

with emphasizing the effect of fire disturbance and the sensitivity of the carbon cycling to climate change. Our experimental design covers total 108 combinations with respects to four major landcover types (deciduous broadleaf, grass, wet and dry conifer), increasing CO₂ fire disturbance, increased/decreased temperature and precipitation. Based on the simulation, we constructed potential vegetation maps of LAI, GPP, and NPP, which were compared MODIS land products. Distinctly distinguishable patterns of regional carbon cycling were identified depending on landcover types. Elevated CO₂ resulted in overall 15% increase in NPP, when it was compared to NPP predicted with pre-industrial CO₂ concentration before 1861. Warmer area was more sensitive to the elevated CO₂ than cooler area. Explicit fire-disturbance simulation produced slightly lower NPP and distinctly scratched patterns but did not alter significantly aerial means, compared to constant fire-mortality simulation. Increased temperature and precipitation were positively related with the increased NPP. The model estimates of regional carbon cycling were more sensitive to temperature than precipitation. Our simulation experiments show the BOREAS region is overall carbon sink but sensitive to geographic location and vulnerable to fire disturbance and future climate change.

B61B-0732 0830h POSTER

Directional Effects on Observations of Land Surface Temperature With AVHRR Over Africa

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We characterized the directional effects on the thermal infrared signal retrieved by the NOAA Advanced Very High Resolution Radiometer (AVHRR). For that purpose, day and night GAC data were processed using the full swath width of the AVHRR/2. We developed a methodology for normalizing the land surface temperature to nadir observation and tested it over continental Africa. The methodology is based on ancillary structural information of the surface as well as empirical and modeled relationships between the scene endmembers. To assess the effectiveness of our method, we apply it to one of the EOS and SAFARI 2000 core sites: Skukuza, South Africa. The directional trends of AVHRR estimates and modeled predictions are consistent and suggest that this approach could be further developed to help reduce the systematic bias in land surface temperature from AVHRR. Our method is general and applicable to other wide field of view sensors such as MODIS.

B61B-0733 0830h POSTER

The MODIS Snow Products - an integral part of the MODIS Land Surface Products

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With Moderate Resolution Imaging Spectroradiometer (MODIS) instruments now operating on the NASA Terra and Aqua satellites, a daily, global coverage stream of high quality information about the earth's surface is being collected and made available to the public. The MODIS archives at the NASA Distributed Active Archive Centers (DAACs) include a

range of data sets, from individual channel radiances to geophysical parameters in swath and resampled gridded formats. The MODIS snow products, produced by the MODIS Science Team and distributed by the National Snow and Ice Data Center DAAC, are a key part of the land surface suite of products. The MODIS snow products are now providing fully automated, daily, global maps of snow cover extent at a spatial resolution of 500-m. The MODIS data from Terra have been produced since October 2000. Ongoing work to improve the performance and utility of the products includes improvements to the use of the MODIS cloud mask, algorithm enhancements to more accurately map snow cover in dense forests, a Climate Modelers Grid, easy to access browse, and plans for a snow albedo product. This paper describes the characteristics, capabilities and limitations of the MODIS snow products, their accessibility from the NSIDC DAAC, and current user support and tools.

URL: <http://nsidc.org/modis>

B61B-0734 0830h POSTER

New Tool for MODIS Multiple Data Ordering: A Case Study Over Lake Michigan

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The Goddard Earth Sciences Distributed Archive Center (GES DAAC) has served as an intermediary between MODIS Data and the user community. This has given us the unique opportunity to communicate with the users and explore better options for accessing and ordering MODIS Data. The MODIS Data Support Team at GES DAAC has developed a much needed tool to aid users to simultaneously order multiple data products, set temporal and spatial search criteria, find appropriate satellite overpass, cloud cover of the scene, and more, all in one interface. The enhanced tool serves as a portal to the GES DAAC Web-based Hierarchical Ordering Mechanism (WHOM), removing, however, some of the drawbacks of WHOM. One of the strengths of the tool is to provide long time series of multiple MODIS Level 1 and Ocean and Atmosphere Level 2 products: something not available from WHOM but so much needed for regional studies.

This presentation will demonstrate the features of the tool using as an example a case study of Ocean Color and Surface Temperature over Lake Michigan. Readers will be guided through the whole process of selecting the relevant data, the spatial and temporal region, submitting order, and finally visualizing the MODIS products. Plans for further developments will be presented as well.

