

Activities

Newsletter

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In this Issue

A Note from the Chair

Science Features

Applications of Stable
Isotopes in Atmospheric-
Biospheric Chemistry

- 3 The Methane Budget
- 7 Nitrous Oxide Loss Processes
- 11 Aerosol Sulfate Sources
- 13 Mass-Independent Isotope Variations
- 18 CO₂ Isotopes and the Carbon Cycle

Announcements

- 19 ACSOE Symposium
Molina Fellowship
- 20 Tropospheric Data Composites Web Site
6th IGAC Scientific Conference
- 22 1999 IGAC SSC, Activities, and Conveners

A Note From the IGAC Chair:

Guy Brasseur

What has the atmospheric-biospheric chemistry community learned in the last ten years ?

What are the remaining questions to address ?

IGAC was created approximately ten years ago and currently operates under the sponsorship of two parent organiza-

tions: the IAMAS Commission on Atmospheric Chemistry and Global Pollution (CACGP) and the International Geosphere-Biosphere Programme (IGBP) of ICSU. Little was known a decade ago about the role of the biosphere in global atmospheric chemistry, about the impact of human activities on the oxidizing capacity of the atmosphere, about the importance of aerosols and chemically active gases in the climate system, or about the role of multiphase chemistry in the troposphere. During the past decade, a large number of projects and major field campaigns have been developed and completed with support from national and international funding agencies. Much progress has also been made through laboratory studies, network observations, data analysis, and modeling. Yet today many questions remain on the agenda of the atmospheric-biospheric chemistry community.

When a group of scientists gathered in Dookie, Australia in 1988 to identify the most pressing questions for the international atmospheric-biospheric chemistry community to address, they greatly influenced the design of many national programs focusing on atmospheric chemistry and established a project—IGAC—that became an integral part of global change research. After ten years of uninterrupted work with many successes, and perhaps a few failures, time has come to address the following questions: What have we really learned over the last 10 years, and what are the remaining scientific questions? We must integrate our knowledge into a coherent framework of results that can be understood not only by experts, but also by decision-makers and the public.

IGAC is therefore initiating a major "integration and synthesis" effort that, hopefully, will engage a significant fraction of the atmospheric-biospheric chemistry community over the next 2 years or so. The purpose is to produce and publish a rather comprehensive report and other more specialized documents that will present and assess progress made not only through IGAC-sponsored research, but in the whole field. For this purpose, the contents of the report have been outlined by a group of about 25 scientists who met in Toulouse, France in November 1998. The chapters and the names of the lead authors for each are shown below. To the right is the proposed and very ambitious timetable for the preparation of the document. I want to emphasize that this integration and synthesis process is entirely open. Colleagues who would like to contribute are therefore strongly encouraged to contact the lead

authors or Ms. Harriet Barker (harriet@ucar.edu) who will coordinate production of the report. The final draft of the document will be discussed and reviewed at a meeting to be held in Aspen, Colorado, USA, in late April – early May, 2000. The final document will provide for the first time a truly international response to the questions raised at Dookie, and will benefit from several similar but somewhat limited efforts made at the national level.

In previous issues of the IGAC newsletter, we have attempted to present a somewhat integrated view on several issues related to the chemistry of the atmosphere and the influence of biospheric processes. The present issue focuses on stable isotopes and their importance for constraining global budgets of chemical elements in the Earth system. In this area also, much progress has been made over the last ten years.

The Changing Atmosphere

"Introduction" (authors tbd)

1. "Changes in the chemical composition of the atmosphere and potential impacts"
(L. Barrie, G. Brasseur, P. Crutzen, D. Jacob, H. Rodhe)
2. "Biosphere/atmosphere interactions"
(M. Andreae, J.-P. Lacaux, P. Matrai, M. Scholes)
3. "Tropospheric ozone and other photooxidants"
(E. Atlas, S. Lal, K. Law, S. Penkett)
4. "Aerosols"
(J. Heitzenberg, F. Raes, S. Schwartz)
5. "An integrated view on the causes and impacts of atmospheric changes"
(L. Barrie, G. Brasseur, P. Crutzen, D. Jacob, H. Rodhe)
6. "A strategic view of future research needs"
(to be written by CACGP members)

Technical Annexes

- a. "Tools: Instrumentation, platforms, and large campaigns"
(T. Anderson, J. Calvert, F. Eisele, U. Schmidt, D. Winker)
- b. "Modeling"
(C. Granier, M. Kanakidou, P. Kasibhatla)

Proposed Integration and Synthesis Timetable

- | | |
|-----------------|---|
| November 1998: | Discuss content of I&S document, adopt outline, and designate lead and contributing authors |
| December 1998: | Finalize list of contributing authors |
| January 1999: | Start working on chapters; several small workshops may be necessary |
| May 1999: | (IGBP Congress) Update IGAC-SSC, SC-IGBP, and wider IGBP community on progress made |
| October 1999: | Lead authors provide draft chapters |
| November 1999: | Meeting of lead authors to discuss content of the chapters; chapters sent to reviewers |
| January 2000: | Chapters modified in consideration of review comments |
| February 2000: | Revised chapters sent to participants of "Aspen Meeting" |
| April/May 2000: | "Aspen Meeting" |
| June 2000: | Chapters finalized and sent to publisher |

Science Features

Measurements and Modeling of Atmospheric Methane Using Stable Carbon Isotopes

Contributed by **Stanley C. Tyler** (*styler@uci.edu*), *University of California, Irvine, U.S.A*

