MINERALS IN THE AIR

Reto Gieré[1] and David J. Vaughan[2]

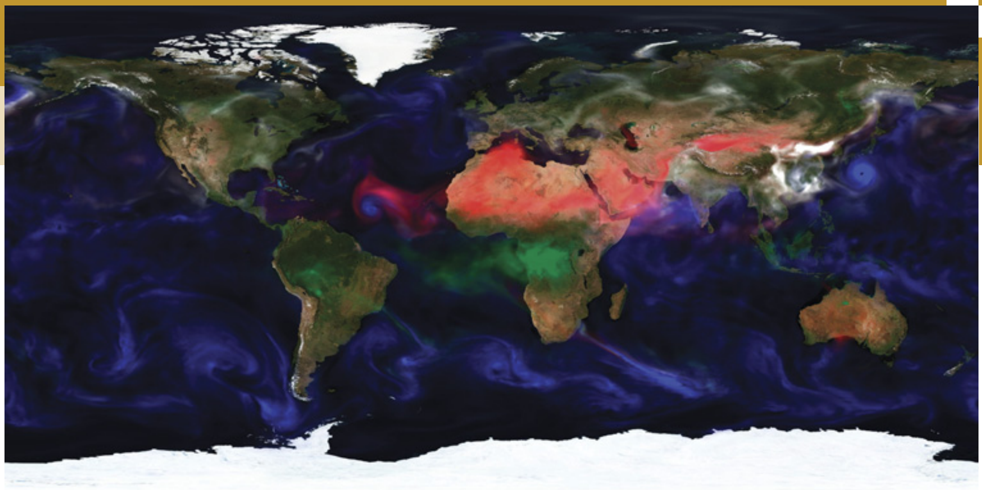

Figure 1 World map showing the distribution of various types of airborne particles: desert dust (red), sea salt (blue), particles emitted from wildfires and biomass burning (green), and anthropogenically emitted sulfates (white, excluding the white areas in the polar regions). Image courtesy of MEEO, Ferrara (www.meeo.it); based on data acquired on September 1, 2011, through the MACC-II project (www.copernicus-atmosphere.eu)

Mineralogists, petrologists, and geochemists do not typically reach for the skies when studying minerals except, perhaps, when threatened by a gigantic cloud of volcanic ash. It is during such events, for example, the April 2010 eruption of the Icelandic volcano Eyjafjallajökull and the 79 CE eruption of Mount Vesuvius described by Pliny the Younger, that humans become aware of the potential impact of airborne minerals. Similarly, major desert dust storms, such as those regularly engulfing cities in the Arabian Peninsula and the seasonal Kosa or Hwangsa storms in East Asia, draw our attention to the presence of minerals in the atmosphere. As previously discussed in *Elements* (Gieré and Querol 2010), atmospheric particulates may have a major impact on local to global climate, the cryosphere, marine and terrestrial ecosystems, agricultural productivity, and visibility, the latter affecting transportation systems. Furthermore, atmospheric particulates can adversely affect human health when inhaled.

Many of these effects are difficult to quantify, mainly due to the challenges involved in determining the physical and chemical characteristics and spatial variability of very small (nano- to micrometer-sized) atmospheric particles. Difficulties also arise because particulate matter may undergo significant changes while airborne. These processes, collectively known as ageing, include particle growth or dissolution due to absorption of moisture, reactions with gases or liquids (including acids), condensation of vapors on the particle surface, redox reactions, and coagulation (Usher et al. 2003; Choël et al. 2006). In understanding these processes, the techniques used in mineralogy can play a decisive role. Applying techniques such as optical and electron microscopy, synchrotron-based X-ray imaging and microspectroscopy, infrared and Raman spectroscopy, BET surface analysis, laser diffractometry, and mass spectrometry to airborne particles can lead to substantial improvements in our knowledge of their properties, behavior, and effects.