B61C MCC: Hall C Saturday 0830h

High Spatial and Spectral Resolution Remote Sensing of Urban Ecology: New Results From NASA EOS Satellite and Airborne Sensors Posters (joint with OS, GC)

Presiding: W L Stefanov, Arizona State University; J Grove, USDA Forest Service

B61C-0735 0830h INVITED POSTER

Multiresolution Morphology and Metabolism of the Metropolis

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Small watershed research is a hallmark of the LTER network, with catchments subject to different treatments used to develop input-output budgets of water,

nutrients and carbon, as well as an understanding of the relations of energy and material cycling to ecological communities and trophic systems. In the Baltimore Ecosystem Study (BES), this approach emphasizes the role of human society as part of the ecosystem such that individual and institutional activity are defined as important aspects of ecological community and trophic system dynamics. We have been adapting a spatial hydroecological modeling approach to operate across the urban-rural gradient, incorporating an explicit description of the drainage sequence, as well as human sources of irrigation water and fertilizer. As human activity tends to produce sharp gradients in land cover and topographic structure (e.g. property lines, drainage infrastructure), the behavior of human dominated ecosystems may require higher resolution information to adequately characterize system structure and function. We hypothesize that our spatial analysis and modeling methods will show greater sensitivity to topographic and land cover information in the suburban sites than in the agricultural or forested ecosystems.

In this paper we concentrate on three of the head-water catchments, including a fully forested catchment (Pond Branch), a suburban catchment (Glyndon) and an agricultural catchment (McDonogh). Continuous discharge gauging by the USGS at each of the three catchments and weekly sampling for stream chemistry have been carried out for all three catchments. Soil moisture has been sampled weekly at a set of sites along a topographic wetness gradient using portable soil moisture meters. Topographically defined flow-path networks were extracted from high resolution digital elevation models (DEMs) at 30m resolution, 5m resolution from photogrammetric sources and at 0.5m from LIDAR. Land cover at these resolutions are also extracted from high resolution airborne imagery and ETM scenes. One of the key features of the catchments we concentrate on is the ecological patch structure along topographic flowpaths and the nature of the land cover and topographic drainage right around the stream channel as these features often have an important role in modifying streamflow generation and water chemistry. Using measured soil moisture and streamflow discharge and chemistry, we test the impact of source data resolutions used to generate topographic and land cover information on our ability to model the measured soil moisture, streamflow and chemistry from these catchments.

B61C-0736 0830h POSTER

Multi-sensor Approaches to Urbanization: Using Astronaut Photography of Earth to Fill Data Gaps

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Scientists studying the rapid growth of urban areas around the globe often must combine a variety remote sensing sources to get data that meets their needs. Depending on research questions, these needs may include observations at specific points in time or with sufficient spatial resolution. Though not widely used for urban studies, astronaut photography can uniquely fill some data gaps. Early photographs taken during the Gemini and Apollo programs in the 1960s represent the oldest remotely sensed records for a number of world cities. The archive of astronaut photography of Earth is maintained in a single location, offers valuable information on urban boundaries over the last 40 years, and can fill gaps in time series studies. Although working with digitized photographs differs from satellite data, such images can be used as 3-band data, georeferenced, and used with image analysis techniques such as supervised classification and texture analysis. The results of simple land cover classifications can approximate results that would be obtained from Landsat. Using digital cameras from the International Space Station, astronauts are now routinely acquiring photographs of urban areas with 6 m or better spatial resolution. These images serve as valuable sources of information that can be analyzed directly or used to verify analyses of other sensor data. Astronaut photographs of cities are available for public searching on the web at NASA Johnson Space Center The Gateway to Astronaut Photography of Earth. The site includes tools for searching the over 400,000 photographs taken to date as well as a special collection, Cities from Space, of outstanding city photographs.

