samples were measured using two different extraction / mass spectrometer systems established previously in the Jena isotope facility. Using the same protocol we have generated CO2-in-air mixtures from NBS-19 and other internationally available carbonate standards for assigning isotopic values to our new carbonate reference material (MAR J1). The isotopic record in a number of batches prepared over months will be discussed. In addition, the relationship with existing CO2-in-air scales (e.g. CG-99, based on a pure CO2 gas) have been evaluated by direct CO2 admixture to synthetic air using the same setup.

A42D-05 1440h

Observations of the Isotopic Compositions of CH_4, H_2, N_2O, and CO_2 in the Stratosphere: Implications for Biogeochemical Tracer Studies and Global Isotope Budgets

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Because various sources and sinks of many trace gases in the atmosphere have distinct isotopic signatures, measurements of the isotopic compositions of these gases in the free troposphere provide a constraint beyond concentration measurements alone on their global budgets. For N_2O, for which the primary sink is photolysis and photooxidation in the stratosphere, Kim and Craig [Science, 1993] first suggested that a flux of isotopically heavy N_2O from the stratosphere could balance the known isotopically light surface sources to produce the observed nitrogen and oxygen isotopic compositions in the troposphere. For most other gases, however, the flux of an isotopic signature acquired through stratospheric photochemistry has been ignored in tropospheric studies, in part due to lack of knowledge of isotopic fractionation processes in the stratosphere and in part due to the idea that the mass of the stratosphere is small compared with that of the troposphere so that the influence of the stratosphere on tropospheric isotopic compositions must be negligible. We have recently quantified the fluxes of isotopically heavy isotopologues for CH_4, H_2, N_2O, and CO_2 from isotopic and trace gas measurements on whole air samples collected from the NASA ER-2 aircraft between 1996 and 2000. In each case, the magnitudes of the fluxes are found to be large enough to influence isotopic compositions in the troposphere. An overview of these fluxes and the implications of the stratospheric observations for the global isotope budgets and/or biogeochemical tracer studies in the troposphere will be given.

A42D-06 1455h

The Stable Isotopes of Atmospheric Methane: Long-Term Observations at Alert (Canada) and Neumayer (Antarctica)

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Ten years records of CH_4 concentration, $^{13}C/^{12}C$-CH_4 and ^2H/H-CH_4 from the background stations Alert, Arctic, (82.45°N) and Neumayer, Antarctica, (70.65°S) are presented. High volume integrated (Alert) and spot (Neumayer) samples are collected at the respective sites and are analysed in Heidelberg using GC-FID technique for mixing ratios, IRMS for $^{13}C/^{12}C$ and ^2H/H ratios, and, in the last two years, a TDLAS system for analysis of the ^2H/H ratio. At Neumayer we observe a seasonal CH_4 cycle with a peak-to-peak amplitude of about 28 ppb; minimum mixing ratios are ocurring in February/March, and maxima in August/September. The seasonalities of $^{13}C/^{12}C$ and ^2H/H are anticorrelated to the mixing ratio and average 0.12 $^o/_{oo}$ ($^{13}C/^{12}C$) and 2.4 $^o/_{oo}$ (^2H/H) peak-to-peak. Seasonal cycles at Neumayer can be explained by the seasonality of methane destruction in combination with a seasonally varying meridional circulation pattern in the atmosphere. The atmospheric OH sink (which contributes about 90% to the total sink of atmospheric methane) is stronger during summer. The long-term trends at Neumayer are 5.8 ppb/yr (mixing ratio), 0.04 $^o/_{oo}$/yr ($^{13}C/^{12}C$) and 0.8 $^o/_{oo}$/yr (^2H/H). At Alert we observe a seasonal amplitude of CH_4 about twice as large as at Neumayer, while the $^{13}C/^{12}C$ and ^2H/H seasonality is larger by a factor of three, with minimum mixing ratios in July, and maxima in January/February (isotopes almost anticorrelated, whereas minimum isotope ratios occur 2-3 month earlier than the maximum mixing ratios). Compared to Antarctica which is far away from any source region additional influences from methane sources lead to the larger seasonalities at Alert: The nearby wetland sources are emitting CH_4 during the summer season but they do not seem to affect much the mixing ratio. This is different for the isotope ratios. High methane concentrations during the winter months are caused by transport of stratified polluted air masses from mid latitudes to the Arctic station during this season. The long-term trends at Alert are 3.6 ppb/yr (mixing ratio), 0.03 $^o/_{oo}$/yr ($^{13}C/^{12}C$) and 1.4 $^o/_{oo}$/yr (^2H/H). At Alert and at Neumayer the mixing ratios are almost constant (except for seasonality) since about three years. From the difference between both stations a fractionation of -7.2 $^o/_{oo}$ ($^{13}C/^{12}C$) and -234 $^o/_{oo}$ (^2H/H) for the mean tropospheric methane sink can be derived. The same results are obtained from the analysis of the southern hemispheric seasonal cycle. With the two approaches one can estimate the isotopic signature of the mean source to -53.9 $^o/_{oo}$ ($^{13}C/^{12}C$) and -275 $^o/_{oo}$ (^2H/H). The continuing long term trend in both stable isotopes shows that in contrast to the mixing ratio the isotopes are still not in steady state with its sources and sinks.

