes and phases

Modelers commonly assume that aerosol particles are spherical. Several justifications are invoked for this assumption. Both absorption and scattering can be easily estimated for spherical shapes, and Liao and Seinfeld (1998) indicate that this assumption does not lead to significant errors. Lacis and Mischenko (1995) also report that an atmospheric radiation model that integrates over the range of particle orientations shows little difference from one based on a spherical assumption. However, other studies indicate that deviations from sphericity can have significant effects on aerosol optical properties (Bohren and Singham, 1991; Pilinis and Li, 1998; Schulz et al., 1999; Korolev et al., 1999). The supposition of sphericity is especially problematical for satellite measurements of aerosol optical properties,

since the scattering geometry of irregularly shaped particles can differ greatly from that of spherical ones.

The sphericity assumption for aerosol particles is unambiguously valid only if they are liquid. Whether a particle is liquid or solid depends on its composition, on the local relative humidity (RH), and on its RH history (Seinfeld and Pandis, 1998). Most salt and organic particles deliquesce at high RH and may remain in a metastable liquid state because of lack of crystallization nuclei as the RH drops (e.g., Cziczo et al.,1997; Cziczo and Abbatt,1999). Aluminosilicate minerals in aerosols do not normally deliquesce. However, our examinations of mineral aerosols by automated scanning electron microscopy show extensive development of hydrophilic sulfate coatings on mineral particles
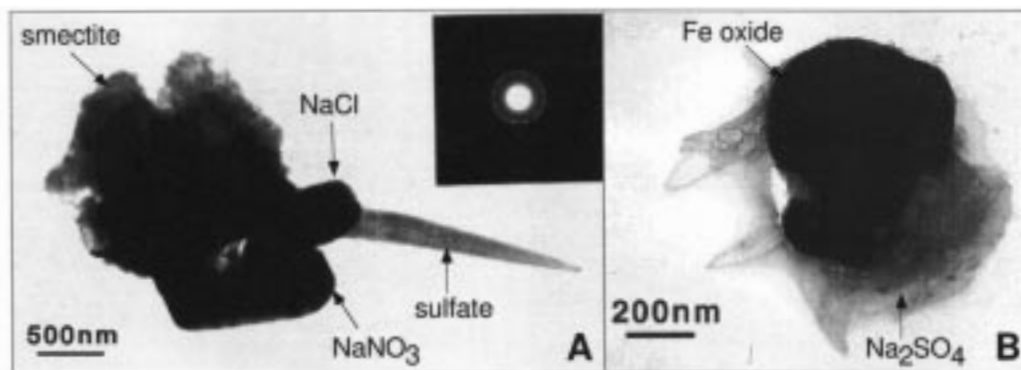
FIG. 6. TEM images of internally mixed terrestrial and marine aerosol particles. A. Terrestrial smectite with sea salt particles. Such an aggregation of mineral dust and sea salt may occur in clouds (cf. the rod-shaped sulfate crystal in Fig. 3B). The selected-area electron diffraction pattern (upper right) confirms the identification of smectite (Azores, North Atlantic Ocean, ASTER/MAGE; after Pósfai et al., 1995). B. Fe oxide emitted from coal burning with Na_2SO_4 (Sagres, Portugal, ACE-2).

(Anderson et al., 1992, 1996). A possible mechanism for the formation of such coatings is heterogeneous oxidation of SO_2 on the particle surfaces. Another mechanism is the scavenging of mineral particles by sulfate-containing cloud droplets. When such droplets evaporate, they leave behind mineral particles physically aggregated with or coated by sulfate. In this manner, otherwise non-deliquescent mineral particles can become cloud condensation nuclei (CCN) if a hydrophilic coating is present. Once hydrophilic, an aerosol particle can undergo many cycles of cloud processing before being removed by dry deposition or precipitation. However, unless deliquesced, their shapes will not be spherical.

In the TEM, as shown by several of the particles in Figures 3 to 5, the shapes of many particles are irregular, in some cases highly complex and even jagged. Some of these crystals may have formed by precipitation in response to evaporation of deliquesced water after sampling/or in the vacuum of the TEM. Clearly, there is a need for experimental work to test that assumption, and that is an area under active study. Much work remains to adequately evaluate the complex shapes of real particles.