Several elements of biological and geological importance occur naturally with two or more stable isotopes. For example, there are two stable isotopes of carbon with atomic mass numbers 12 and 13, and a radioactive isotope with atomic mass number 14. The relative amounts of any two isotopes of the same element vary because natural differences in isotope composition of biogeochemical compounds result from processes of formation and destruction which fractionate the isotopic pools representing substrate and product [Hoefs, 1987]. Because of isotopic fractionation, biogeochemical researchers can exploit measurements of isotope ratios in compounds found in various earth, ocean, and atmospheric systems to study a wide variety of processes. The measurements can also be used as tracers to study flux rates among compartments of the biotic and abiotic environment including cycling of carbon, nitrogen, sulfur and other elements in various forms including trace gas species.

The differences in carbon isotopic composition among various compounds are usually very small (often only on the order of a few parts per thousand or less) and must be measured both accurately and precisely to be useful in biogeochemical studies. Only about 1 in 10^{12} carbon atoms has mass 14. Because of this, the use of ^{14}C is usually restricted to radioactive counting techniques which provide gross information about biogeochemical cycling (in addition to its main purpose of age dating material containing carbon). Conversely, because about 1 in 89 carbon atoms has mass 13, differences in the stable isotope ratio of $^{13}\text{C}/^{12}\text{C}$ among various compounds can be measured quite precisely, allowing detection of very small differences. The measurement results are nearly always expressed in δ notation, using the following equation where $^{13}\text{C}/^{12}\text{C}_{\text{sample}}$ is the carbon isotope ratio in a sample and $^{13}\text{C}/^{12}\text{C}_{\text{standard}}$ is the carbon isotope ratio of Pee Dee Belemnite carbon, a conventional standard:

$$\delta^{13}\text{C} = \left[\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} - 1 \right] \times 1000$$

Isotopic information provides a major constraint on estimates of the global methane (CH_4) budget and its sources and sink processes. The latter include CH_4 loss

from reaction with OH, Cl and O(^1D), as well as consumption by soil bacteria. Ehhalt [1974] first determined a budget relating sources and sinks of CH_4 to its atmospheric burden. In doing so, he divided sources into fossil fuel (radiocarbon dead) and biogenic (radiocarbon modern) categories and estimated that dead CH_4 sources accounted for roughly 10–20% of all atmospheric CH_4 . Subsequent studies of $^{14}\text{CH}_4$ by Wahlen *et al.* [1989a], Manning *et al.* [1990], and Quay *et al.* [1991] have resulted in similar fossil fuel estimates.

Stevens and Rust [1982] proposed that a mass-weighted stable carbon isotopic balance between CH_4 sources and sink processes and the $\delta^{13}\text{C}-\text{CH}_4$ value in the atmosphere would help constrain the CH_4 budget. They illustrated their contention using atmospheric data from rural Illinois and information on CH_4 sources and sinks available at the time. They used a flux-weighted average value for the $\delta^{13}\text{C}$ of CH_4 entering the atmosphere and allowed for a slight ^{13}C enrichment in the resulting atmospheric CH_4 isotopic value from its partial chemical loss by reaction with OH, the principal CH_4 sink. (CH_4 remaining in the atmosphere is slightly enriched in ^{13}C because of the OH preference for reacting with $^{12}\text{CH}_4$ over $^{13}\text{CH}_4$. This phenomenon is known as a "kinetic isotope effect," or KIE for short.) Resulting calculations by Stevens and Rust helped apportion CH_4 sources according to whether they were relatively ^{13}C -heavy or ^{13}C -light with respect to atmospheric CH_4 . Since that beginning, additional measurements of atmospheric $\delta^{13}\text{C}-\text{CH}_4$ have further constrained the CH_4 budget, provided information on seasonal cycles in CH_4 sources and sink processes, and helped elucidate recent trends in CH_4 mixing ratio [e.g., Wahlen *et al.*, 1989a; Quay *et al.*, 1991; Lowe *et al.*, 1991, 1994, and 1997; Thom *et al.*, 1993; and Tyler *et al.*, 1993 and 1999].

One effective measurement protocol is to conduct multi-year regularly scheduled CH_4 isotope monitoring at fixed surface sites representing well-mixed background air to compare to other widely spaced sites [i.e., Quay *et al.*, 1991; Lowe *et al.*, 1991, 1997; and Tyler *et al.*, 1993, 1999]. From observations, nearly all surface sites monitored have an appreciable but variable seasonal cycle in $\delta^{13}\text{C}-\text{CH}_4$ with less negative values (^{13}C -enriched) in summer and more negative values (^{13}C -depleted) in winter. The cycle appears to be source driven, particularly in the northern hemisphere, although some of the seasonality can be explained by a seasonal increase in OH in warmer months which enriches the CH_4 isotope ratio.

Isotopic measurements of atmospheric CH_4 can be used along with model calculations to provide explanations for observed CH_4 behavior. For example, using a rela-

tively simple one-dimensional (1D) box model with coarse resolution, the $\delta^{13}\text{C}-\text{CH}_4$ seasonal cycle in the Southern Hemisphere, represented by data taken at Baring Head, New Zealand (41°S), can be explained partly by the KIE of CH_4 reaction with OH , but the amplitude is large enough to indicate that the cycle is partially source driven, possibly by biomass burning during the austral spring [Lassey *et al.*, 1993; Lowe *et al.*, 1997]. Similarly, the global mean $\delta^{13}\text{C}-\text{CH}_4$ value of $\sim -47\text{‰}$ as determined from stations regularly monitored in the Northern Hemisphere and from less frequent measurements in the Southern Hemisphere, when coupled with $^{14}\text{CH}_4$ measurements, implies that about 11% of the total CH_4 release rate is derived from biomass burning [Quay *et al.*, 1991].

