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The temporal and spatial distribution of boundary-layer ozone was studied during June 2000 at Summit, Greenland by surface-level measurements and vertical profiling from a tethered balloon. Three weeks of continuous ozone surface data and 133 meteorological and 82 ozone vertical profile data sets were collected from the surface to a maximum altitude of 1400 m above ground. The lower atmosphere at Summit was characterized by the prevalence of high stability conditions with strong surface temperature inversions. These inversions succumbed to neutral to slightly unstable conditions between approx. 9.00 and 18.00 hrs local time with the formation of shallow mixing heights of typically 70-250 m above the surface. Surface ozone ranged from 39 to 68 ppbv and occasionally had rapid changes of up to 20 ppb in 12 hours. The diurnal mean ozone mixing ratio showed distinct cycles indicating meteorological and photochemical controls of surface ozone. Vertical profiles were within the range of 37 to 76 ppb and showed strong stratification in the lower troposphere. A high correlation of high ozone/low water vapor indicated the transport of high tropospheric/low stratospheric air into the lower boundary layer. An approx. 1 to 4 ppb decline of ozone towards the surface was frequently observed within the neutrally stable mixed layer during midday hours. These observations suggest that the boundary-layer ozone and ozone depletion/deposition to the snowpack are influenced by photochemical processes that follow diurnal dependencies.

A12B MC: 133 Monday 1330h

Current Understanding of Tropospheric Aerosol: Advances in Laboratory and Field Measurements II

Presiding: A M Middlebrook, NOAA Aeronomy Laboratory; R S Dasselkamp, Pacific Northwest National Laboratory

A12B-01 1330h

Laboratory Studies of Sulfuric Acid Aerosol Formation, Growth and Coagulation

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Laboratory measurements involving nucleation, condensation, and coagulation of sulfuric acid are described. Studies were carried out using a laminar flowtube at atmospheric pressure coupled to an aerosol mass spectrometer (AMS). A sulfuric acid reservoir heated to a known temperature was connected to the flowtube via heated tubing. Dry filtered nitrogen carrier gas was pre-heated and passed over the reservoir entraining an equilibrium density of the H₂SO₄(g) to the flowtube. The entrance to the flowtube was heated to a temperature above that of the reservoir, establishing a well-characterized decreasing temperature profile along the flowtube axis. Supersaturation (and consequent nucleation and growth) conditions were reached at a position within the flowtube determined by the temperature profile and the H₂SO₄ vapor pressure. The number and mass distributions of the particles formed in this way were measured on-line by the AMS at the flowtube exit. With the entrance of the flowtube at 150 C, particles were first observed at a H₂SO₄ vapor pressure of 10-4 torr forming particles at a number density of 104 cm⁻³. As the pressure increased to 3x10-2

torr, the particle number density increased to 107 cm⁻³. However, the median diameter increased only from 40 to 50 nm. At pressures higher than 4x10-3 torr, the size distributions were observed to exhibit broadening and a new mode appeared near 60nm, consistent with coagulation. A third mode appeared at H₂SO₄ pressures near 3x10-2 torr indicating further coagulation. This work is a first time on-line laboratory observation of sulfuric acid microphysics spanning nucleation and coagulation processes. The features of the apparatus enabling absolute detection of mass and number distributions will be discussed.

A12B-02 1345h INVITED

Phase Transitions of Aqueous Atmospheric Particles

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The physical state of atmospheric particles affect their optical properties, their chemical reactivity, and their atmospheric lifetime. Accordingly, the prediction of particle phase is critical for accurate atmospheric modeling. Atmospheric aqueous particles, due to their small size (submicron), can deeply supercool with respect to freezing (e.g., 40 K) and deeply supersaturate (e.g., S = 35) with respect to relative humidity before crystallization begins via homogeneous nucleation. Atmospheric mineral dusts, incorporated as inclusions within aqueous particles, provide active surfaces to induce crystallization heterogeneously and thus drastically reduce the extent of supercooling (e.g., 20 K) or supersaturation (e.g., S = 5). This talk will present laboratory and theoretical work on several systems, including sulfates, nitrates, and mineral dusts. The results are crucial to providing a quantitative microphysical model that couples the interactions of these particle classes in the atmosphere.