Mixing state

Parcels of air contain mixtures of many different particle types. Atmospheric scientists draw a sharp distinction between what they call internal and external mixtures. The distinction is important because mixing state affects radiative properties. In an external mixture, each individual particle consists of a single material, and so can be considered homogeneous. Internal mixtures, on the other hand, contain more than one material—i.e., they are polyphasic, more like a tiny rock than an individual mineral. The transition from an external to an internal mixture takes place by coagulation of particles, coalescence of particles in clouds, and gas-aerosol transfer reactions such as the uptake and oxidation of SO_2 on dust particles.

Most atmospheric radiation models assume that aerosols are externally mixed because the specification of optical properties is much easier than for internal mixtures. The assumption of external mixing has significant impacts on the calculated radiative properties. For example, the single-scattering albedo for internal mixtures of aerosols is generally lower than for external mixtures. In the next section, more details are discussed for mixtures of soot and sulfate aerosols.

Many aerosol particles are, in fact, internally mixed. We see such mixtures of different sea salts (Figs. 3 and 4), silicates and marine minerals (Figs. 5 and 6), and different types of anthropogenic species (Figs. 7 and 8). In fact, we observe a wide combination of mixture types. We will return to this subject below, in the section on soot and sulfate aerosols.
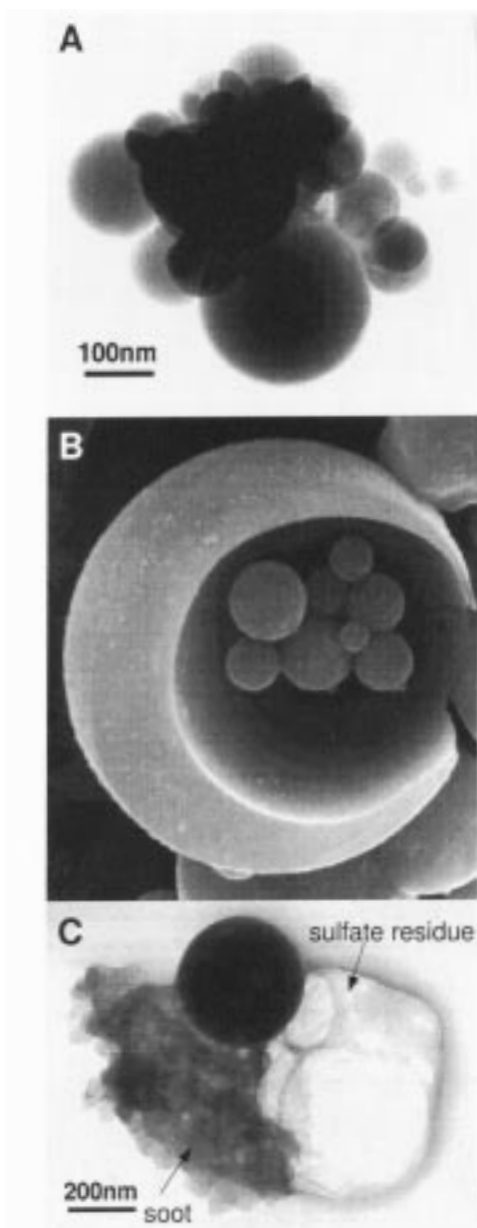
FIG. 7. SEM and TEM images of fly-ash particles. A. TEM image of an aggregate of submicron silica spheres collected in the marine boundary layer (Canary Islands, North Atlantic Ocean, ACE-2). B. SEM image of fly-ash. The hollow fly-ash particle (cenosphere) contains smaller fly-ash spheres. The largest hollow sphere is roughly 5 m across (by Gary Aden, Arizona power plant source). C. TEM image of internal mixture of fly-ash, soot, and sulfate. The sulfate was evaporated by the TEM electron-beam, leaving behind only S-bearing residues that outline its former shape (Canary Islands, North Atlantic Ocean, ACE-2).

