

Probing the surface chemistry of mineral particulates and organic matter

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Introduction

Particulate matter in the atmosphere (aerosol) is a critical component in determining climate and climate change of the Earth. The chemical composition of particulate matter may affect climate directly, by scattering and absorbing solar radiation, and indirectly, by acting as cloud condensation nuclei, forming clouds. Clouds can reduce the incident radiation falling on the surface of Earth, increase solar heating and suppress rainfall. Thus, the concentration and chemical composition of particulate matter forming atmospheric aerosol can produce a weaker water cycle, which has a direct effect on the quality and availability of fresh water; a global issue.

Atmospheric aerosol is not chemically inert; particles may provide a site for chemical reaction or be a reaction partner in a chemical reaction. Reactions will alter the chemical and physical properties of the particle, consequently altering how the particle will interact with solar radiation and thus affect global climate.

A large portion of the total coarse (1-10 microns) atmospheric aerosol fraction consists of mineral particles containing species such as TiO_2 , SiO_2 , Fe_2O_3 and Al_2O_3 .

The climatic effects of the mineral dust in the atmosphere are unknown. The International Panel on Climate Change (IPCC)^[1] classifies the level of scientific understanding as “very low”, and assessing mineral dust may have a warming effect of up to 0.4 W m^{-2} or cooling effect of up to 0.6 W m^{-2} . Note greenhouse gases have a warming effect of 2.5 W m^{-2} . The mineral aerosol may also act as cloud condensation nuclei i.e. seed particles for nucleation of water to form cloud droplets, the scientific understanding of this mechanisms is also “very low” any the cooling resulting may be up to 2.5 W m^{-2} (i.e. almost as large as the greenhouse gas warming).

Mineral dust provides a reactive oxide surface within the atmosphere for chemical reactions. The surface may catalyse slow gas-phase reactions, including the interchange of nitrogen oxide species NO_x to HONO.

The aim of this work is to investigate the range of methodologies that are viable for introducing mineral particulates to an optical laser trap. If this can be achieved at a scale amenable with microscope studies it will enable the investigation of reactions of individual mineral particles with atmospheric gases. Ultimately such a technique could determine both the products and possible phase (and hence size) changes that accompany the reactions so that the climatic effects of mineral particles in the atmosphere can be better understood. Phase changes

and alterations in hygroscopicity of atmospheric particles are critical to cloud formation and cloud albedo.

The reaction and phase changes accompanying the atmospheric reactions were to be followed using Raman spectroscopy, as previously achieved for sea-water droplets.^[2] The laser-tweezers Raman-microscope is the only technique presently viable to study these reactions chemically and morphologically at the moment.

The key part of the study hinges on our ability to trap and retain single micron sized particulates in air for periods in excess of 10 minutes. There is reasonable evidence in the academic literature to indicate that this is possible.

Previous studies^[4] have shown that glass beads of a few microns in diameter can be optically trapped in air using a single beam optical gradient trap. We attempted to repeat this work using several dry samples of various micron-sized glass beads on plates of different materials. The plates were resonated briefly using a piezoelectric ceramic ring at a frequency of 25.8 kHz (see Figure 1). The energy created from generating a standing wave across the glass plate are sufficient to break the attractive Van der Waal's forces acting between the plate and the beads, i.e. the particles should start to bounce. Placing the optical trap above the bead and with the combination of radiation and scattering forces should allow the capture of the airborne bead. The resonant vibrations are only required for the brief period during the trapping procedure.