I can illustrate further how measurements and modeling of isotopic CH_4 are used to answer questions about atmospheric CH_4 and its sources and sinks processes from some of the research being done at UC Irvine. In so doing, I will also address areas where more questions have arisen, how these are being resolved, and show how the results of many researchers globally, all working toward a common understanding of the CH_4 budget, must be used to succeed.

At UC Irvine we have established time series of CH_4 measurements at Niwot Ridge, Colorado (1989–present) and Montaña de Oro, California (1995–present). The mea-

surements at both locations include CH_4 concentration and $\delta^{13}\text{C}$ (approximately bi-weekly) and ^{14}C (less frequently). Our overall precision of measurement on CH_4 mixing ratio and $\delta^{13}\text{C}$ from air samples is ± 5 ppb and $\pm 0.05\text{‰}$, respectively. In Tyler *et al.* [1993] we reported on measurements of $\delta^{13}\text{C}-\text{CH}_4$ at Niwot Ridge (40°N) for the period 1989 to 1992 (Figure 1). Those data showed a distinct difference between winter and summer values, with the $\delta^{13}\text{C}$ of CH_4 being approximately 0.5‰ lighter in winter than in summer (a curve fit of the form $y = a + b \cdot t + c \cdot \sin(\omega \cdot t) + d \cdot \cos(\omega \cdot t)$ had an $r^2 = 0.63$ with seasonal amplitude 0.3‰ for the 4 year period) and also showed a trend in $\delta^{13}\text{C}-\text{CH}_4$ of $-0.10\text{‰}/\text{year}$ over the four years.

We also maintain intercalibration programs of isotopic measurements of CH_4 samples with the National Institute of Water and Atmospheric Research, New Zealand (NIWA) and of CH_4 mixing ratios in air with the National Oceanic and Atmospheric Administration, Boulder, Colorado (NOAA). Through a sample exchange program with NIWA, a subset of the air samples collected at Montaña de Oro and Baring Head is measured by both laboratories while still in its original canisters. The obvious advantage to intercalibrating between the two isotope data sets is that each research group can incorporate the others' published data for other sites and dates into its own global calculations. Measurements reported by Lowe

et al. [1991, 1994, and 1997] have consistently shown a seasonality in CH_4 mixing ratio and $\delta^{13}\text{C}$ of CH_4 from Baring Head for the period 1988–1996. The seasonal amplitude variation in $\delta^{13}\text{C}$ of CH_4 has a range of 0.6‰ peak to peak while the period from mid-1991 to end of 1992 saw $\delta^{13}\text{C}$ drop by $\sim 0.2\text{‰}$.

We have used a 2D tropospheric photochemical model developed at UC Irvine to make model calculations of atmospheric CH_4 and its sources and sinks. The model has been described in detail in Gupta [1996] and Gupta *et al.* [1998]. In brief, it has a horizontal resolution of 10° and extends from the surface to 24.5 km with a vertical resolution of 0.5 km. Transport coefficients (advective and diffusive) are derived from the Geophysical Fluid Dynamics Laboratory general circulation model [Plumb and Mahlman, 1987]. A reasonably complete gas phase photochemical scheme containing only CH_4 as a parent hy-