A12B-03 1415h

Ice Phase Transitions by Atmospheric Aerosol Particles of Varied Composition

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This paper describes laboratory and field study measurements of water uptake and ice nucleation by surrogate and real atmospheric aerosol particles. Laboratory measurements of water uptake are made using a humidified tandem differential mobility analyzer (HTDMA) and a cloud condensation nucleus (CCN) instrument operating at 20 to 30 °C. Measurements of ice nucleation are made using a continuous flow ice-thermal diffusion chamber (CFDC) operated to -60 °C for relevance toward understanding cirrus cloud formation.

Extending earlier laboratory studies of single composition aerosols, we are investigating water uptake and ice nucleation rates and mechanisms by mixed aerosols of various types, including sulfate-nitrate, sulfate-organic, mineral oxide-sulfate and black carbon-sulfate types. Methodologies will be described and results will be summarized.

Field measurements are planned to study heterogeneous and homogeneous ice nucleation by free tropospheric aerosols at a high altitude laboratory. The field

study will include measurements of the compositions of aerosols that activate ice formation by homogeneous and heterogeneous ice nucleation mechanisms. This aspect of the study will be facilitated by interfacing the CFDC to the PALMS (Particle Analysis by Laser Mass Spectrometry) instrument. This combined instrument system was tested in the laboratory to quantify sampling efficiencies and validate specificity for sampling ice nucleus aerosol particles. Initial field data, if available at conference time, will be compared and contrasted with the results obtained for laboratory surrogate particles.

A12B-04 1430h

Heterogeneous Reactions on Mineral Dust: Surface Reactions of Sulfur Dioxide, Ozone, Nitric Acid and Acetic Acid on Oxide and Carbonate Particles

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The role of heterogeneous reactions on particulate matter present in the Earth's atmosphere remains an important question in tropospheric chemistry. It has been proposed in several modeling studies that mineral dust may provide reactive surfaces for trace atmospheric gases. Laboratory studies can provide some answers concerning the kinetics of these reactions so that heterogeneous chemistry can be quantitatively assessed in atmospheric chemistry models. In our work, the heterogeneous chemistry of trace atmospheric gases including sulfur dioxide, ozone, nitric acid and acetic acid on oxide (e.g. hematite, corundum and quartz) and carbonate (e.g. calcite) particles has been investigated. These particles are used as models for mineral dust found in the atmosphere. FT-IR spectroscopy is used to interrogate the surface of the particles as they are exposed to trace atmospheric gases in order to gain additional insight into the surface chemistry. Initial uptake coefficients on powdered samples have been measured using a Knudsen cell reactor so as to quantify the rates of these reactions. The uptake kinetics have been measured as a function of powder sample mass to insure that realistic surface areas are used in the calculation of the initial uptake coefficient. The heterogeneous reaction rates are then compared to known gas-phase chemical and photochemical reaction rates for the trace atmospheric gases investigated. From this comparison, the atmospheric implications of these heterogeneous reactions are discussed.

A12B-05 1445h

Kinetics of Trace Gas Uptake by Liquid Surfaces

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Over the past quarter century atmospheric scientists have gradually come to realize that "heterogeneous" or "multi-phase" gas/liquid processes play a major role in the chemistry of the Earth's lower atmosphere. As we better appreciate the role of atmospheric heterogeneous processes their complex nature has become clear. The uptake of pollutants by atmospheric aerosol particles and cloud droplets and their subsequent chemical transformation often depends not only on simple mass accommodation and re-evaporation, but also on a range of other chemical and mass transport parameters, including: gas and liquid phase diffusion, solubility, and both liquid surface and bulk liquid reaction.

We have developed two novel experimental laboratory techniques, the droplet train/fast flow reactor and the bubble train reactor, to deconvolve these processes. In addition, much more sophisticated phenomenological models have been developed to address the full range of chemical and physical processes that come into play both in the laboratory and the atmosphere. This review will focus on the results of uptake measurements using these techniques for over three dozen atmospheric trace gases by aqueous and aqueous acid surfaces representing the liquid content of the tropospheric clouds and aerosols where a large fraction of atmospheric heterogeneous processing occurs. We will also present initial studies involving organic liquid surfaces motivated by recent realizations that a significant fraction of the mass of tropospheric aerosol material is organic in nature.