URL: <http://eol.jsc.nasa.gov>

B61C-0737 0830h INVITED POSTER**Urban Mapping Validation at Venice With Satellite and Aircraft Data**Michael Abrams¹ (mike@lithos.jpl.nasa.gov)Stefano Pignatti² (pignatti@lara.rm.cnr.it)Luigi Alberotanza³ (direzione@isdgm.ve.cnr.it)¹Jet Propulsion Lab, 4800 Oak Grove Dr., Pasadena, CA 91109, United States²CNR-Progetto LARA, Via Monte d'Oro, 11, Rome 00040, Italy³ISDGM-CNR, S. Polo 1364, Venice 30125, Italy

As part of a validation project for EO-1 satellite data, a large number of data sets were analyzed to map the urban environment of the city of Venice. Satellite data included 30-m EO-1 Advanced Land Imager (ALI) data with 9 broad bands in the 0.43-2.35 micron region; 30-m EO-1 Hyperion hyperspectral scanner data with 192 bands in the 0.45-2.35 micron region; 30-m Landsat Thematic Mapper data; 15 and 30-m ASTER data with 9 bands in the 0.52 to 2.4 micron region; 8-m MIVIS hyperspectral aircraft scanner data with 102 bands in the 0.4 to 12 micron region; and 4-m Ikonos data with 4 bands in the VNIR. The data were analyzed to isolate different instrument factors: spatial resolution and spectral bands. The materials looked for were: old tile roofs, new tile roofs, zinc roofs, asphalt pavement, trachyte pavement, limestone pavement, grass and trees. In the 30-m data, all pixels were spectrally mixed, so materials that were identifiable were not pure classes. New roofs, old roofs, grass, and trees form large enough areas to be separable, though materials were mixed with shadows and other materials. Increased spatial resolution improved classification accuracy, and allowed more different materials to be identified. Similarly, more spectral bands improved classification accuracy. The best results were obtained with MIVIS 102-channel, 8-m data, that allowed all types of materials to be mapped both spatially and spectrally. EO-1 ALI data were better than Landsat TM due to the improved signal-to-noise, and the additional spectral bands. Hyperion data suffered from low signal-to-noise, and so the full advantage of hyperspectral data was not available for this site. Operational multispectral satellites generally do not have sufficient spatial resolution to be extremely effective for mapping urban areas. The data are good for separating general classes of materials, useful for runoff models. Higher spatial resolution (<10 m) is necessary to spatially separate urban materials. Most classes can be separated with Ikonos, for example, with 4-m pixels. But the limited number of spectral bands prevents separation of subtle differences, such as the presence of limestone.

B61C-0738 0830h INVITED POSTER**Investigation of Spectral Characteristics of Urban Surface Materials Using Field Measurements and Hyperspectral HyMap Data**Uta Heiden¹ (+49-331-2881197; heiden@gfz-potsdam.de)Sigrid Roessner¹ (+49-331-2881196; roessner@gfz-potsdam.de)Karl Segl¹ (+49-331-2881193; segl@gfz-potsdam.de)Hermann Kaufmann¹ (+49-331-2881190; charly@gfz-potsdam.de)¹GeoForschungsZentrum Potsdam, Telegrafenberg A17, Potsdam 14471, Germany

Recent developments of remote sensing technologies allow the acquisition of data with a high spectral and spatial resolution. The high information content of hyperspectral data enables the detailed analysis urban surface materials. This yields the potential for an automated identification of urban surface materials based on their spectral shape. The base for such an analysis is a detailed knowledge about spectral characteristics of urban surface materials.

This study aims at investigating the spectral characteristics of urban surface materials throughout the reflective wavelength range. For this purpose urban surface materials have been systematically measured with a field spectrometer. Furthermore the measurements have been analyzed and stored in a spectral library. For the systematic assessment of materials the urban surface is categorized in regard to its degree of surface sealing resulting in urban surface cover types. The resulting categories form the thematic frame for the assessment of urban surface materials. Sealed surfaces are analyzed in terms of variations in material and color. Non-sealed surfaces, such as soil and vegetation are investigated in regard to their special urban properties. The obtained spectral library is used to explore the spectral information content of airborne hyperspectral HyMap data, which have been acquired for the study area of Dresden, Germany. In the result 79 spectral classes could be distinguished based on

these data. They represent spectrally different materials (e.g. zinc and asphalt). They also contain spectral variations of the same material, which are caused by different roof geometries, color and other coating, age and intensity of use.

The results of this investigation show the high spectral variability of urban surface materials in the field measurements and in the hyperspectral data. This high information content yields the potential for area-wide automated assessment of urban surface materials.