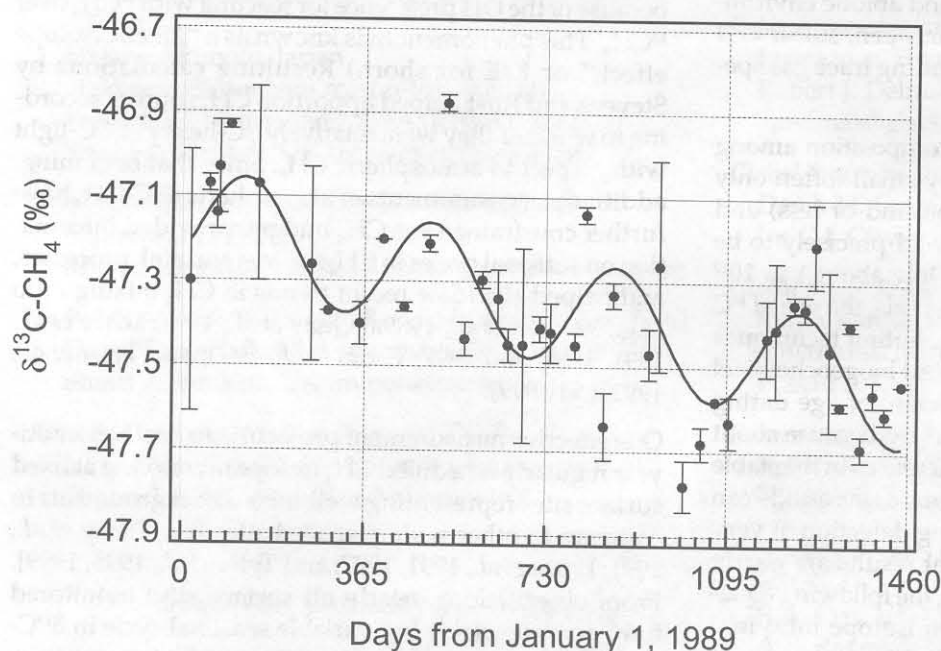


Figure 1. $^{13}\text{C}/^{12}\text{C}$ ratio in atmospheric CH_4 at Niwot Ridge, Colorado from January, 1, 1989 to December 31, 1992, measured by isotope ratio mass spectrometry and expressed relative to PDB carbonate in per mil (‰). Curve fit to data is unweighted least squares fit (1 harmonic) of form $y = -47.26 - 2.760\text{E}-4 \times T + 0.0219 \sin(\omega T) - 0.1269 \cos(\omega T)$ with T in days relative to January 1, 1989 and $\omega = 2\pi/365$. Slope is equal to $-0.10\text{‰}/\text{year}$ over the four years. Error bars are one standard deviation from the average of multiple samples. [Adapted from Tyler *et al.*, 1993]

Source	Emission Strength in Tg/yr	$\delta^{13}\text{C}$, ‰
Lake	64	-59*
Swamps	85	-56*
Tundra	5	-55*
Rice paddies	90	-59
Animals	85	-62
Landfills	42	-50
Gas venting and leakage	53	-38
Oceans	5	-40
Coal minings	27	-37
Biomass burning	42	-26
Termites	32	-57

The average $\delta^{13}\text{C}$ of these sources is -52.16‰.

* Between 70°N and 90°N, $\delta^{13}\text{C}$ values were decreased to -65‰.

Table 1. Estimated annual global emission strengths and corresponding $\delta^{13}\text{C}$ values for various categories of CH_4 used in model calculations.

drocarbon with parameterized tropospheric heterogeneous losses is included. All species including CH_4 and its isotopic species are calculated with the time dependent photochemical scheme up to 16.5 km. Above 16.5 km, hydroxyl and chlorine radical concentrations are prescribed on a monthly basis and their values are adopted from the Oslo 2D tropospheric-stratospheric global model.

In Gupta *et al.* [1996] we used annual surface sources of CH_4 based on published research by ourselves and others to initiate the model. Methane source magnitudes and distributions were slightly modified from those appearing in Fung *et al.* [1991]. The assigned average $\delta^{13}\text{C}-\text{CH}_4$ for individual sources was adapted from source budgets appearing in Cicerone and Oremland [1988] and newer information from additional CH_4 source studies. The adopted source magnitudes and assigned $\delta^{13}\text{C}-\text{CH}_4$ values data appear in Table 1.

We examined the dependence of the distribution of atmospheric $\delta^{13}\text{C}-\text{CH}_4$ on the KIEs associated with various CH_4 sinks (i.e., OH, Cl, O(¹D), and soil bacteria). We also investigated the changes in both mixing ratio and $\delta^{13}\text{C}$ of CH_4 observed between the years 1989 to 1993 by considering changes in the strengths of these sinks and the relative likelihood of postulated changes in CH_4 sources. In doing so, we used the general features of observed $\delta^{13}\text{C}-\text{CH}_4$ data as reported by Tyler *et al.* [1993] for Niwot Ridge and Lowe *et al.* [1994] for Baring Head and the then-recent data from the NOAA/CMDL network of measurement stations reported in Dlugokencky *et al.* [1994] which indicated that CH_4 growth rate, easily discernible between about 1978 and 1990 (e.g., Rasmussen and Khalil [1981]; Steele *et al.* [1987 and 1992]; Blake and Rowland [1988]), had nearly leveled off (almost no net change was observed between 1991 and 1992).

To assess the effects of KIEs in the CH_4 loss processes, we successively added KIEs to the reference loss function (simulation A1) which included only the KIE of the reaction of CH_4 with OH. Additional simulations were named A2 (soil sink KIE included) and A3 (soil and Cl sink included). In the simulation, the generally accepted values for all CH_4 loss KIEs were used. They were as follows: $k_{12}/k_{13} = 1.0054$ for the OH sink with no temperature dependence over the range of atmospheric temperatures simulated [Cantrell *et al.*, 1990], $k_{12}/k_{13} = 1.022$ for the soil sink again with no temperature dependence [Tyler *et al.*, 1994], and $k_{12}/k_{13} = 1.043 \cdot \exp(6.455/T)$ for the Cl sink, where T is in Kelvin [Saueressig *et al.*, 1995].

Figure 2a shows the calculated steady state latitudinal distributions of $\delta^{13}\text{C}-\text{CH}_4$ at the surface. The calculations show that the inclusion of KIEs of CH_4 sinks other than OH has a significant effect on modeled distributions of $\delta^{13}\text{C}$ of atmospheric CH_4 . In the simulation shown, the estimated source function from Table 1 was purposely chosen to match model-calculated and observed CH_4 mixing and carbon isotope ratios at 40°N and 40°S for case A3. Another similar source function could have been chosen to match observations to model output using case A1 or A2, the point being that any reasonable source function will result in differences of approximately 2‰ for surface $\delta^{13}\text{C}-\text{CH}_4$ values as the KIEs above are added successively as in Figure 2a. From this it is clear that determining values for KIEs of all CH_4 reactions can be as important as determining an accurate CH_4 source function. The magnitude of the carbon KIE as well as the strength of the overall chemical sink both must be considered when evaluating $\delta^{13}\text{C}$ of CH_4 .