A12B-06 1520h INVITED

Interactions between Aerosols and Photochemistry in the East Asia Troposphere

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In this paper we explore the question of how aerosol impact tropospheric chemistry. We address this issue using regional models of the troposphere that couple aerosol processes with photochemical and biogeochemical cycles. There is a growing body of observational data that suggests that aerosols such as mineral oxides and black carbon may provide important reactive surfaces. However, very little is known regarding the mechanisms by which aerosol impact these cycles. Mechanisms for the interaction of O₃, NO_y and SO_x, with aerosol surfaces are postulated, and used to calculate heterogeneous removal rates and subsequent influence. The focus will be on our work in East Asia, where anthropogenic particles along with wind blown soils represent major surface areas for chemical reactions (especially in the spring). Results indicate that the presence of mineral aerosol may significantly alter the chemical size distribution of particulate sulfate and nitrate, thus influencing the lifetimes of these species and altering physical and radiative aerosol properties. In addition the surfaces may alter the photochemical oxidant cycle by perturbing NO_x partitioning between gas and particulate phases, and providing additional reaction pathways. Also the impact of aerosol on photolysis rates may also be significant, and this aspect will be addressed in the paper. However, these calculations remain highly uncertain, due in part to the fact that these surfaces have not been widely studied from a reactive surface standpoint, and basic information on sorption and reaction rates are not well known, and due to the lack of field experiments designed to investigate the role of aerosols in tropospheric chemistry. Results of recent laboratory studies at the University of Iowa will also be presented and discussed. Some results from preliminary analysis of recent large field experiments in East Asia (e.g., from Trace-P and Ace-Asia), may also be presented.

A12B-07 1550h

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The heterogeneous conversion of N₂O₅ to HNO₃ which occurs on the surface of aqueous aerosols in the planetary boundary layer is an important step in the removal of nitrogen oxides from the atmosphere. A series of experiments in the large Aerosol Chamber at the FZ-Juelich revealed that the reaction probability $\gamma_{N_2O_5}$ on metastable and deliquescent sulfate aerosols is about 0.02, i.e. 2 out of 100 collisions of N₂O₅ with the particle surfaces lead to formation of HNO₃. The $\gamma_{N_2O_5}$ on sulfate aerosols is fairly independent of the aerosol substrate and the relative humidity. However, in a few experiments, we observed a reduction of $\gamma_{N_2O_5}$ on sulfate aerosols by a factor of 2-7. Reduced $\gamma_{N_2O_5}$ were

measured on aerosols which were kept for over a day in the chamber. This suggests an effect of aging of the particles.

In a series of experiments, effects of drying of the particles (recrystallization), imperfect mixing of the chamber and a nitrate effect could be excluded. By GC-MS we detected several biogenic hydrocarbons in our chamber air. These hydrocarbons originate from outside air since our air cleaning system is not very efficient in removing hydrocarbons. The ozonolysis of the biogenic hydrocarbons induces particle formation. O₃ is used with NO₂ for in-situ generation of N₂O₅ in the chamber. In the presence of sulfate aerosol the oxidized species will condense on the preexisting aerosol surfaces. In two experiments the aerosol was coated by addition of α -Pinen into the chamber (11.4 ppb and 1.22 ppm respectively) and subsequent ozonolysis. A dependence of the reaction probability on the α -Pinen concentration was observed. Thus, it can be concluded that the reaction probability of N₂O₅ depends on the thickness of the organic film on the aerosol surface. An organic coating introduces an extra transport barrier for the heterogeneous hydrolysis of N₂O₅.

The reduction of the reaction probability by an organic coating or scarcity of water due to a large organic solute fraction could have severe consequences for the nitrogen oxide cycle. The tropospheric NO_x-cycle could be imbalanced or require a shift to greater importance of NO₃-reactions.

A12B-08 1605h

New Flow Tube for in situ Measurements of Optical Spectra and Particle Size Distributions of Aqueous Aerosol Particles of Tropospheric Composition.