Depending on source, formation, and ageing, airborne solid particles encompass a wide variety of natural and anthropogenic materials, including sea-salt particles, silicates (such as clays and quartz), oxides (including those of iron and uranium), sulfates (gypsum, anglesite), carbonates (calcite, dolomite), alloys (such as those of iron and manganese), glass (particularly volcanic ash), biogenic material (pollen, spores, plant fragments, algae, bacteria, brochosomes), and combustion-derived carbonaceous particles (such as soot). The characterization of such particles helps us to understand key interactions between the atmosphere and the solid Earth, its hydrosphere, and its biosphere.

An example is research to determine the ultraviolet and visible light absorption properties of clays (Hoang-Minh et al. 2010), as this mineral group is prominent in desert dust clouds and, therefore, plays a critical role in modifying solar and terrestrial radiation. Such interactions, which strongly depend on the optical properties of the airborne particles, result in a direct change of the radiation balance of the atmosphere and the Earth's surface (Mahowald et al. 2011). This modification to the radiation budget, known as a *direct radiative effect*, leads, in turn, to changes in the surface temperature of both land and ocean with concomitant indirect effects on ecosystems, as recently discussed on the basis of coral growth rates (Kwiatkowski et al. 2013). Airborne minerals and other aerosol particles also have *indirect effects* on the radiation balance, because they are capable of acting as cloud condensation nuclei or ice-forming nuclei, thus modifying cloud properties and precipitation (Stevens and Feingold 2009). Both the direct and the indirect radiative effects influence climate, but the magnitude of this climate impact is associated with considerable uncertainties, largely because we do not know enough about the properties of the particles in the atmosphere and their so-called "mixing state," i.e. whether they occur as single-phase or multiple-phase particles (Pósfai and Buseck 2010). These phenomena can be further complicated by mixing with carbonaceous materials produced by biomass burning, which is carried out on a very large scale in areas such as Central Africa and Southeast Asia (Fig. 1) as part of the agricultural cycle (Hand et al. 2010).

Airborne particles can also have a direct impact on ecosystems, both terrestrial and marine, by modifying their chemical compositions. This process has been investigated extensively with regard to deposition of nutrients contained in airborne particles. In this case it represents what is described as an *ecosystem fertilization* mechanism. Aeolian dust, for example, provides one of the dominant external sources of iron and other nutrients, such as phosphorus and silicon, to the surface waters of the open ocean (Jickells et al. 2005). Here, the dust-derived nutrients stimulate phytoplankton growth, which, in turn, increases the uptake of CO_2 from the atmosphere through conversion into biomass (Baker and Croot 2010). However, because the speciation of these nutrients is one of the main controlling factors in determining particle solubility and bioavailability (Schroth et al. 2009), the global models of ocean fertilization can be refined only if both the chemical and the mineralogical compositions of dust from various sources are better known. Globally, the most important dust-source areas, those which have received most attention, are located in the arid regions of the lower and middle latitudes (e.g. the Bodélé Depression in Chad). However, important dust sources also occur at high latitudes, such as in proglacial regions and in areas exposed through glacial retreat (Prospero et al. 2012). With increasing global temperatures and the associated shrinkage of glaciers, ice caps, and ice sheets, high-latitude dust sources could become more important globally in providing nutrients to various ecosystems. Dust deposition, however, may also have negative effects on ecosystems due to increases in the turbidity of the seawater and due to the possible delivery of pathogens (examples include fungal spores and bacteria) and toxins contained in the dust clouds.

The influence of airborne mineral particles on climate and ecosystems is a major topic of current research. Another key area of research is that concerning the impact of mineral dusts on human health, especially with respect to particles in the nanometer size range where properties

1 Institut für Geo- und Umweltnaturwissenschaften, Albert-Ludwigs-Universität, 79104 Freiburg, Germany
E-mail: giere@uni-freiburg.de

2 Williamson Research Centre for Molecular Environmental Science, and School of Earth, Atmospheric and Environmental Sciences, University of Manchester Manchester M13 9PL, UK
E-mail: david.vaughan@manchester.ac.uk