Phase identification/speciation

No species identification is complete without knowing its structural state. Identification of the structures of crystalline aerosol particles (such as minerals) is important for obtaining information about their refractive indices and other physical properties. Also, particles that were partly or totally liquid may crystallize during or after sampling, and their structures can provide indirect information about their compositions. The most commonly used method for mineral identification in aerosols is x-ray diffraction (e.g., Leinen et al., 1994; Caquineau et al., 1997), which is a bulk method and so provides only limited information regarding structural state and speciation for all but the most abundant particle types. Except for TEM, none of the analytical methods used by atmospheric scientists is capable of determining structural states for individual particles, and so structural states are generally ignored. Speciation also is commonly overlooked.

Soot and Sulfate Aerosols

Soot and sulfate aerosol particles are abundant, are mainly of anthropogenic origin, and have pronounced effects on radiative forcing. We discuss them here because they bear a close relation to minerals (many species in fact have mineral analogues), are important and have been studied intensively, and illustrate many of the principles discussed in this paper.

Combustion of fossil fuels releases SO_2, which is then oxidized to sulfate in the atmosphere. Aerosol sulfates are also atmospheric reaction products of natural processes such as volcanic and planktonic emissions of sulfur gases (Spiro et al., 1992). Sulfates scatter short-wave radiation and thus produce a negative forcing, ie., cooling.

Soot is another major component of the tropospheric aerosol. It results from combustion of fossil fuels, as well as from mass burning during both controlled and wild fires (e.g., Crutzen and Andreae, 1990; Kuhlbusch et al.,1996; Kuhlbusch and Crutzen, 1996; Andreae, 1997). Soot particles absorb radiation and thereby produce a positive forcing, i.e., a net warming.

Soot and sulfate provide good examples of the assumptions discussed in the previous section. Most models assume that they are externally mixed. We have observed just the contrary. By using high-resolution TEM, we have found soot intergrown with sulfates in aerosol particles collected from marine
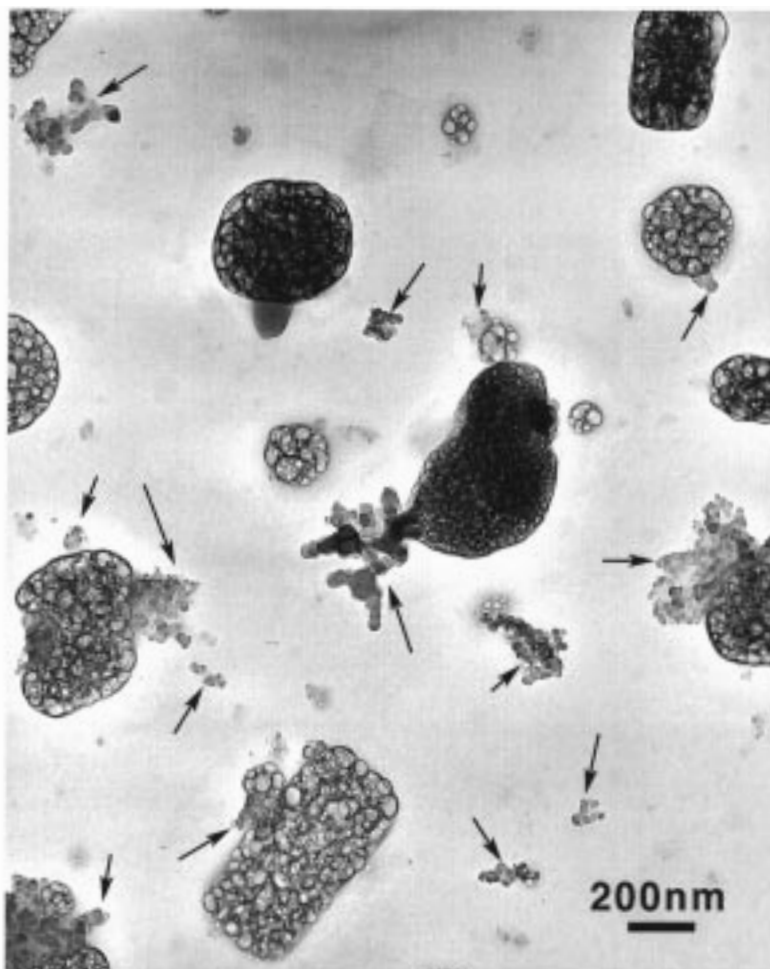
Fig. 8. TEM image of an assemblage of internally and externally mixed soot (arrowed) and ammonium sulfate. The bubbles formed as a result of the decomposition of the ammonium sulfate particles from electron-beam damage (Sagres, Portugal, ACE-2).

