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Recent studies have shown that tropospheric sulfate aerosols commonly contain 50 % by mass organic species. The influence of these organics on the chemical and physical properties of sulfate aerosols is not fully established. We have determined the ice nucleation temperatures for particles composed of eutonic mixtures of ammonium sulfate with a series of dicarboxylic acids. Measurements of the low temperature vapor pressures of the eutonic solutions were also made in order to develop a calibration curve to convert the freezing temperatures to ice saturation ratios. We find that for a given water activity, the freezing temperature is constant and is independent of the mole fraction of organic in solution. While this observation was predicted by *Koop et al.* [2000], the freezing temperatures observed in the present study are somewhat higher than those found in the emulsion studies used to develop the *Koop et al.* [2000] theory.

A42E-08 1525h

Mass and Composition Modification of (NH4)2SO4 Aerosols by Dicarboxylic Acid Formation in Clouds: Implications on Cloud Physics

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We present a chemical mechanism focused on the in-cloud production of sulfate and small dicarboxylic acids (< C6), which are a major part of organic aerosol fractions. The mechanism is applied to a size resolved aerosol model that calculates production rates for sulfate and organic aerosol mass. It is found that cloud processing of aerosol leads to (1) a modified aerosol mass distribution and (2) a modification of the hygroscopic behavior across the aerosol size spectrum due to the formation of different organic fractions in each aerosol size class. We present analysis of the conditions under which these modifications are significant for particle activation and cloud drop number concentration. We also evaluate the relative importance of the sulfate/organic mass fraction (i.e., composition) and variables such as updraft velocity and aerosol size distribution parameters in determining drop concentrations. The results show that, in general, the main fraction of organic aerosol mass produced by cloud chemistry consists of glutaric and oxalic acid. These acids are relatively soluble and do not change the water uptake of the particles significantly compared to pure ammonium sulfate. However, we find that high fractions of less soluble organics (e.g., adipic acid) can change the hygroscopic behavior of the aerosol population.

A42F MCC: 3018 Thursday 1600h

Isotopic Constraints on Global Budgets of Atmospheric Gases II

(joint with B, H, OS, PP)

Presiding: **T Roeckmann,** Max-Planck-Institut für Kernphysik**; J Rudolph,** Centre for Atmospheric Chemistry, York University

A42F-01 1600h

The changing isotopic composition of atmospheric N2O determined from the University of Heidelberg air archive

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The construction of a realistic global isotope budget of atmospheric N2O requires the knowledge of temporal trends in its isotopic composition. Due to the long atmospheric lifetime of N2O of about 130 years, those temporal trends are exceedingly small. Thus, it has not been possible to determine temporal changes from direct atmospheric measurements, and only recently the small trends of a few thousands of a permil per year could be established using measurements on air trapped in polar firn (Sowers et al., 2002, Röckmann et al., 2003). The University of Heidelberg regularly collects air samples at various atmospheric monitoring stations and has set up an archive of atmospheric samples that goes back to 1988. We have recently analyzed the isotopic composition of N2O from a suite of archived air samples (1990 to 2002) from the Neumayer station in Antarctica. Using a high-precision continuous-flow IRMS system we have derived the small trends in the isotopic composition of atmospheric N2O over the past 13 years from actual atmospheric samples. The good agreement of N2O mixing ratios (which are also obtained from the isotope ratio measurement) with other observations confirms the integrity of the samples after the long storage times. The results show slowly decreasing trends in the 15N and 18O content of atmospheric N2O, in agreement with the firn air observations. These trends are caused by the increase in the atmospheric N2O mixing ratio since pre-industrial times. Global isotope budget calculations using these trends (Röckmann et al., 2003) imply that the global average isotopic source signature is lower today than in pre-industrial times, providing independent evidence that increased soil emissions are responsible for the observed increase of N2O in the atmosphere.

A42F-02 1615h INVITED

Compound Specific Stable Isotope Ratio Measurements, a new Tool to Study the Atmospheric Chemistry of Volatile Organic Compounds

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Stable isotope ratio measurements of volatile organic compounds (VOC) are a relatively new, but rapidly developing method, which has great potential to improve our understanding of the atmospheric chemistry of VOC. The dependence between measured stable isotope ratio, atmospheric reactions, atmospheric mixing and transport, and isotope ratio of emissions is rather complex, especially for VOC with atmospheric residence times shorter than the timescales required for global scale mixing. However, for a number of VOC the problem is simplified due to a, compared to the variability of the emissions, large isotope fractionation due to atmospheric removal reactions. Under these conditions isotope ratio measurements can be used to determine the average degree of atmospheric processing of the studied VOC if the kinetic isotope effects for the atmospheric reactions and the stable isotope ratio of the emissions are known. In this presentation the possibilities, conditions, and limitations for the use of stable isotope ratios of VOC are discussed and examples are presented. This includes deficits in our present knowledge as well as new possibilities for the extension of stable isotope ratio measurements for studies of the atmospheric chemistry of VOC.