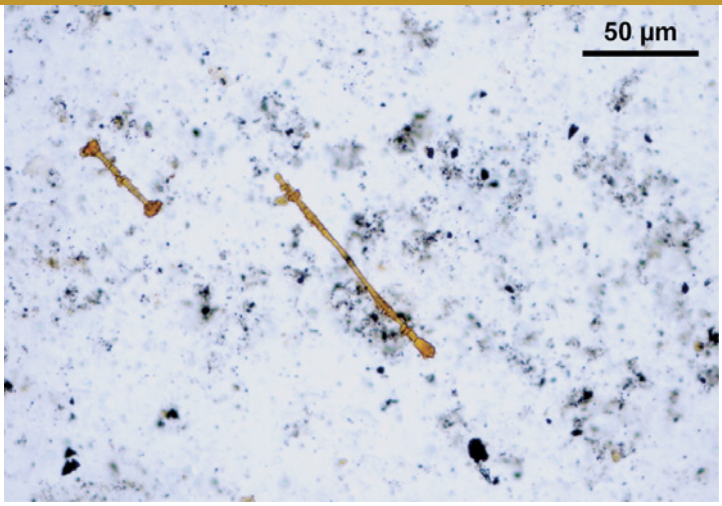

FIGURE 2 A photomicrograph of dust particles recovered from human lung tissue. The tissue contains numerous fine particles as well as two orange-colored objects, which are mineral fibers coated with iron compounds. SAMPLE COURTESY OF SILAG (WWW.SILAG.ETHZ.CH)

may differ significantly from those of larger particles. Millions of airborne particles enter the human respiratory system with each breath we take. Once inhaled, coarse particles may be deposited on the surfaces of the conducting airways of the upper respiratory system, whereas fine particles (generally defined as those with a diameter of <2.5 µm and known as $PM_{2.5}$) can migrate to the deepest parts of the lung where the gas exchange takes place (Plumlee et al. 2006). Ultrafine particles (<0.1 µm) may even penetrate through the cell tissue that lines the lung and then translocate to other parts of the body. The inhaled particles can interact with the lung fluid or with various types of cells present in the lungs. These interactions may have adverse health effects, both acute and chronic, and may also lead to the formation of endogenous particles, such as calcite and apatite, and of Fe^{3+}-rich coatings on inhaled fibrous minerals (FIG. 2). In addition to being dependent on size, the interactions are influenced by other particle characteristics, including structure, chemical composition, shape, surface area and reactivity, sorptive properties, and solubility.

Epidemiological and toxicological studies have shown that exposure to $PM_{2.5}$ is linked to increases in mortality and hospital admissions due to respiratory and cardiovascular diseases (Englert 2006). There is increasing evidence, however, that coarser particles may also produce adverse health effects (Brunekreef and Forsberg 2005). The adverse health effects include chronic bronchitis, exacerbation of asthma, fibrosis, and lung cancer (Fubini and Fenoglio 2007). The mechanisms behind these diseases and their dependence on particle properties are still poorly known; they are thought to involve excessive production of free radicals (which can lead to oxidative damage to cell membranes, proteins, and DNA) and the release of chemical substances that trigger and perpetuate inflammation (Donaldson and Tran 2002; Schoonen et al. 2006). To improve our knowledge of these biochemical processes, it is essential to perform careful toxicological experiments with human lung cells and tissue cultures. However, detailed characterization of the particles used in such experiments is only rarely reported in the medical literature (Könczöl et al. 2012). Additional information about the nature and abundance of particles in human lungs and their possible role in disease development comes from microscopic investigations of fluids that are extracted from the lung or from lung tissue samples excised during biopsy or autopsy.

Although great efforts have been made to reduce particulate emissions, airborne particles still pose a significant threat to human health in many areas. Moreover, the success in cutting traffic emissions, especially diesel soot, through the installation of particle filters in vehicles has been partially negated by increased emissions resulting from biomass combustion. The recent increase in the use of wood as a cleaner alternative to fossil fuels has led to air pollution problems in both urban and remote areas, especially during winter months. Emissions from biomass combustion contain numerous chemical compounds, including mineral particulates with phases such as quartz, cristobalite, and various carbonates, halides, and sulfates. Little is known about the health effects of particles emitted by biomass combustion (Naeher et al. 2007); they may be as serious as those associated with diesel-exhaust particulates (Corsini et al. 2013). A large-scale, European Union–funded research project (www.biocombust.eu) is currently tackling these important issues. In these and other aspects of the study of atmospheric particles, clearly we can say that "mineralogy matters."