A42D-07 1510h

Carbon-13 Evidence of the Causes of the Atmospheric Methane Concentration Increase Since 1700AD and of a Varying Methane Budget Beforehand

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The causes of the major increase in the concentration of atmospheric methane since 1700 AD are investigated. We measured d13CH4 in air extracted from Antarctic ice cores and firn and in air archived from Cape Grim, Tasmania. This was done using a newly developed GC-IRMS technique that analyses very small air samples with high precision. The results show that d13CH4 increased over the past century, consistent with the addition of isotopically enriched sources from anthropogenic activity. However a large increase (about 1.5 per mil) in d13CH4 from 1700AD back to about 1500AD was also observed. This was quite unexpected as it was previously assumed, based on the small observed changes in methane concentration, that the pre-anthropogenic methane budget was approximately in balance. Explanations for the cause of this d13CH4 increase invoke changes in enriched sources such as biomass burning with compensating changes in biogenic (mainly wetland) sources, or changes in a strongly fractionating sink.

A42D-08 1525h

Changes of Methane and Nitrous Oxide in the Atmosphere : new Constraints From Stable Isotope Analyses in Polar Firn and ice.

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Methane and nitrous oxide are two greenhouse gases playing a major role in atmospheric chemistry ; methane largely affects the oxidative capacity of the atmosphere whereas nitrous oxide participates in many atmospheric chemical reactions involving O_3 and NO_x in the stratosphere. A sharp increase in the mixing ratios of both gases has been observed since the beginning of the pre-industrial era, implying an increase of anthropogenic sources. Although these gases are important in global climate changes, their budget remains poorly known. The evolution of their isotopic composition in the atmosphere brings additional constraints as it represents the final signature of their budgets and reflects changes in the relative contribution of sources and sinks. We have measured preindustrial air from polar firn air and ice cores that will lead to the long term evolution of these gases. A continuous flow technique is used at the Laboratory of Glaciology and Geophysics of Environment (LGGE) in Grenoble, France to measure $\delta^{13}CH_4$, whereas a similar technique is used at the Max Planck Institute for Nuclear Physics, in Heidelberg, Germany to measure $\delta^{15}N_2O$ and $\delta N_2{}^{18}O$. Samples from both Antarctica (Vostok, Dome C, Berkner Island) and Greenland (North GRIP) were used. We will present these results and their tentative interpretation based on a diffusion model of gas isotopes in polar firn and on simple atmospheric box approaches.

URL: http://w3.agu.org

A42E MCC: 3016 Thursday 1340h

The Organic Aerosol Component: Impact on Reactivity, Optical Properties, Hygroscopicity, and Cloud-Condensation Properties III

(joint with AE)

Presiding: **G D Smith,** University of Georgia**; T Mentel,** Institut für Chemie und Dynamik der Geosphäre Juelich

A42E-01 1340h

Aerosol mass spectrometer measurements of organic aerosol

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Organic species are known to be ubiquitous and comprise a significant component of ambient aerosols. Identifying the sources, chemical compositions, and loadings of particulate organics remains a difficult, yet important problem as organic components may affect the formation, hygroscopicity, growth, reactivity, and radiative effects of ambient particles. Unraveling this complexity inherently must rely on chemical information (such as off-line filter analyses and collector/concentrator techniques), but also on real-time instruments that are capable of combining particle phys-

ical measurements (size, density) with chemical speciation information. The Aerodyne Aerosol Mass Spectrometer (AMS) has been deployed on many different measurement platforms around the world and is generating a rich data set capable of providing insight into the complexity of particulate organics. Highlights of the aerosol measurements will be presented. Although the AMS cannot uniquely classify individual organic compounds, it has been become evident that classes of organic compounds can be identified. These include the identification of a size-resolved chemical signature for fresh diesel and gasoline particulate emissions. Electron impact ionization mass spectral signatures of oxidized organic components and the temporal and spatial relationships between the signatures for fresh organic emissions and aged/oxidized organic components. Laboratory studies on soot and other organic aerosols will also be presented within this context.