particles over the northern Atlantic, equatorial Pacific, Southern, and Indian oceans, and from polluted continental regions in Europe and the United States (Figs. 9 and 10). In fact, wherever we look in detail at aerosol sulfates we observe at least small amounts of soot in a significant number of particles (Pósfai et al., 1998, 1999; Buseck and Pósfai, 1999). These internal mixtures are so fine grained that they are only observable by high-resolution measurements. It remains to be determined if the reverse is true. In marine areas such as were sampled during the ACE-1 experiment, the soot particles were too small and had low contrast, so we did not attempt to count those that were not in sulfates.

The effects of such internal mixtures have been considered in several recent studies (Haywood and Shine, 1995; Pilinis et al., 1995; Andreae et al., 1986; Haywood et al., 1997; Tang, 1997). The most detailed investigation to date is that by Fuller et al. (1999), who calculated the absorption cross sections for soot/black carbon in a variety of configurations and aggregation states. Their results are complex and show that the radiative properties depend on a variety of parameters that include particle size and shape, degree of crystallinity, type of aggregation, density of aggregates, and type (internal or external) and extent of mixing with non-absorbing materials such as sulfate. The position of the soot within an
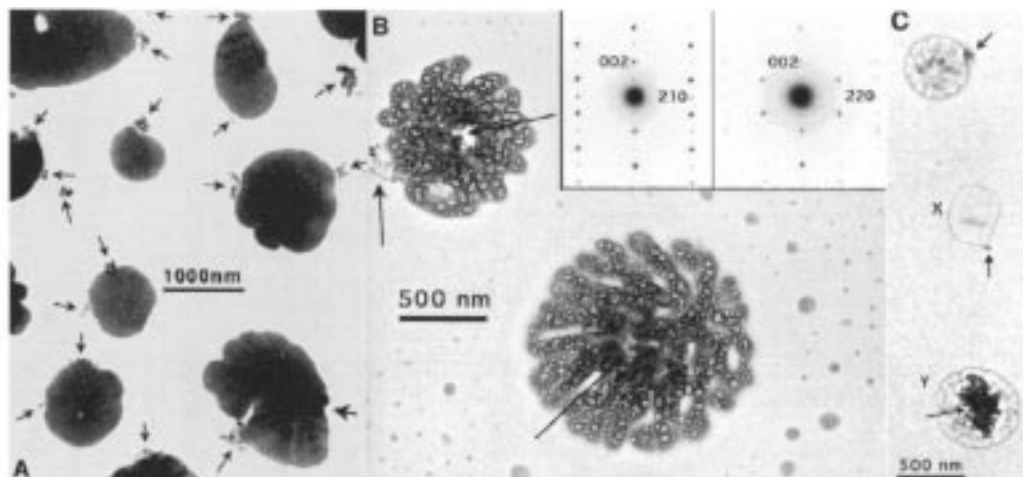
FIG. 9. TEM images of ammonium sulfate containing soot. A. Ammonium sulfate particles internally mixed with soot (small arrows) and fly-ash spheres (larger arrow in the lower-right corner), Azores, North Atlantic Ocean, ASTER/MACE (after Pósfai et al., 1999). B. Ammonium sulfate with soot inclusions. The rings of small ammonium sulfate particles formed during the dehydration of the large central particle. The inserted selected-area electron diffraction patterns were obtained from a similar particle and are consistent with the structure of ammonium sulfate. C. Soot inclusions (arrowed) and residues after evaporation of ammonium sulfate particles by the electron-beam. B and C are from Tasmania, Southern Ocean, ACE-1 (from Pósfai et al., 1995).

encapsulating sulfate host also affects the absorption and scattering properties. We think it is reasonable to expect effects of comparable magnitude on the seemingly abundant internal mixtures involving minerals with one another and with other species. Their results "suggest the importance of the determination of the physical state of the soot particles and their immediate environment when ascribing characteristic values for their absorption and scattering efficencies." We interpret that statement as indicating that TEM measurements are needed.