A42F-03 1630h

Use of Carbon Isotopes in the Analysis of the Tropospheric Carbon Monoxide Budget

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The budget of carbon monoxide (CO) includes emissions from combustion of fossil fuels and biomass, as well as chemical production from the oxidation of methane and higher hydrocarbons, with the primary sink being reaction with OH. The lifetime of CO is on the order of months, so CO serves as a good tracer of pollution long distances from source regions. The CO isotopic signature varies depending on the type of emissions, and thus can provide additional information about the contributions of different emissions. Measurements of ^{13}CO have been made at a number of locations, showing distinct seasonal and interannual variations. We have added ^{13}CO and its precursors (CH_4 and other hydrocarbons) to the NCAR/MPI/GFDL global chemical transport model MOZART, including the ^{13}C emissions and fractionation rates, to assist in the interpretation of the ^{13}CO measurements. The individual emission types have been 'tagged' for different regions, to further quantify the CO budget.

A42F-04 1645h INVITED

Deuterium Enrichment in Atmospheric Molecular Hydrogen and the Global Isotopic Budget

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Molecular hydrogen (H_2) is the second most abundant reduced gas in the atmosphere (after methane) with a globally averaged mixing ratio of $\sim$ 530 ppbv. Its largest sources are photochemical oxidation of methane (CH_4) and non-methane hydrocarbons (NMHCs) while other recognized sources include biomass burning, fossil fuel burning, nitrogen fixation, and ocean degassing. The potential for a future H_2 based fuel-cell economy has significant implications for the atmospheric H_2 budget. As with other volatile fuels, escape of H_2 during production, storage, and transfer processes is inevitable. Future increases in anthropogenic H_2 emissions may potentially lead to higher atmospheric concentration; this could have several as yet poorly understood consequences including moistening of the stratosphere, destruction of stratospheric ozone, and increased lifetimes of other reduced gases such as CH_4. As with other atmospheric trace gases, the stable isotopic content of H_2 has the potential to help quantify various aspects of its production and destruction. The average deuterium content of H_2 (expressed as δD_{H2}) is enriched by $\sim$130 $^{o}/_{oo}$ relative to Vienna Standard Mean Ocean Water although those H_2 sources that have been measured are typically depleted in deuterium. We have recently shown that production of H_2 via the oxidation of methane results in δD_{H2} that is enriched by 210 $^{o}/_{oo}$ (Rahn et al., 2003), shedding light on this puzzling enrichment. These results will be placed in the context of the overall H_2 isotopic budget and the potential effect of future anthropogenic perturbations on the isotopic budget will be discussed. Rahn et al., *Nature, 424*, 918-921, 2003.

A42F-05 1700h

17O as a new tracer of the hydrological cycle

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The abundances of 18O and deuterium in the present and past hydrologic cycle have proven to be an important tool in earth systems science. In contrast, the abundance of 17O in precipitation has thus far been assumed to carry no additional information to that of 18O. Here, we demonstrate, using known constraints on oxygen isotope abundances from the O2 cycle and existing data about the natural abundance of 17O in water, that the relationship between the discrimination against 17O and 18O in water may vary. This relationship (or slope) was found to be lower for kinetic transport effects then for equilibrium effects, with very low temperature sensitivity. As a result, the 17O excess (defined similarly to deuterium excess) of precipitation is controlled primarily by kinetic effects during evaporation and ice formation and therefore, in contrast to the deuterium excess, is independent of the temperature at the site of evaporation (and condensation). This makes the 17O excess a unique tracer that complements 18O and deuterium, and may allow a decoupling of changes in the temperature of the ocean that serves as the vapor source from changes in the relative humidity above it. In addition, the 17O of ice caps is influenced by kinetic effects in ice formation, and therefore measurement of ice 17O can be used as an additional constraint for better understanding and parameterization of these effects.