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In studies of the heterogeneous hydrolysis of N₂O₅ in the presence of aqueous aerosols in the Aerosol Chamber at the FZ Jlich we applied FTIR absorption spectroscopy for the determination of trace gases. In the FTIR spectra we also observed broad absorptions of several 10 to a few 100 cm⁻¹ widths that clearly arise from species in the condensed aerosol phase: liquid H₂O, NO₃⁻, SO₄²⁻, HSO₄⁻. Moreover, the aerosol droplets caused extinctions over several 1000 cm⁻¹ by IR scattering. This allows for in-situ observation of changes in the condensed aerosol phase, like the shift of the sulfate/bisulfate equilibrium or the growth by water condensation. The IR absorptions of the condensed aerosol phase provide useful extra information in process studies, if they can be quantified. Clapp, Miller and Worsnop [1] developed a method to extract cross sections (and refractive indices) from IR spectra, just based on the fact that condensed phase absorption and scattering extinction by aerosol particles occur in the same IR spectrum. They did not measure the aerosol size distribution and assumed lognormal distributions. If the size distribution is measured independently further the degrees of freedom are removed and the method can be extended for calibration of aerosol instruments.

We therefore set up an aerosol flow tube in which IR spectroscopy on a 8 m light path and aerosol size distribution measurements in the range from 20 nm - 10 μ m can be performed simultaneously. We measured sulfate aerosols at several relative humidities (dry, metastable, deliquescent) and will present first results for ammonium sulfate - measurements and Mie-calculations.

[1] M. L. Clapp, R. E. Miller, D. R. Worsnop, J. Phys. Chem.,99 (1995), 6317

A12B-09 1620h

Estimating Natural Variability of Asian Aerosols; Relationship of ACE-Asia to the 1990s

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We have constructed a multi-year climatology of global aerosol distributions using the aerosol assimilation methodology described in Collins et al (2001) and Rasch et al (2001). This climatology provides 3-dimensional estimates of aerosol concentration and optical properties (broken down by constituent) and aerosol direct radiative forcing. We use this climatology to identify characteristic variations in aerosol distributions (near the surface and at altitude) in the ACE-Asia region in terms of: monthly mean properties; frequency of occurrence of intense dust storms; and relative contributions of anthropogenic and natural

aerosols to the region. During the dust event in April 2001, which was measured by the ACE-Asia observing network, dust was transported from Asia into the interior of the continental U.S. We analyze the properties of this dust event in relation to other dust events in the latter 1990s.

A12B-10 1635h

The Influence of Organic Coatings on the Hygroscopic Properties of Atmospheric Particles

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The chemical composition of atmospheric particles is an important factor governing their light scattering properties, their ability to act as media for chemical transformations and their ability to act as cloud condensation nuclei. Field measurements have indicated that organic material is a significant component of the mass of atmospheric aerosol particles. We have initiated studies using a quartz crystal microbalance (QCM) to examine the uptake and loss of water onto organic-coated surfaces in a controlled environment. Our preliminary results will be presented here.

A12B-11 1650h

Aerosol Influence on Cloud Optical Depth and Albedo Over the North Atlantic Shown by Satellite Measurements and Chemical Transport Modeling

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The Twomey effect of enhanced cloud droplet concentration, optical depth, and albedo due to anthropogenic aerosols is thought to contribute substantially to radiative forcing of climate change over the industrial period. However, present model-based estimates of this indirect forcing are highly uncertain. Satellite-based measurements would provide global or near-global coverage of this effect, but previous efforts to use satellite observations to identify and quantify enhancement of cloud albedo due to anthropogenic aerosols have been limited, largely because of strong dependence of albedo on cloud liquid water path (LWP), which is inherently highly variable. Here we examine satellite-derived cloud radiative properties over a one-week episode for which a chemical transport and transformation model indicates that sulfate aerosol in a remote area of the North Atlantic experienced a substantial excursion due to transport from Northern Europe. Despite the absence of discernible dependence of optical depth or albedo on modeled sulfate loading, examination of the dependence of these quantities on LWP readily permits detection and quantification of increases correlated with sulfate loading which are otherwise masked by variability of LWP, demonstrating brightening of clouds due to the Twomey effect on a synoptic scale. Median cloud-top spherical albedo was enhanced over the episode, relative to the unperturbed base case for the same LWP distribution, by 0.04 to 0.15. Examination of the dependence of cloud optical depth and albedo on LWP should be broadly applicable to identification of enhancement by anthropogenic aerosols and well suited for global-scale characterization by satellite measurements.