Rock-forming Minerals (RFM) in the Troposphere

Although the RFM are abundant in the troposphere, no studies even closely approaching that of Fuller et al. (1999) for soot have been devoted to the RFMs. Liao and Seinfeld (1998) calculated the forcing effects of minerals, although their calculations are based on integrated atmospheric optical measurements and are independent of the composition and speciation of the particular dust types. Sokolik and Toon (1996, 1999) initiated more extensive studies through their measurements of 11 important minerals; they have thereby amassed the largest data set, by far, on optical properties and radiative

effects of minerals in the troposphere. They conclude that it will be highly important to determine the state of aggregation for minerals such as hematite, and also that more data are required on the regional and global scales to quantify the size-resolved composition of (mineral) dust, and thus the radiative effects of minerals.

We believe that their abundance and consequent large surface areas for gas deposition and catalytic activity will bring increasing attention to the role of minerals in the troposphere. Their effects on climate will, because of their more localized distribution than gases, be more regional than global. However, some minerals will, similarly to soot, produce warming and thus could be considered "greenhouse particles" whereas others, similarly to sulfates, will produce negative forcing and thus tend toward cooling, acting like "icehouse particles." Their details and net effects on the radiative processes in the troposphere remain to be determined.

Regulatory and Health Issues

It is well known that certain mineral aerosols produce health-threatening diseases (e.g., asbestosis, silicosis, etc.), and the insult-producing materials are regulated by the U.S. Environmental
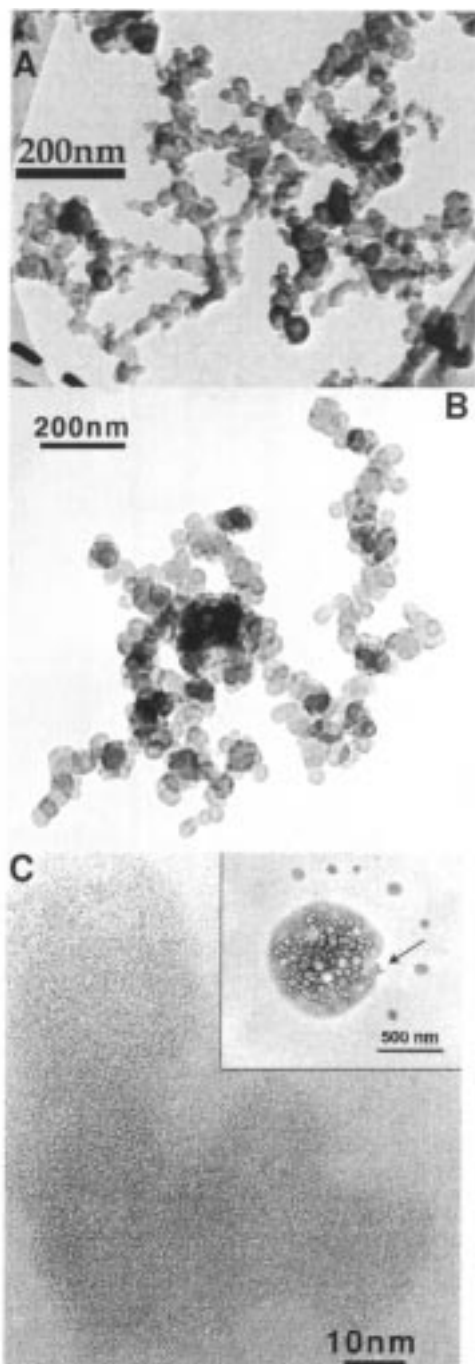
FIG. 10. TEM images of soot. A, B. Chain-like soot aggregates (A = Phoenix, Arizona after Katrinak et al., 1993; B = Sagres, Portugal, ACE-2). C. High-resolution TEM image of the arrowed soot aggregate showing the onion-like structure of soot spheres (Southern Ocean, ACE-1; after Pósfai et al, 1999).