B61C-0739 0830h POSTER**Assessment of Landscape Fragmentation Associated With Urban Centers Using ASTER Data**William L Stefanov^{1,2} (480-965-5507; will.stefanov@asu.edu)¹Department of Geological Sciences, Arizona State University, Tempe, AZ 85287, United States²Center for Environmental Studies, Arizona State University, Tempe, AZ 85287, United States

The role of humans as an integral part of the environment and ecosystem processes has only recently been accepted into mainstream ecological thought. The realization that virtually all ecosystems on Earth have experienced some degree of human alteration or impact has highlighted the need to incorporate humans (and their environmental effects) into ecosystem models. A logical starting point for investigation of human ecosystem dynamics is examination of the land cover characteristics of large urban centers. Land cover and land use changes associated with urbanization are important drivers of local geological, hydrological, ecological, and climatic change. Quantification and monitoring of urban land cover/land use change is part of the primary mission of the ASTER instrument on board the NASA Terra satellite, and comprises the fundamental research objective of the Urban Environmental Monitoring (UEM) Program at Arizona State University. The UEM program seeks to acquire day/night, visible through thermal infrared data twice per year for 100 global urban centers (with an emphasis on semi-arid cities) over the nominal six-year life of the Terra mission. Data have been acquired for the majority of the target urban centers and are used to compare landscape fragmentation patterns on the basis of land cover classifications.

Land cover classifications of urban centers are obtained using visible through mid-infrared reflectance and emittance spectra together with calculated vegetation index and spatial variance texture information (all derived from raw ASTER data). This information is combined within a classification matrix, using an expert system framework, to obtain final pixel classifications. Landscape fragmentation is calculated using a pixel per unit area metric for comparison between 55 urban centers with varying geographic and climatic settings including North America, South America, Europe, central and eastern Asia, and Australia. Temporal variations in land cover and landscape fragmentation are assessed for 9 urban centers (Albuquerque, New Mexico, USA; Baghdad, Iraq; Las Vegas, Nevada, USA; Lisbon, Portugal; Madrid, Spain; San Francisco, California, USA; Tokyo, Japan; and Vancouver, Canada). These data provide a useful baseline for comparison of human-dominated ecosystem land cover and associated regional landscape fragmentation. Continued collection of ASTER data throughout the duration of the Terra mission will enable further investigation of urban ecosystem trends.

B61C-0740 0830h POSTER**Analysis of Brush Fire Scars in Semi-Arid Urban Environments: Implications for Future Fire and Flood Hazards Using Field and Satellite Data**Tamara Misner¹ (412-624-8773; tam85@pitt.edu)Michael Ramsey¹ (412-624-8773; ramsey@ivis.eps.pitt.edu)Ramon Arrowsmith² ((480) 965-3541; ramon.arrowsmith@asu.edu)¹University of Pittsburgh, Department of Geology Planetary Science, 4107 O'Hara Street, Pittsburgh, PA 15260, United States²Arizona State University, Department of Geological Sciences, Box 871404, Tempe, AZ 85287, United States

The number of forest fires has increased dramatically over the past five years in the western United States, due to both human and natural causes. These fires commonly expand rapidly as a function of vegetation, climate as well as past and present fire fighting practices. Many urban areas, such as Phoenix, AZ have experienced extreme population growth rates over the past 50 years. A majority of the development now

occurring is in desert areas that have once burned, or are currently threatened by the potential of brush fires. These regions northeast of the city of Phoenix have experienced numerous fires over the past two decades that have been expensive to fight, and caused a considerable amount of property damage. This region is also currently targeted as one of the prime suburban growth corridors in a metropolitan area. As people expand into these environments there is an increased risk of fire, and the potential of subsequent flooding focused within the scars. Therefore, the ability to predict and control fires is increasingly important in these rapidly growing areas. Remote sensing together with detailed field data has been used to characterize areas scarred by past fires with the goal of assessing the risk for burning in the future.