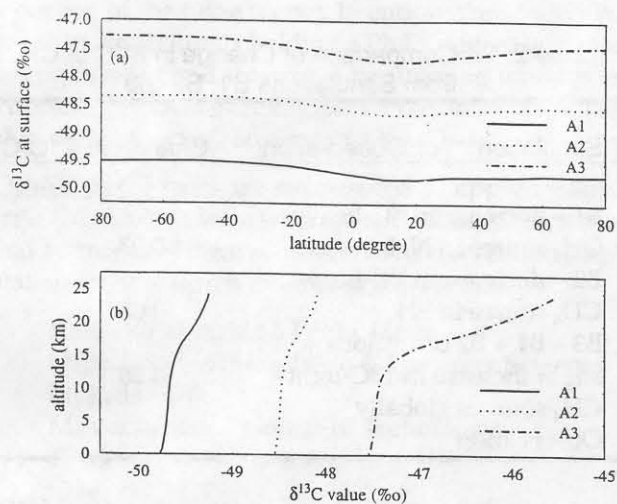


Figure 2. Calculated steady state (a) surface latitudinal distributions and (b) vertical profiles of $\delta^{13}\text{C}-\text{CH}_4$ values at 50°N for January for the three cases A1, A2, and A3. See text for more details. [Adapted from Gupta *et al.*, 1996]

Figure 2b shows the steady state calculated vertical profiles of $\delta^{13}\text{C}-\text{CH}_4$ at 50°N for the month of January for three cases A1, A2, and A3. Inclusion of a KIE due to Cl enriched $\delta^{13}\text{C}$ at 18 km by 0.95‰ compared to the corresponding surface value, whereas the enrichment was only 0.31‰ when this KIE was omitted. Because CH_4 reaction with Cl is the sink with the largest carbon KIE, it has a significant effect on atmospheric $\delta^{13}\text{C}-\text{CH}_4$ vertically in spite of its much smaller effect on total atmospheric CH_4 oxidation. Even so, comparisons between model-calculated and observed differences between surface and upper air sample $\delta^{13}\text{C}$ values were discrepant. The difference in $\delta^{13}\text{C}-\text{CH}_4$ between stratospheric and surface level air observed by Brenninkmeijer *et al.* [1995], Wahlen *et al.* [1989b], and our own measurements from the NASA AASE-II program was larger than could be accounted for by Gupta *et al.* [1996] in model calculations using the sink magnitudes and KIE values described.

The 2D model in Gupta *et al.* [1996] has also been used to help explain the abrupt changes in CH_4 mixing ratio growth rate in the period from 1989 to 1993. The use of CH_4 isotopic data provides an important check on any explanation because any postulated change in CH_4 sources must simultaneously account for changing trends in $\delta^{13}\text{C}-\text{CH}_4$ as well as in CH_4 mixing ratio. Once again, features of the observed $\delta^{13}\text{C}-\text{CH}_4$ data as reported for Niwot Ridge [Tyler *et al.*, 1993] and for Baring Head [Lowe *et al.*, 1994] over the time period in question were compared to model simulations to explain the causes of atmospheric CH_4 changes.

As shown in Table 2, CH_4 growth rate reported in both the Northern and Southern Hemispheres for 1992 was accompanied by reported decreases in $\delta^{13}\text{C}-\text{CH}_4$ in each hemisphere. Model simulations B1, B2, and B3 were de-

signed to compare various explanations for the decrease in CH_4 growth rate. One can see that no single explanation (including decreased loss of CH_4 from former USSR pipelines and gas fields proposed by Dlugokencky *et al.* [1994] and changes in seasonal biomass burning patterns in the Southern Hemisphere proposed by Lowe *et al.* [1994]), but rather a combination of changes in both light and heavy sources of CH_4 , coupled with recent changes in OH concentration brought about by ozone depletion and the eruption of Mt. Pinatubo, were needed to explain changes in the observed CH_4 mixing ratio observed in that time period.

Although isotopic information has provided major constraints on the global CH_4 budget and its sources and sink processes, there are several areas where more investigations are needed. For one thing, we need to arrive at consensus values for the KIEs of the CH_4 sinks. For example, currently there are two determinations for the carbon KIE in the reaction between CH_4 and $\text{O}(^1\text{D})$. Davidson *et al.* [1987] reported that the carbon KIE of $\text{O}(^1\text{D})$ is very small (i.e., ~ 1.001 at 297 K) on the basis of one measurement made during the course of investigating the $\text{CH}_4 + \text{OH}$ reaction. More recently, Saueressig *et al.* [1998] reported it as 1.0115 ± 0.0006 (2σ) at 295 K.