A42E-02 1355h

Hygroscopic Organic Aerosols in the Great Smoky Mountains: Chemical Characteristics and Origins

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Water uptake by hydrophilic organic aerosols can be especially important in rural locations. An especially sizeable fraction of the aerosol organics in these more remote locales tends to be polar, due to the importance of biogenic emissions and the substantial photochemical alteration of primary nonpolar anthropogenic emissions that have been transported long distances from urban areas. As part of the Southeastern Aerosol and Visibility Study (SEAVS), 42 daytime and 10 nighttime filter samples of fine aerosols were collected during the period from July 15 to August 25, 1995 at the Great Smoky Mountain National Park, Tennessee (U.S.A.). Samples were extracted and derivatized to enable identification and quantification of the water-soluble organic compounds (WSOCs). The identified species were chemically classified into 7 groups: (1) monocarboxylic acids, (2) hydroxy-carboxylic acids, (3) dihydroxy-carboxylic acids, (4) dicarboxylic acids, (5) hydroxy-dicarboxylic acids, (6) polyols, and (7) other water-soluble organic compounds. Species concentrations ranged from <1 ng/m^3 to >200 ng/m^3. Dicarboxylic acids were the most dominant identified compound class, and succinic acid was the most abundant dicarboxylic acid. The dominance of succinic acid over oxalic acid observed in this study contrasts with what has been reported for a number of other rural areas. This unique concentration distribution of dicarboxylic acids found in daytime SEAVS samples suggests to us that: (1) most WSOCs collected in the SEAVS samples were mainly generated from secondary photochemical reactions, especially during the first half of the sampling campaign, and (2) high relative humidity at the sampling site may have contributed to the high abundance of succinic acid. Concurrent trends in malic acid and malonic acid concentration support the hypothesis that succinic acid is being oxidized via hydroxyl radical addition. Analogous to the conversion of 3-hydroxy-propanoic acid to malonic acid, these measurements suggest that 4-hydroxy-butanoic acid could serve as a major precursor contributing to abundant succinic acid in the daytime samples. Nocturnal WSOCs exhibited different chemical compositions and lower concentrations than the daytime WSOCs. It appears that a diurnal-to-nocturnal ratio of succinic acid larger than 0.3 may indicate an atmospheric environment dominated by photochemical reactions, rather than by primary emissions.

A42E-03 1410h

Hygroscopic Characteristics of Organic Laden Ambient Aerosols in Yosemite National Park

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Water absorption by inorganic compounds can be modeled with some degree of certainty; however, water uptake by ambient organic aerosols remains speculative. To improve the understanding of organic hygroscopicity, an aerosol characterization study was conducted at Yosemite National Park, California, starting in July and ending in the first week of September 2002. High time resolution measurement (15-minute time increments) of PM2.5 ionic species (Cl-, SO42-, NO3-, Na+, NH4+, K+, Mg2+, and Ca2+) were measured using PILS (Particle-Into-Liquid-System)/IC (Ion Chromatography). Commercially available annular denuders and a PM2.5 cyclone (URG) were used upstream of the PILS/IC to remove particles greater than 2.5 ìm and acidic and basic gases. A dual wavelength aethalometer and an R&P particulate carbon monitor were used to measure carbon on a semi-continuous basis while a DRUM sampler allowed for semi-continuous estimates of concentrations of elements associated with crustal material. Standard IMPROVE type samplers were used to measure 24-hr integrated samples of these same aerosols. Two nephelometers operated in tandem, one dry and the other with a controlled humidity environment, were used to measure f(RH) = bscat(RH)/bscat,dry , where bscat(RH) is the scattering coefficient measured at some relative humidity and bscat,dry is the scattering coefficient measured at RH $<10\%$. The aerosol composition was highly variable in time, with a strong diurnal cycle. Organic carbon mass was observed to be, on the average, 70% of the fine mass with days where its contribution was well over 95% of the mass. Measurements of carbon isotopes revealed the fraction of carbon from biogenic sources to range from approximately 73 to 95%. Water soluble potassium was highly correlated with carbon mass, suggesting the influence of wood smoke. The ionic fraction of the aerosol consisted primarily of ammonium sulfate and in most cases nitrate was in the form of sodium nitrate. Fine soil mass was less than 1% of PM2.5 mass. The ambient aerosol was observed to deliquesce on days when the inorganic and organic aerosol were approximately equal in concentration; however, on days when the organic component was dominant, only smooth f(RH) curves were observed. Equilibrium models, exercised in combination with Mie scattering theory, were used to predict atmospheric aerosol water content and associated increases in aerosol scattering coefficient. The analyses suggest that in most cases the hygroscopic growth of inorganic salts alone could account for the observed increase in scattering as a function of relative humidity.