Space and airborne data from ASTER, Landsat ETM, SIR-C, TIMS and balloon-based cameras have been combined within a GIS model to characterize existing fire scars northeast of Phoenix, AZ. These data sets were used to quantify the relationship of fire scar age to vegetative recovery, and to determine the control of local topography on fire behavior. In addition, detailed field topographic surveys were combined with sediment trap data to contrast erosion rates in severely burned and unburned catchments. Initial results imply a slightly higher erosion rate in the scars and therefore increased flooding risks. The combination of remote sensing data analyses with a GIS database, constrained by careful geomorphic and sedimentological investigations, may permit city officials and urban planners to better calculate potential risks for both future fire and flood hazards within the region. By examining the spatial variability of numerous scars in one location, and given the potential to evaluate their relative ages automatically, it should be possible to establish fire recurrence intervals around any urban area. This can be compared with lightning frequency, climate, vegetation, and terrain characteristics to vastly improve the characterization of hazards associated with semi-arid environment brush fires.

B61C-0741 0830h POSTER**Using Hyperspectral Imagery for Ocean Process Studies in Monterey Bay, California**Andrew M Fischer¹ (607-255-5449; amf26@cornell.edu)John P Ryan² (rjyo@mbari.org)¹Cornell University, Department of Earth and Atmospheric Sciences 2154 Snee Hall, Ithaca, NY 14853, United States²Monterey Bay Aquarium Research Institute, 7700 Sandholt Road, Moss Landing, CA 95039, United States

Hyperspectral remotely sensed imagery is promising technology for coastal marine science. High-resolution snapshots from airborne platforms reveal detailed ocean structure, from which information on the processes that shape the coastal marine environment can be derived. The Airborne Visible/Infrared Imaging Spectrometer (AVIRIS) sensor was flown aboard the ER-2 aircraft over Monterey Bay on October 13, 2000. Upwelling radiance and downwelling irradiance were measured just above the surface of the water during the overflight. CTD casts, inherent optical property (absorption and attenuation) measurements at CTD stations, and continuous underway sea surface temperature, salinity, fluorescence, attenuation and absorption measurements were also taken. The 5 AVIRIS flight lines, consisting of 33 scenes, were mosaicked into a composite image of Monterey Bay and the adjacent ocean. The image was radiometrically corrected and transformed into map space. FLAASH, a commercial release software, was used for atmospheric correction and optimized for use over water. Spectra in the atmospherically corrected image were compared with in situ measurements. Surface chlorophyll estimates, derived from reflectance values of the composite image, reveal fine scale coastal ocean structure. The imagery, combined with in situ data, illustrate the dynamic processes that shape the coastal marine environment of Monterey Bay. Future considerations in adapting hyperspectral imagery to ocean process studies are also addressed.

B61C-0742 0830h POSTER**Seasonal Variation in Sea Surface Chlorophyll Patterns of the Northern Gulf of Mexico as Determined by Satellite Remote Sensing**Richard L. Miller¹ (Richard.Miller@ssc.nasa.gov)Jinchun Yuan¹ (Jinchun.Yuan@ssc.nasa.gov)Rodney T. Powell² (rpowell@lumcon.edu)Michael J. Dagg² (mdagg@lumcon.edu)

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The sea surface concentration of chlorophyll in the northern Gulf of Mexico was derived from satellite remote sensing for the period of July 2001 to June of 2002. High resolution (L1A data, with 1 km spatial resolution) Sea-viewing Wide Field of view Sensors (SeaWiFS) data were used to calculate chlorophyll with the OC4 algorithm for all the clear and partly cloudy days. The chlorophyll pattern shows strong seasonal variation. In offshore areas, a single annual phytoplankton bloom was observed with chlorophyll concentration increasing in fall and winter to reach a maximum of 0.35 mg m⁻³ in February, and decreasing in spring and summer to a minimum of 0.1 mg m⁻³ in July. In coastal regions from the Texas shelf through Mississippi Sound, phytoplankton blooms were observed in February and July. During the bloom in summer, patches of high chlorophyll surface waters were injected into offshore waters. The chlorophyll concentration decreased from ~10 mg m⁻³ near the mouth of the Mississippi River and on the Louisiana shelf to ~5 mg m⁻³ on the Texas shelf and the Mississippi Sound. The temporal and spatial distribution of the phytoplankton bloom in summer coincides with reported annual hypoxia events.

