# Atmospheric-Particle Research: Past, Present, and Future

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## INTRODUCTION

Except when wistfully daydreaming, admiring the sunset, or perhaps worrying about the weather for the day's field work, our attention and gaze as earth scientists is downward. No "Hans Guck-in-die-Luft"[2] are we. And yet, a refocusing of interest upwards to the atmosphere, and the minerals and other particles in it, can be useful and rewarding.

As a starting geology faculty member, I encountered a bizarre situation that also seemed like a splendid opportunity and challenge. As elsewhere, air pollution was hotly discussed in Phoenix in the late 1960s. Its sources were in fierce dispute—nearby copper mines and smelters? vehicular traffic? desert dust? incinerators? local industries? pollutants from California?—and there was pressure from the government in Washington, DC, to solve the problem. However, state legislators did not want "the Feds" involved in state issues. As is still the case, "the Feds" was a dismissive term used by local politicians for federal officials in Washington. This argument seemed unusual because our state, like most entities across the globe, had no research capacity to understand, and even less to control, the sources of the dust and other pollutants that were evident to anyone breathing the air or looking upwards when outdoors.

Here was an opportunity for conducting societally significant research by studying the minerals and other particulate constituents of the atmosphere. They are, after all, an integral part of the Earth system, affecting nutrient distribution, rainfall, and, of course, climate. The challenge of studying airborne particles may seem strange to those of us who were raised on traditional geology, mineralogy, and geochemistry. However, it will make sense in the context of this issue of *Elements*. As stated by Guest Editor Gieré, the goal is to "explore the atmosphere as an exciting new research area for mineralogists and geochemists."

Airborne particles are ubiquitous and are an important focus of studies in the atmospheric sciences because of their huge effect on climate. Although the largest mass fraction consists of minerals—making airborne particles a logical topic of study for mineralogists—this realm of the natural environment has largely been left to chemists and physicists.

Most aerosol particles are less than one micrometer in diameter, with many a few nanometers or less. These sizes present no problems for bulk (ensemble) measurements, but the detailed study of such small aerosol particles requires instruments able to analyze them individually. These are mainly aerosol mass spectrometers and electron microscopes.

Aerosol mass spectrometers analyze particles, one at a time, as they pass through a laser beam that counts and fragments them. They then enter a spectrometer that determines the mass distribution of the fragments, from which they and their parent molecules are identified. Measurements produce extensive data sets with good statistical reliability, but details regarding the nature of coatings, intergrowths, and other complexities must be inferred because the particles are not imaged.

Electron microscopes, in contrast, provide high-quality spatial details about the individual particles, but measurements are made off-line. Although electron microscopes yield poorer statistics, they provide information that is unavailable by other techniques. They are widely used and thus familiar to mineralogists, and the data they produce (e.g. Pósfai and Buseck 2010) are of potential interest to all who combine a fascination with minerals with a desire to do environmental research.

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2 From an 1844 children's poem by H. Hoffman about a boy who runs into trouble because he is forever looking upwards instead of watching where he is going (http://en.wikipedia.org/wiki/Struwwelpeter)


**Figure 1** Clouds formed around exhaust particles along ship tracks in the northeastern Pacific Ocean. These particles are smaller and more numerous than in natural marine clouds, making the track clouds more reflective and thus brighter than the regular clouds. NASA MODIS satellite image; http://earthobservatory.nasa.gov/IOTD/view.php?id=37455

## AEROSOL PARTICLES, CLIMATE, AND CLOUDS

Climate change and the use of climate modeling for assessing future changes are critical topics (IPCC 2007). Aerosol particles interact with solar radiation and influence climate in complex ways; the specifics depend on the optical properties of the particles, which are in turn influenced by their sizes, compositions, crystal structures, agglomerations, and geometries. Assessing the impact of the particles poses major challenges.

Additional complexity is provided by clouds, which consist of myriads of droplets. The process is hard to imagine when in an airplane flying through a cloud, but each droplet formed around an aerosol particle. Clearly, particles have a major influence on cloud development, and clouds obviously have a major influence on climate.

A key question is which particle types form effective cloud condensation nuclei (CCN) and thus favor cloud formation. Effective particles need to be hygroscopic (or have coatings that are) and have diameters larger than ~60 nm. There is much interest in the origin of such particles, how smaller particles grow to an effective size, and the role of pollutants in cloud development (Fig. 1).

Sophisticated instruments are used to collect particles from both within and between cloud droplets in order to determine which types are active. TEM measurements in gases can also be made within small semi-enclosed chambers inserted into the column of electron microscopes. Such environmental cells have recently been used to study reactions as a function of relative humidity and to determine which types of aerosol particles form ice nuclei (Freney et al. 2009).

## MINERALOGICAL AND GEOCHEMICAL INSIGHTS NEEDED

Many atmospheric scientists lack technical familiarity with solids and are casual when referring to them. As mineralogists, it is incumbent upon us to do better. Because of experience with solids, including the chemical analysis of small regions, geoscientists can provide important insights into the study of aerosol particles. The following are examples where such perspective and experience help.

### *Particle Shape and Structure*

Mie theory, a solution of Maxwell's equations for the scattering of electromagnetic radiation, is widely used for calculating the optical properties of individual spherical particles, and most climate models assume that particles can be approximated as spheres. However, observations of individual solid particles using electron microscopes show that few, if any, are actually spherical, and many have highly complex shapes (Fig. 2a). Some particles, like soot, can be approximated as fractal, but for others there is currently no practical model that can be applied.

There is confusion about "structure" and whether the term refers to morphology or crystallography. Atmospheric scientists, many of whom are mainly concerned with surfaces, widely use the former meaning. By contrast, mineralogists and other solid-state scientists use the term to convey the atomic or molecular geometric arrangement.