REFERENCES

Baker AR, Croot PL (2010) Atmospheric and marine controls on aerosol iron solubility in seawater. Marine Chemistry 120: 4-13

Brunekreef B, Forsberg B (2005) Epidemiological evidence of effects of coarse airborne particles on health. European Respiratory Journal 26: 309-318

Choël M and 5 coauthors (2006) Fast evolution of tropospheric Pb- and Zn-rich particles in the vicinity of a lead smelter. Atmospheric Environment 40: 4439-4449

Corsini E and 9 coauthors (2013) Comparison of wood smoke PM2.5 obtained from the combustion of fir and beech pellets on inflammation and DNA damage in A549 and THP-1 human cell lines. Archives of Toxicology: doi:10.1007/s00204-013-1071-z

Donaldson K, Tran CL (2002) Inflammation caused by particles and fibers. Inhalation Toxicology 14: 5-27

Englert N (2006) Fine particles and human health—a review of epidemiological studies. Toxicology Letters 149: 235-242

Fubini B, Fenoglio I (2007) Toxic potential of mineral dusts. Elements 3: 407-414

Gieré R, Querol X (2010) Solid particulate matter in the atmosphere. Elements 6: 215-222

Hand VL and 5 coauthors (2010) Evidence of internal mixing of African dust and biomass burning particles by individual particle analysis using electron beam techniques. Journal of Geophysical Research: Atmospheres 115: D13301, doi:10.1029/2009jd012938

Hoang-Minh T, Le TL, Kasbohm J, Gieré R (2010) UV-protection characteristics of some clays. Applied Clay Science 48: 349-357

Jickells TD and 18 coauthors (2005) Global iron connections between desert dust, ocean biogeochemistry, and climate. Science 308: 67-71

Könczöl M and 10 coauthors (2012) Cellular uptake and toxic effects of fine and ultrafine metal-sulfate particles in human A549 lung epithelial cells. Chemical Research in Toxicology 25: 2687-2703

Kwiatkowski L and 7 coauthors (2013) Caribbean coral growth influenced by anthropogenic aerosol emissions. Nature Geoscience 6: 362-366

Mahowald N and 8 coauthors (2011) Aerosol impacts on climate and biogeochemistry. Annual Review of Environment and Resources 36: 45-74

Naeher LP and 6 coauthors (2007) Woodsmoke health effects: a review. Inhalation Toxicology 19: 67-106

Plumlee GS, Morman SA, Ziegler TL (2006) The toxicological geochemistry of Earth materials: an overview of processes and the interdisciplinary methods used to understand them. Reviews in Mineralogy & Geochemistry 64: 5-57

Pósfai M, Buseck PR (2010) Nature and climate effects of individual tropospheric aerosol particles. Annual Review of Earth and Planetary Sciences 38: 17-43

Prospero JM, Bullard JE, Hodgkins R (2012) High-latitude dust over the North Atlantic: Inputs from Icelandic proglacial dust storms. Science 335: 1078-1082

Schoonen MAA and 5 coauthors (2006) Mineral-induced formation of reactive oxygen species. Reviews in Mineralogy & Geochemistry 64: 179-221

Schroth AW, Crusius J, Sholkovitz ER, Bostick BC (2009) Iron solubility driven by speciation in dust sources to the ocean. Nature Geoscience 2: 337-340

Stevens B, Feingold G (2009) Untangling aerosol effects on clouds and precipitation in a buffered system. Nature 461: 607-613

Usher CR, Michel AE, Grassian VH (2003) Reactions on mineral dust. Chemical Reviews 103: 4883-4939