B61D MCC: 132 Saturday 0830h Mass Independent Isotope Fractionation: New Frontiers in Isotope Biogeochemistry I (joint with A, V, GC, PP)

Presiding: G Michalski, University of California, San Diego; B Alexander, University of California, San Diego; J Savarino, Laboratoire de Glaciologie et Gophysique de l'Environnement

B61D-01 0830h

Mass Independent Isotope Effects and Their Occurrence in Nature

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It has been nearly 20 years since the discovery of a chemically produced mass independent isotope effect by Thiemens and Heidenreich. Subsequent to that time there has been a great deal of progress in developing a physical chemical theory to account for the effect. In particular, recent work by R. Marcus and colleagues has advanced understanding of the effect considerably.

There are now many know examples of mass independent isotopic compositions in nature, in fact, with the exception of water, all atmospheric molecules possess mass independent isotopic compositions. This includes O₂, O₃, CO₂, H₂O₂, N₂O, CO, and atmospheric aerosol sulfate and nitrate. In addition, sulfur in aerosol sulfate is mass independently fractionated and it is now known that the anomalies are preserved in Miocene Volcanic samples, Namibian desert sulfate, Pre-Cambrian sulfate and sulfide (sulfur isotopes), and sulfates from the Antarctic dry valleys. Polar ice samples are also known to preserve the mass independent isotopic anomalies. In addition, secondary minerals from the SNC Martian meteorites possess both sulfur and oxygen isotopic anomalies which are used to understand atmospheric-regolith coupling. In all cases where mass independent isotopic compositions have been observed, understanding of the particular cycle has been advanced.

B61D-02 0845h INVITED

Mass Independent Isotope Effect in Ozone and in the Earliest Processed Solids in the Solar System

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The main concepts in a theory are described for the mass-independent isotope effect in ozone formation discovered by Thiemens. They include (1) the relative lifetimes of the symmetric (OOQ*, OOO*) and asymmetric (OOQ*) vibrationally excited ozone intermediates, Q is ¹⁷O or ¹⁸O, (2) the differences in zero-point energy in the two exit channels of a dissociating

OOQ* molecule, and (3) "weak" deactivating collisions. The first plays a major role under the usual ("scrambled") conditions and causes the mass-independent isotope effect. The second produces large and unusual mass-dependent isotopic effects observed by Mauersberger under "unscrambled conditions," but cancels exactly under the scrambled conditions. Their theoretical basis is described. The third plays a role under both sets of conditions. We also discuss whether analogous concepts, particularly the first, are applicable to the formation of the earliest processed solids in the solar system, the calcium-aluminum-rich inclusions in meteorites, for which a mass-independent isotope effect was first observed by Clayton.

URL: <http://chemistry.caltech.edu/faculty/marcus/index.html>

B61D-03 0925h

The Temperature Dependence of Positional Resolved ¹⁸O Fractionation in Ozone

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The formation of ozone by the well known Chapman reaction O + O₂ + M → O₃ + M shows a large and unusual isotope effect. Laboratory predictions of oxygen fractionation in ozone molecules containing singly substituted ¹⁷O or ¹⁸O match well with both tropospheric and stratospheric observations. Quantitative modelling and understanding of isotope transfer from ozone into other atmospheric species (CO₂, N₂O, etc.), however, remains difficult or even impossible, since the positional fractionation in atmospheric ozone either is not accurately known (for ¹⁶O¹⁶O¹⁷O vs. ¹⁶O¹⁷O¹⁶O) or, when accurate measurements exist, published values obtained by different techniques seem to be in striking difference (for ¹⁶O¹⁶O¹⁸O vs. ¹⁶O¹⁸O¹⁶O).

Here we present mass spectrometric measurements of a temperature study of ozone forming rate coefficient ratios and oxygen fractionation values in ⁵⁰O₃, ⁵²O₃ and ⁵⁴O₃. The results are combined with the findings of earlier symmetry specific diode laser absorption spectroscopic (TDLAS) measurements in order to predict the temperature dependence of [¹⁶O¹⁶O¹⁸O]/[¹⁶O¹⁸O¹⁶O]. By numerical simulation of the isotope kinetics of ozone sample preparation in other symmetry resolving studies employing fourier transform far infrared (FTFIR) spectroscopy it is demonstrated that the seemingly differences in dependence of [¹⁶O¹⁶O¹⁸O]/[¹⁶O¹⁸O¹⁶O] between TDLAS experiments in the mid IR and the FT experiments in the far IR are not caused by experimental artefacts, but are rather due to the different temperature conditions in the two sets of experiments.