### *Mixing State*

When modeling the effects of aerosol particles on climate, it is important to know their mixing state, that is, whether they occur as single or multiple phases, called externally or internally mixed, respectively. If the phases were solid, a geologist would call them minerals and aggregates, respectively. For internally mixed particles, there is also commonly an implication regarding single or multiple sources (Seinfeld and Pandis 2006), and additionally, they have been divided into heterogeneous and homogeneous mixtures.

The mixing-state distinctions can be challenging. In contrast to much conventional wisdom, we find that many, and perhaps most, solid particles are heterogeneously internally mixed—i.e. they contain several discrete phases—a result that has potential significance for their reactivity and for climate models.

### *Coatings and Core–Shell Configurations*

Coatings of one species on another are widespread among atmospheric particles, and they give rise to one type of internal mixture. However, as with particle shape, modeling such coatings presents serious challenges. A common assumption is that coatings and other internal-mixing geometries can be adequately represented as spherical cores of one species concentrically surrounded by a shell of another species (Fig. 2b). However, TEM observations show that such core–shell particles rarely, if ever, exist.

If we accept the observations that most solid aerosol particles (a) are not single-phase (i.e. not externally mixed), (b) are irregularly shaped rather than spherical, and (c) do not have core–shell configurations, the challenge is to determine whether the approximations currently used will yield acceptable answers when modeling climate change. Our recent measurements show differences on the order of 30% or more between real and idealized particles, but this conclusion is based on a limited number of measurements. It remains to be determined whether such discrepancies are too low (or too high) for most aerosol particles and whether such errors are significant, given the other uncertainties in climate modeling.

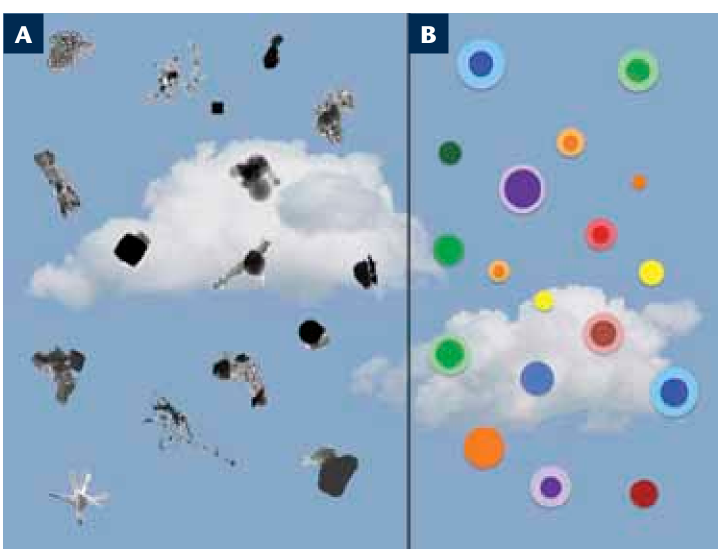


**Figure 2** Comparison of (**A**) real and (**B**) idealized aerosol particles. (**A**) TEM images of actual particles (from Arizona, Mexico, southern Africa, Saudi Arabia, the United Arab Emirates, and Japan; images by K. Adachi, J. Bradley, T. Kojima, J. Li, M. Pósfai). The particles range from 200 nm to a few micrometers in their largest dimension. They are examples and not necessarily representative or average particles. (**B**) Cartoon of spherical single-phase and core–shell particles representing external and internal mixtures, respectively. The colors and sizes are arbitrary.

### *Geoengineering*

Several implications arise from the offsetting effects of reflective particles on the warming produced by greenhouse gases (GHGs) such as $CO_2$. One is that as particle emissions are reduced through improved technology and controls, the net cooling effect of particles will decrease and warming from the GHGs will become an increasingly severe problem.

Artificial injection of particles such as sulfates into the atmosphere to produce cooling and counteract GHG warming has been proposed. Such geoengineering is attracting much attention. However, there is concern because of unanticipated consequences of large-scale tinkering with natural processes (e.g. Andreae 2007). Weather patterns could be affected, resulting in flooding in some areas and droughts in others. If rainfall patterns are changed, the consequences for food production and nutrition could be severe. Moreover, if weather modification is initiated, who is responsible for the consequences of deciding to discontinue the program—or to continue it indefinitely? The topic is being vigorously debated and is sure to produce more controversy in coming years.

## OPPORTUNITIES FOR FUTURE RESEARCH

Aerosol particles are much more complex in their shapes, compositions, and mixing states than has been commonly assumed. Far greater statistical depth is needed to categorize the various particle types, including specific airborne minerals, and to define their physical and chemical features. Once that information is available, parameterization of the typical characteristics and variations will be critical. The means for doing such work on a large scale have yet to be developed. Also, since solid particles might be involved in geoengineering schemes, their study could be an interesting research area for geoscientists.

Determining the identities and fraction of CCN that are organic is a complex problem where organic geochemists can make important contributions. Experience with isotope and trace element mass spectrometry as well as other measurement techniques for small samples can be put to good advantage regarding species identification and the origin and subsequent history of particles in the atmosphere.

Analyses based on ensemble measurements and climate models based on remote (satellite) measurements provide information of a totally different sort from analyses of individual particles. No one currently knows how to span these knowledge and scale gaps, how to incorporate accurate individual-particle information into climate models, or even how essential it is to do. It also remains to be determined whether the conclusions derived from different models, for example, as presented in IPCC (2007), represent the effects of compensating errors or whether the assumptions in the models are accurate.

Many geoscientists have extensive experience with studying small quantities of highly complex materials, a skill that is readily applicable to investigations of atmospheric particles, including organic ones. Studies of atmospheric mineralogy, viewing mineralogy broadly, offer a research arena of great importance and potential.

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