More KIE studies may be one key to resolving the discrepancy between observed and calculated $\delta^{13}\text{C}-\text{CH}_4$ values in the upper atmosphere. This discrepancy is currently very large at 11-13 km and gets worse with increasing altitude (i.e., 2D model generated $\delta^{13}\text{C}-\text{CH}_4$ values from Bergamaschi *et al.* [1996] are not in agreement with measured values from Sugawara *et al.* [1997] for upper stratospheric samples). It would also help to have more upper air samples measured for CH_4 mixing and isotope ratio. To that end we recently began a collaboration with

Table 2. Comparison of Change in $\delta^{13}\text{C}$ of CH_4 and Its Growth Rate Derived from Simulations B1, B2, B3

Simulation*** or Observation	Change in $\delta^{13}\text{C}-\text{CH}_4$ (‰/yr)*		Change in CH_4 Growth Rate (ppb / year)**	
	40°N	40°S	40°N	40°S
B1 – decrease in ^{13}C -heavy CH_4 source in NH	-0.07	-0.02	-8	-1
B2 – decrease in ^{13}C -heavy CH_4 source in SH	-0.08	-0.12	-1	-4
B3 – B1 + B2 conditions + slight increase in ^{13}C -light CH_4 sources globally	-0.20	-0.19	-8	-3
Observation	-0.20	~ -0.20	-9.8	-3.4

* -- changes calculated by the end of Dec., 1993 relative to Dec., 1991, model simulations from Gupta *et al.* [1996], observations from Tyler *et al.* [1993] and Lowe *et al.* [1994]

** -- changes calculated by the end of Dec., 1992 relative to Dec., 1991, model simulations from Gupta *et al.* [1996], observations from Dlugokencky *et al.* [1994]

*** -- all simulations include changes in OH concentration brought about by ozone depletion and the eruption of Mt. Pinatubo

Profs. D.R. Blake and F.S. Rowland at UC Irvine to measure CH₄ mixing ratio and δ¹³C in air samples collected by aircraft. Thus far we have participated in the NASA missions GTE PEM-Tropics A (samples for isotopic analysis were taken from 2° to 27°S latitude at sea level to 11.3 km) and SONEX (over the Atlantic Ocean between 38° and 66°N at altitudes of 3 to 12 km).

Finally, a source function with seasonally-resolved magnitudes of both source strength and isotope ratio is not presently available. Therefore, although it is possible to provide a match within a few 0.10‰ between observed and calculated δ¹³C-CH₄ values at the few surface locations reported on globally, one obtains only a relatively poor match between measured seasonal differences in δ¹³C-CH₄ at either of two sites representing mid Northern and Southern Hemispheric surface CH₄ and model-calculated intra-annual differences [e.g. Gupta *et al.*, 1996; Tyler *et al.*, 1999]. A source function which includes seasonal changes in the δ¹³C of emitted CH₄ requires additional measurements designed to study processes controlling the isotopic signature of CH₄ sources [Reeburgh, 1996]. Better global coverage of the surface in the form of routine measurements at many more sites, all of which have been intercalibrated against each other, would also allow for better resolution of the source function. Fixed surface sites and shipboard sampling transects such as those reported on by Lowe *et al.* [1999] would both contribute toward this coverage.

This article has offered several examples of how stable carbon isotopic measurements help determine the behavior of CH₄, a key greenhouse gas. Continued studies of atmospheric CH₄ and its sources and sinks using stable isotope measurements are in order. More atmospheric measurement data (better global coverage at the surface and many more above-surface observations), improved CH₄ source functions for the models (based on additional source/sink studies), and agreed upon KIEs of CH₄ loss processes will all contribute to further understanding of the CH₄ budget. Ultimately, this is of critical importance because most researchers believe that human-induced changes in CH₄ sources brought about by increasing population will increase global CH₄ emissions unless mitigation strategies are attempted for some of the anthropogenically controlled sources (Intergovernmental Panel on Climate Change, 1996). Deciding which strategies and policies to mitigate CH₄ emission are feasible, which are working, and what the societal impacts are will depend on measurements and models such as those described here which help to understand the CH₄ atmospheric budget, its changes over time, and its link to natural and managed ecosystems.

Editor's Note: Reference lists have been omitted from all articles due to space limitations. They are available on the IGAC web site (<http://web.mit.edu/igac/www/>) or in hardcopy upon request from the IGAC Core Project Office (igac@mit.edu).

Isotopic discrimination during nitrous oxide loss processes: An important piece of the N₂O global atmospheric budget

Contributed by Thom Rahn <trahn@ucsd.edu> and Martin Wahlen (mwahlen@ucsd.edu), Scripps Institute of Oceanography, University of California, San Diego, USA

Introduction

There are five species of interest when analyzing N₂O isotopes: the abundant isotopomer ¹⁴N¹⁴N¹⁶O and the rare isotopomers ¹⁴N¹⁵N¹⁶O, ¹⁵N¹⁴N¹⁶O, ¹⁴N¹⁴N¹⁷O and ¹⁴N¹⁴N¹⁸O. The two ¹⁵N species are indistinguishable with current mass spectrometric techniques. The two rare oxygen species have in the past been assumed to be mass-dependently related although it has recently been shown that there is a slight mass-independent enrichment of ¹⁷O in tropospheric samples [Cliff and Thiemens, 1997] which is as yet unaccounted for. Isotopic values are typically reported as ratios of the heavy-to-light species relative to those in a standard such that $\delta = [(R_{\text{sample}}/R_{\text{std}}) - 1] \times 1000$ (expressed in units per mil).

Because the isotopomers of interest are isobaric with those of CO₂ (masses 44, 45, and 46) and since CO₂ in natural environments is generally ~1000 times more abundant, traditional methods of isotopic analysis employed techniques involving selective decomposition of N₂O and subsequent analysis of products. For this reason, the isotopic standards for N₂O have been atmospheric N₂ for ¹⁵N and either atmospheric O₂ or Standard Mean Ocean Water for the oxygen isotopes. (Atmospheric O₂ has become the de facto standard for the oxygen isotopes.) In the case of current analytical techniques (with the exception of ¹⁷O analyses), N₂O is now routinely separated from CO₂ and fed directly into a mass spectrometer. It is then referenced to a nitrous oxide gas standard with known isotopic values relative to N₂ and O₂.