Therefore, the temperature dependence of end member enrichment of atmospheric ⁵⁰O₃ seems now to be well characterized for the first time and it can be used in quantitative modelling of isotope transfer from ozone into other atmospheric molecules.

B61D-04 0940h INVITED

Isotope transfer from O₃ to CO₂ in light of the ozone isotope anomaly

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An increasing amount of information is presently becoming available about the anomalous oxygen isotopic composition of atmospheric ozone. Due to its active role in atmospheric chemistry, the ozone isotope anomaly is transferred to a number of atmospheric constituents. The well established transfer to CO₂ via O(¹D) is responsible for the strong ¹⁷O and ¹⁸O enrichments of CO₂ in the stratosphere. However, in stratospheric CO₂ the ¹⁷O enrichment is considerably larger than the ¹⁸O enrichment, opposite to the situation for ozone, which implies a preferential transfer of ¹⁷O. New laboratory experiments are being carried out to study this transfer, which may involve an additional anomalous fractionation process. At the same time, detailed position resolved investigations of the ozone isotopic composition also provide new information about

the isotope transfer, which primarily involves the terminal oxygen atom. In light of these new data we evaluate various possible scenarios for the CO₂ - O₃ isotopic exchange.

B61D-05 0955h

Oxygen Isotope Anomalies in Carbon Dioxide: From the Laboratory to the Stratosphere

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A number of studies have suggested that the oxygen isotope anomaly in stratospheric CO₂ (defined as Δ¹⁷O = δ¹⁷O - 0.516 * δ¹⁸O) can be used as a tracer of integrated chemistry and transport in the stratosphere,¹ of stratosphere-troposphere exchange,² of gross carbon exchanges between the terrestrial biosphere and atmosphere,³ and, through the impact of anomalously fractionated CO₂ on the O₂ reservoir, of gross global primary productivity on millennial timescales through ice core measurements of O₂.⁴ Bringing these applications to fruition, however, requires a more fundamental understanding of the source and mechanism(s) of the anomalous fractionation in CO₂ than is currently available. Several new suites of laboratory and field measurements that address the source(s) of the oxygen isotope anomaly in CO₂ will be presented. Measurements of Δ¹⁷O of CO₂ from whole air samples collected from the NASA ER-2 aircraft and their correlation with trace gases measured in situ while the samples were being collected, such as N₂O and O₃, provide important new information as to the source and mechanism(s) of the anomalous enrichment in the stratosphere. Laboratory investigations of the reaction CO₂ + O(¹D) in a crossed molecular beam, of photochemical kinetics and isotope measurements in irradiated CO₂ / O₂ mixtures, and of isotope effects in the photolysis of CO₂ at different wavelengths are providing additional information. These new laboratory and field data will be discussed and compared with previous studies.

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How Large is the Mass Independent O-17 Anomaly in the Atmosphere?

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The isotopic composition of atmospheric oxygen is controlled by biological mechanisms, the hydrological cycle and stratospheric photochemistry. The biological mechanisms include photosynthetic oxygen production of identical isotopic composition as the substrate water and oxygen uptake by various mechanisms with mass dependent fractionation. Fractionation in the hydrological cycle is also mass dependent. In contrast, stratospheric photochemistry also removes oxygen, but fractionates the isotopic composition of the remaining gas in a mass-independent way. As a result atmospheric oxygen becomes anomalous (O-17 depleted) with respect to oxygen of the global atmosphere that would have been produced in the absence of stratospheric photochemistry. For estimating the magnitude of this anomaly, it is necessary to know the triple isotope fractionations of the relevant global processes. In the present research we carried out experiments in order to determine the ratio between the discriminations against O-17 and O-18 in dark respiration and in photorespiration. The obtained values are 0.518 and 0.506 respectively, and are different than in meteoric water fractionation (0.525). Assuming that the latter value applies to leaf-water (the substrate of all terrestrial photosynthesis), we estimate the magnitude of the anomaly as 258 permeg. This figure is significantly larger than 117 permeg estimated from stratospheric mass balance. Alternatively, by talking the 117 permeg value as representative of the anomaly, we calculate the ratio between the discriminations against O-17 and O-18 in leaf water as 0.511. Clearly, if we are to correctly estimate the atmospheric anomaly, careful determination of the triple isotope composition of global leaf-water is a prerequisite.