A42F-06 1715h

Multiply-Substituted Isotopologues of Atmospheric Gases

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Stable isotope geochemistry is principally concerned with bulk isotopic compositions of natural materials (e.g., d13C). In atmospheric gases, these bulk compositions effectively depend only on abundances of molecules containing one rare isotope (e.g., 16O13C16O). However, the common di- and tri-atomic atmospheric gases also contain ca. 10-5 to 10-6 mole fraction of molecules containing two or more rare isotopes (e.g., 18O13C16O). These rare isotopologues are an untapped resource of constraints on physical chemistry and geochemical budgets. There are sparse data on the vapor pressures and chemical kinetics of multiply-substituted isotopologues, and the reduced partition functions of some were estimated by Urey (1947) and Bigeleisen and Mayer (1947). These studies demonstrate that these rare isotopologues have unique thermodynamic and kinetic properties, and thus that routine measurements of them could uniquely constrain geochemical problems. However, distributions of these rare isotopologues in nature are essentially unknown. We have developed a gas source mass spectrometer for analysis of doubly substituted isotopologues of N2, NO, CO, O2, CO2 and N2O at their naturally occurring abundances (in addition to the common and singly substituted isotopologues of these gases); associated sample preparation techniques and standardization protocols have been developed for CO2, N2O and are in progress for O2. Capabilities of this instrument vary with the abundances of the isotopologue of interest; external precision for the most abundant (e.g., 18O13C16O; 40 ppm of natural CO2) is typically $\pm$0.03 per mil, 1s, whereas that for more rare species (e.g., 18O12C18O; ca. 4 ppm of respective molecules) is typically $\pm$0.1 to 0.2 per mil, 1s. Accuracy based on comparisons to standards having the stochastic distribution of isotopes is similar to external precision. Interferences are the greatest analytical difficulty, with hydrocarbon fragments and recombination products being the most common and recalcitrant problem. The most extensive use of this instrument to-date has been to measure abundances of 18O13C16O in air and in experimental products. Preliminary results for 18O13C18O, 15N14N18O and 14N15N18O will also be reviewed, as will expected data for 18O18O and 17O18O if sufficiently complete. Near-surface air in southern California in mid-2003 is characterized by a 0.72 per mil enrichment in 18O13C16O relative to the abundance predicted for a stochastic (random) distribution of 18O and 13C among all CO2 isotopologues. This enrichment can be attributed to enhanced thermodynamic stability of 18O13C16O during air-sea and air-leaf water exchange which generates ca. 0.9 per mil enrichments modulated by anthropogenic emissions, fires and diffusive fractionations during photosynthesis all of which slightly (less than 0.1 per mil) reduce 18O13C16O mixing ratios. Variations in 18O13C16O in air with time and location will constrain the mean temperature of air-sea and air-leaf water exchange (and thereby add to the interpretation of d18O of CO2), and contributions from anthropogenic emissions and biomass burning. We will present data comparing southern California and Alaska during summer, 2003 as examples of these effects. Photolysis experiments on N2O demonstrate that photochemical reactions can generate large (up to tens of per mil) enrichments in multiply substituted isotopologues relative to their predicted stochastic abundance. Potential uses of such effects to constrain the physical budgets and physical chemistry of atmospheric gases will be discussed.

A42F-07 1730h

Modeling and measurements of oxygen isotope tracers of sulfate formation: Implications for the sulfur budget in the marine boundary layer

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Measurements of the mass-independent fractionation (MIF) in the oxygen isotopes of sulfate provide information on the relative oxidation pathways of sulfate formation(Savarino et al. 2001). The oxidation pathway has important implications for the effect of sulfate aerosols on climate, because it regulates whether this process can form a new particle in the atmosphere (gas-phase oxidation by OH) or forms on an already existing particle (aqueous-phase oxidation by H_2O_2 and O_3). Both present and past measurements of the MIF of sulfate show that O_3 is an important aqueous-phase oxidant in the sulfur cycle with regional (Lee, 2001), climatic (Alexander et al., 2001) and anthropogenic (Alexander et al., in preparation) variations. However, most global climate models do not consider O_3 to be an important oxidant for sulfate formation, primarily due to the assumption that most aqueous-phase oxidation of SO_2 occurs in clouds with pH values at which H_2O_2 will be the dominant aqueous-phase oxidant. Oxidation on alkaline aerosols such as sea salt or mineral dust could provide this missing O_3 oxidation pathway, as has been previously suggested in the literature. We report measurements of the MIF of sulfate collected on aerosol filters from two INDOEX cruises that show large $\Delta^{17}O$ values in the ITCZ region of the Indian Ocean. These measurements are compared with results from the GEOS-CHEM model of atmospheric chemistry and climate. The $\Delta^{17}O$ values of sulfate in the GEOS-CHEM model are calculated off-line based on the relative sources of sulfate. In addition to gas-phase oxidation by OH and in-cloud oxidation by H_2O_2 and O_3, O_3 oxidation of S(IV) on alkaline sea salt aerosols has been implemented in the GEOS-CHEM model. Results from the model indicate that the large $\Delta^{17}O$ values of sulfate measured within the ITCZ can be explained by oxidation of S(IV) by O_3 on sea salt aerosols. This process can affect the predicted climate forcing of sulfate aerosols by perturbing the amount of sulfate formed through gas-phase oxidation, and also by affecting the lifetime of sulfate that forms on coarse aerosols. The implications of this change on the sulfur budget in the marine boundary layer will be discussed.