Nitrous oxide is a trace gas that is produced during microbial energy exchange reactions involving both reduced (NH₃) and oxidized (NO₃⁻) forms of nitrogen. A portion of the N₂O that is produced escapes to the troposphere where it is chemically inert. The commonly accepted model holds that nitrous oxide ascends to the stratosphere where it is photolyzed by ultraviolet radiation (90% of the total loss); oxidized by excited atomic oxygen (10% of loss); or returned to the troposphere during stratosphere/troposphere exchange processes. The bulk of the N₂O photolysis, as demonstrated in Figure 1, occurs on the shoulder of the cross section spectrum, between the Schumann-Runge bands and Herzberg continuum of O₂ absorption, rather than at the peak. While in the atmosphere, N₂O actively absorbs infrared radiation and thereby contributes to greenhouse warming. A portion of the N₂O destroyed by the reac-

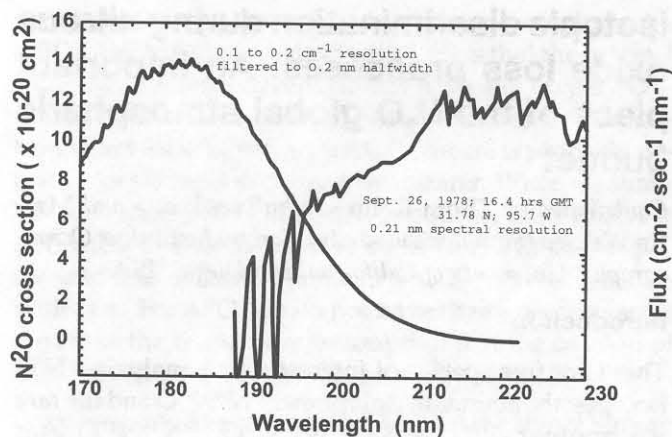


Figure 1. High resolution N_2O cross section from Yoshino *et al.* [1984] and the actinic flux as measured at 40 km by Herman and Mentall [1982] (0.21 nm resolution).

tion with $O(^1D)$ provides the principle natural source of NO , which initiates the catalytic NO_x cycling of stratospheric ozone. The current tropospheric concentration, which is increasing at a rate of $\sim 0.25\%$ per year, is about 313 ppbv and the estimated atmospheric lifetime is approximately 120 years. Because of its influence on the Earth's radiative budget and its increasing concentration, nitrous oxide has been selected as one of the six gases slated for regulation by the Kyoto Protocol of 1997.

Despite the importance of nitrous oxide and its incorporation in the Kyoto Protocol, its global budget is poorly characterized. Estimates of the natural sources of N_2O range from 1 to 5 Tg N/yr for oceanic sources and 3.3 to 9.7 Tg N/yr from tropical and temperate soils [IPCC, 1995]. The atmospheric increase is considered to arise primarily from application of fertilizers to cultivated soils but animal waste, biomass burning, fuel combustion, and industrial processes also contribute. The estimated range of the sum of the anthropogenic sources is 3.7 to 7.7 Tg N/yr [IPCC, 1995]. In an effort to reduce the error in these estimates, investigations of the stable isotopic signatures of the various sources and sinks have been carried out by several research groups [see Moore, 1974; Yoshida and Matsuo, 1983; Wahlen and Yoshinari, 1985; Yoshinari and Wahlen, 1985; Kim and Craig, 1990; Kim and Craig, 1993; Yoshinari *et al.*, 1997; Naqvi *et al.*, 1998; Dore *et al.*, 1998].

Isotopic considerations

The stable isotopic composition of atmospheric trace gases provides information about their origin and fate that cannot be determined from concentration measurements alone. Biological source and loss processes, such as bacterial production of CH_4 or photosynthetic consumption of CO_2 , are typically accompanied by isotopic selectivity associated with the kinetics of bond formation and destruction. Thermodynamic considerations also predict isotopic differentiation between phases and/or

reactants under equilibrium conditions. Of the three important biologically mediated greenhouse gases, our understanding of the isotopic budget of nitrous oxide lags far behind that of carbon dioxide and methane. This is due in part to problems inherent in collection and analytical techniques which hamper our ability to make measurements of very high precision. It is also due to the fact that a limited data base and a wide range of observed isotopic values for each of the major natural sources has made it difficult to assign unique values to each of the source terms.