A42E-04 1425h

Amplification of Black Carbon Absorption by Internal Mixing With Secondary Organic Aerosol Mass

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Atmospheric soot or black carbon (BC) might have a significant warming influence on local and global climate. During its residence time within the atmosphere freshly emitted BC is aged by microphysical processes like coagulation, the condensation of low and semi-volatile gaseous compounds, and cloud cycling. Especially the latter two processes dominate the atmospheric ageing and result in an internal mixture by the inclusion of BC in transparent host particles composed of organic or inorganic material. It is well known from several theoretical investigations that internally mixed BC has an amplified mass specific absorption cross section. When accounting for the internal aerosol mixing in global circulation models a doubling of the climate warming potential of BC was found compared to the external case. However, these studies use relatively simple particle models to calculate the optics of the aerosol particles. Since the overall diversity and complexity of the atmospheric aerosol morphology could not be accounted for in optical models, lab investigations which simulate the atmospheric BC ageing processes under realistic conditions are desirable to get a more reliable assessment of the direct climate forcing by anthropogenic BC emissions. The large aerosol chamber AIDA of Forschungszentrum Karlsruhe is well suited to simulate atmospheric aerosol aging processes over a wide range of temperature and pressure conditions. The absorption and scattering properties of BC internally mixed with SOA mass were investigated at the AIDA facility. BC particles were coated in situ by secondary organic material generated by the ozonolysis of α-pinene. A significant increase of the specific BC absorption cross section in the visible by a factor of more than 1.8 can be inferred from the experiments. The measured optical properties are compared with theoretical investigations using a concentric core shell model to calculate the optical properties of the internally mixed BC aerosol.

URL: http://www.aerosoloptics.de

A42E-05 1440h

Organic cloud condensation nuclei: the effect of phase, surface tension, trace soluble species, and oxidative processing on particle activation.

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The ability of organic aerosols to act as cloud condensation nuclei (CCN) will be discussed. A variety of laboratory experiments will be presented which address several key questions concerning organic particle activation. Does the particle phase impact activation? How does surface tension play a role and can a trace amount of a surface active species impact activation? Does a trace amount of a highly soluble species impact the activation of organic particles of moderate to low solubility? Can the activation properties of organic aerosols be enhanced through oxidative processing? To systematically address these issues, the CCN activity of various diacids such as oxalic, malonic, succinic, adipic and azelaic acid have been studied, as well as the addition of trace amounts of nonanoic acid and ammonium sulfate to examine the roles of surface active and soluble species, respectively. The first examination of the role of oxidative processing on CCN activity has involved investigating the effect of ozone oxidation on the activity of oleic acid particles.

A42E-06 1455h

Water Uptake and Ice Nucleation of Particles containing Humic Materials

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Aerosols can influence cloud nucleation and thus, may alter climate. While much is known about sulfate aerosol, recent field studies show that atmospheric particles contain significant masses of organic species, such as dicarboxylic acids and larger polycarboxylic acids, resembling the humic materials in soil. The presence of these compounds may alter the water uptake and deliquescence characteristics of particles and their ability to form clouds. Using a humidified tandem differential mobility analyzer (HTDMA) we have measured the water uptake by pure humic material and by mixed humic material/ammonium sulfate particles as a function of relative humidity. We find that the water uptake behavior varies with the type and source of the humic material. In most cases, the pure humic materials take up very little water and the mixed organic/ammonium sulfate particles take up a reduced amount of water relative to pure ammonium sulfate. We have also measured the ice nucleation behavior of humic acid aerosols. Results of the water uptake and cloud nucleating ability of aerosols will be presented, and atmospheric implications discussed.

A42E-07 1510h

Ice Nucleation in Internally Mixed Ammonium Sulfate/Dicarboxylic Acid Particles

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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.