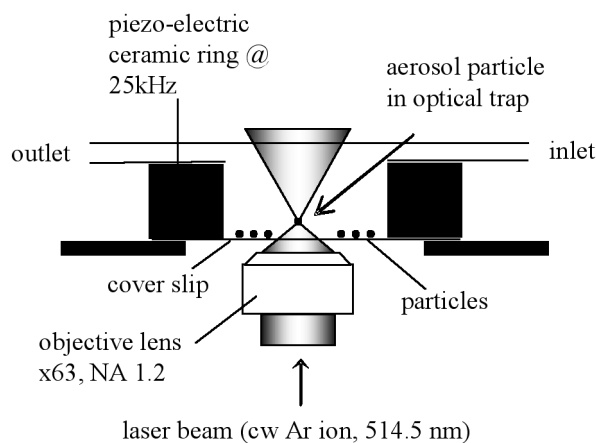


Figure 1. Schematic diagram of the trapping apparatus.

A range of piezoelectric elements was used across different resonant frequencies to repeat the literature method^[4]. However, the reported result could not be replicated under

our experimental conditions using a range of bead types and glass surfaces. Three other methods were investigated for mineral particle production (1) particle nebulisation (2) dehydration of aqueous droplets of halite solution and (3) abrasion. These methods all produced aerosol particles in a stream of gas but the particles tended to be charged by collisions and difficult to trap owing to a combination of electrostatic forces and high particle velocity when entering the trapping region. Many minerals were investigated with pure simple salts, e.g. NaCl, showing the most promise, and compounds such as silica and clay showing less promise. Several routine methods of removing the charge or producing a Boltzman distribution of charge on the particle were attempted but were not successful. The dehydration of aqueous halite solutions showed sufficient promising to merit future investigation. A concentrated aqueous solution of NaCl was nebulised and a large droplet was held in the laser trap. The cell buffer gas was dried and water from the droplet started to evaporate. The droplets were observed to shrink with the loss of water vapor. Crystallization and development of solid facets were observed however the forming particle was had no axis of symmetry and as such it was ejected by an imbalance in trapping forces just before final and full crystallization.

The feasibility of analyzing organic matter particles was also considered. Humic material as cloud condensation nuclei has recently become of interest in atmospheric science.^[9] Here we used benzoic acid in water as a proxy for humic material and investigated whether it was possible to study the heterogeneous reaction between ozone and aqueous droplets of benzoic acid. The oxidation of a soluble species in an aqueous droplet with a gas-phase species had not been attempted before using optical levitation combined with Raman spectroscopy.

The experiment was a success, and figure 2 illustrates the reaction of ozone with benzoic acid (red line) in relation to a small size change (black line) of the droplet. This preliminary work will be written up for publication as a potential reaction of importance in cloud droplet chemistry.

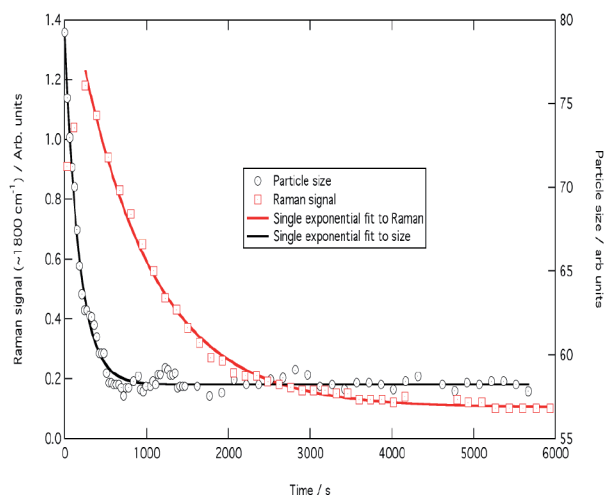


Figure 2. Change in droplet size and benzoic acid concentration during the reaction with ozone as a function of time.

Conclusions

- Optical levitation of mineral particles is very difficult due to a combination of (i) electrostatic forces, when removing particles from surfaces, and (ii) high particle velocities when introducing the particles in a gas stream.
- Laser Raman tweezers can be used to study heterogeneous reactions between bulk aerosol phases and gas-phase oxidants.
- Generating solid particles in the optical trap by evaporation of chemical reactions show promise for future work.

References

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