Protection Agency (EPA). These problems tend to be localized geographically and are relatively straightforward to manage. A broader set of issues are related to ambient aerosols, and the EPA has dealt with these through the so-called PM (particulate matter) 2.5 and PM 10 standards from §109 of the Clean Air Act. These standards regulate the total mass of particles with diameters of 2.5 μm or less (with 15 and 65 μg M^{-3} as annual arithmetic mean and 24-hour average concentrations, respectively). The PM 10 standard is concerned with particles 10 μm or less in diameter (with 50 and 150 μg M^{-3} as annual arithmetic mean and 24-hour average concentrations, respectively).

The basis for the 2.5 and 10 μm diameter cutoffs is related to the sizes of particles that penetrate the lungs and the naso-pharyngeal systems, respectively. Although one of the goals of the Clean Air Act is to protect and improve the quality of the air we breathe, the PM standards totally ignore the compositions of the inhaled particles. With the exception of a few specified substances, there is no regulatory need or incentive to know the mineralogy of the inhaled particles. It remains for scientists and policymakers to decide whether such species- and coating-independent regulations serve the needs of society.

There is another problem related to the PM standards. The amount of mineral dust in the air exhibits great variations, both geographically and temporally. Volcanic eruptions can inject vast quantities of SO_2 (which rapidly turns into aerosol) plus particulate matter into the atmosphere (Andronova et al., 1999). Forest fires and dust storms in arid regions such as the southwestern United States also can produce sporadic events that vastly exceed EPA standards. Federal regulations accommodate such occasions by the possibility of excluding "exceptional events" produced by natural processes. Such somewhat localized events are relatively easy to identify and thus exclude.

Prospero (1999) provides an example of another type of dust-producing event that can be far more difficult to recognize because of its subtlety. At times, large quantities of minerals from northern Africa are transported across the Atlantic and deposited throughout large areas of the southeastern United States (Perry et al., 1997). These depositional events tend to be most severe during the summers, which is also the period when air pollution problems are most intense. Prospero (1999) points out that, somewhat surprisingly, the highest individ-

ual PM 2.5 soil concentrations were found in the southeastern United States rather than in the arid Southwest. African dust also commonly impacts the Caribbean Islands (Arimoto et al.,1992, 1995), and there is abundant evidence that dust from Asia has important impacts over large areas in and bordering the Pacific Ocean (Tsunogai et al., 1985; Arimoto et al., 1990; Fan et al., 1996; Jaffe et al., 1999).

The evidence for long-range transport of dust complicates environmental regulations solely based on mass loadings. Identification of such distant source regions requires chemical and mineralogical fingerprinting.

Conclusion

By mass, minerals comprise the greatest part of the aerosol particles in the troposphere, the part of the atmosphere that we inhabit. They have, with prominent exceptions, been largely overlooked by atmospheric scientists, although increasing attention has been devoted to them recently. They are important as absorbers and scatterers of radiation and thus can have important effects on climate, most especially on local and regional scales because of their relatively localized spatial and temporal distributions.

Because aerosol particles are small in dimension and large in number, most analyses have been on large numbers of particles, with averaged bulk compositions and properties as the results. Such bulk measurements have important limitations. The radiative, health, and visibility effects of aerosol particles are caused by the cumulation of individual rather than averaged particles, and therefore there is much reason for studying particles individually.

Transmission electron microscopy is well suited to the study of individual aerosol particles. Many widely used assumptions in global climate models are seen to be of limited validity when individual particles are examined. Thus, spherical shapes, extent of mixing of phases, and particle speciation are all problematical, but can be resolved through individual-particle TEM studies. A difficulty is that deliquesced species lose their water in the vacuum of the electron microscope, and therefore these important aerosol types dehydrate and change their character. With this important limitation, aerosol particles can be studied on an individual basis, their most private details can be determined through TEM, and they represent a far richer and more complex world than commonly is assumed.

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