A42F-08 1745h

Seasonal Atmospheric Chemistry at Summit, Greenland Based on N and O Isotopes of Nitrate

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Nitric acid (HNO_3), or nitrate (NO_3^-) is the major sink for reactive nitrogen oxides (NO_x) in the atmosphere. Ice core records of NO_3^- could provide information about past reactive nitrogen chemistry and oxidative capacity of the atmosphere. However, processes that take place in the surface snow (e.g., evaporation, photolysis) can affect the final NO_3^- concentrations that are archived in the ice cores, making it difficult to interpret past changes in atmospheric chemistry or climate. The isotopic composition of NO_3^- in surface snow provides an additional constraint on the effect of post-depositional processing in the upper meter of snowpack on the NO_3^- content measured in glacial ice cores. Furthermore, the isotopes of NO_3^- in ice cores have the potential to allow for reconstruction of sources of NO_x and aspects of atmospheric chemistry in the past. Snow pit samples (sampled every 3 cm to 1 m) collected at Summit, Greenland during August 2001 show seasonal variation in N and O isotopes of NO_3^-. $\delta^{15}N$ of NO_3^- in the upper meter of snow ranges from -15 to +16 per mil (vs. atmospheric N_2), with higher values found in summertime snow. The $\delta^{15}N$ of snowpack NO_3^- falls in the range reported for NO_3^- in precipitation from other parts of the world. $\delta^{18}O$ of NO_3^- in the snowpack ranges from 65 to 80 per mil (vs. VSMOW), similar to high values observed for rainwater and aerosol NO_3^-. In contrast to the $\delta^{15}N$, the $\delta^{18}O$ of NO_3^- is lower in summertime snow than in wintertime. Preliminary analyses also show diurnal variation in the isotopes of NO_3^- during summer, with depletion of ^{15}N and ^{18}O at "night" followed by enrichment during the "day." The similar behavior of the N and O isotopes is suggestive of a simple physical mechanism for the diurnal change, such as photolysis or evaporation. The seasonal $\delta^{15}N$ and $\delta^{18}O$, however, vary in opposite directions suggesting that these processes are not the dominant mechanism determining the seasonal signals. Our hypothesis is that isotope ratios preserved in the snow are determined by seasonal changes in atmospheric chemistry rather than post-depositional processes. To first order, we can explain the variation in $\delta^{18}O$ of NO_3^- as a switch in the reactions that produce HNO_3 from NO_x from predominantly homogeneous reactions in the summer ("day chemistry" influenced by OH) to predominantly heterogeneous reactions in the winter ("night chemistry" more influenced by ozone). Given our current information, the seasonal change in $\delta^{15}N$ of NO_3^- may be determined by seasonal changes in chemistry (i.e., ozone concentrations and its effect on the fraction of NO_x as NO_2), the source of NO_x, or both.

A42G MCC: 3016 Thursday 1600h

Results From the SOLVE II/VINTERSOL Mission II *(joint with C)*

Presiding: **M R Schoeberl,** NASA Goddard Space Flight Center**; L R Poole,** NASA Langley Research Center

A42G-01 1605h INVITED

An Overview of the Second SAGE III Ozone Loss and Validation Experiment (SOLVE-II)

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The SOLVE II Field mission was a field campaign designed to investigate polar ozone loss, polar stratospheric clouds, processes that lead to ozone loss, the dynamics of the polar stratosphere, and to acquire correlative data needed to validate satellite measurements of the polar stratosphere. The campaign was closely coordinated with VINTERSOL-EUPLEX campaigns. This combined international campaign was staged over the course of the winter of 2002-2003. SOLVE-II measurements were made from the NASA DC-8 aircraft, ozonesondes and other balloon payloads, ground-based instruments, and satellites. In particular SOLVE-II was designed to validate the Meteor-3M/Stratospheric Aerosol and Gas Experiment (SAGE) III satellite mission. We will review the overall objectives of the combined campaigns, discuss some of the broad observations of the winter of 2002-2003, and highlight the major findings of this campaign.

A42G-02 1625h INVITED

Arctic Stratospheric Ozone Loss in Winter 2002/2003 as Observed During the European VINTERSOL Campaign

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The first phase of the European Validation of International Satellites and Ozone Loss (VINTERSOL) program was focussed on stratospheric ozone loss and related processes and satellite validation in the 2002/2003 Arctic winter. Over the winter several measurement campaigns employing balloons, ozone sondes, aircraft, and satellite data focussed on PSC formation, halogen activation, and ozone loss processes. The talk will give an overview of the activities carried out and will highlight the major results on the formation of NAT particles, chlorine activation and partitioning, and ozone loss processes.