The isotopic signature of tropospheric N_2O is commonly reported as $\delta^{15}N = 7.0\%$ and $\delta^{18}O = 20.7\%$ [Kim and Craig, 1990] although inter-laboratory averages vary by 3 and 4% for $\delta^{15}N$ and $\delta^{18}O$, respectively [see Moore, 1974; Yoshida and Matsuo, 1983; Yoshida *et al.*, 1984; Wahlen and Yoshinari, 1985; Kim and Craig, 1990; Cliff and Thiemens, 1997; Rahn and Wahlen, 1997]. The measured isotopic signature of N_2O emitted from terrestrial environments is nearly everywhere depleted relative to the tropospheric average. The averages of known measurements from terrestrial sources, including fertilized lands, are $-14.6 \pm 11.9\%$ for $\delta^{15}N$; and $8.2 \pm 7.1\%$ for $\delta^{18}O$ [Kim and Craig, 1993; Casciotti, 1997; T. Pérez, pers. comm]. Oceanic surface waters are observed to be typically depleted in both ^{15}N and ^{18}O [Yoshida *et al.*, 1984; Kim and Craig, 1990; Dore *et al.*, 1998] although it is proposed that in certain upwelling areas there may be isotopically enriched deep waters introduced to the surface [Yoshinari *et al.*, 1997]. The observation that the source terms are depleted relative to the tropospheric reservoir led Kim and Craig [1993] to propose that the enrichments which they observed in the stratosphere might provide the necessary balance. A conundrum resulted when it was shown by Johnston *et al.* [1995] that the fractionations associated with the major N_2O loss terms, photolysis and photooxidation, were not great enough to account for the observed stratospheric values. Rahn and Wahlen [1997] subsequently verified that stratospheric N_2O is indeed enriched in the heavy stable isotopes of both N and O (see Figure 2). These stratospheric results have led to speculation that the anomalous enrichment might provide evidence of novel excited state photochemical sources of nitrous oxide [McElroy and Jones, 1996; Prasad, 1997; Prasad *et al.*, 1997; Zipf and Prasad, 1998]. In particular, Zipf and Prasad [1998] suggest that highly vibrationally excited O_3 could react with N_2 to form N_2O and O_2 and that this reaction could account for as much as 8% of the global source of nitrous oxide. Such photochemical sources would significantly alter our understanding of the geochemical cycle of N_2O . The results of Rahn and Wahlen [1997], however, are in good agreement with a Rayleigh distillation loss model indicating that no significant source products are interfering with the isotopic signature of the destruction mechanism. Source processes, should they

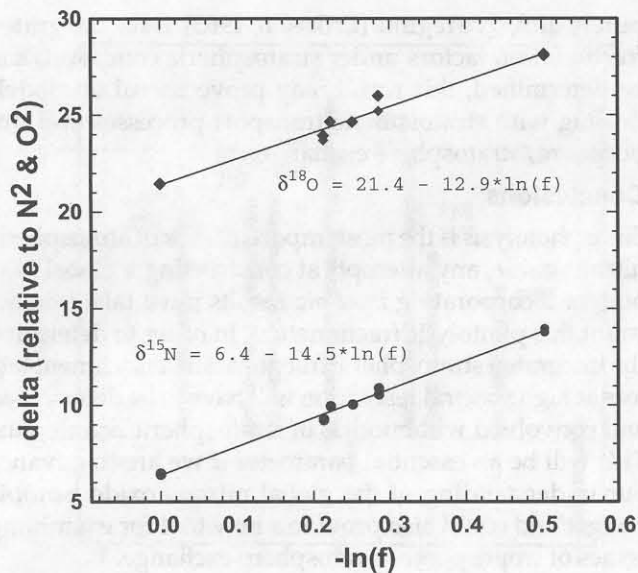


Figure 2. Lower stratosphere (between 14 and 19 km) isotopic enrichments of ^{15}N and ^{18}O . The results compare favorably with a Rayleigh distillation model where $R = R_0 f^{(a-1)}$: with R and R_0 equal to the residual and initial heavy-to-light isotope ratios; f , the fraction of tropospheric N_2O remaining; and a , the ratio of heavy-to-light destruction rates. Note that the regressions pass through tropospheric values at $\ln(f) = 0$. A single sample from 22.4 km (not shown) shows reasonable agreement for ^{18}O and an increased enrichment for ^{15}N indicating the possibility of competing processes at higher altitudes. The figure is based on Figure 1 of Rahn and Wahlen [1999].

exist, would therefore have to be able to mimic the Rayleigh distillation model, or be associated with negligible fractionation, or represent a very minor portion of the global budget.

Photolytic fractionation

An alternative explanation for the isotopic enrichment of stratospheric N_2O has been provided by Yung and Miller [1997]. They have proposed a wavelength-dependent mechanism for the photolytic fractionation of N_2O based on subtle shifts in the zero point energy with isotopic substitution. The wavelength dependence allows for the minimal fractionation observed by Johnston *et al.* [1995] near the peak of the absorption cross section at 184.9 nm yet predicts increasing fractionation at longer wavelengths where the bulk of the stratospheric N_2O photolysis takes place. This principle is demonstrated graphically in Figure 3 using the absorption cross section spectral function recommended by Selwyn *et al.* [1977]. The curve representing the ^{18}O substituted species (dashed curve) is slightly blue shifted, by -27.5 cm^{-1}

[Yung and Miller, 1997], relative to the normal curve (both calculated at 300 K). Cross sections are nearly equal in the region of the curve crossing at the absorption peak but a clear separation is observed on both shoulders. The inset plot of Figure 3 details the highlighted section on the higher wavelength shoulder. Pointed out are the cross sections at 185 nm for the normal curve ($14.00 \times 10^{-20} \text{ cm}^2$) and the blue shifted N_2^{18}O curve ($13.96 \times 10^{-20} \text{ cm}^2$). Analogous to determining the kinetic fractionation for a chemical reaction, the photolytic fractionation factor will be equal to the ratio of the heavy to light cross sections or $\alpha = 0.9971$. When expressed as an enrichment factor, where $\epsilon = 1000(\alpha - 1)$, $\epsilon_{185} = -2.9\text{‰}$. The theoretical enrichment factors can be calculated and plotted as a function of wavelength. As can be seen in Figure 4, the wavelength dependent enrichment factor, ϵ_λ , is initially posi-

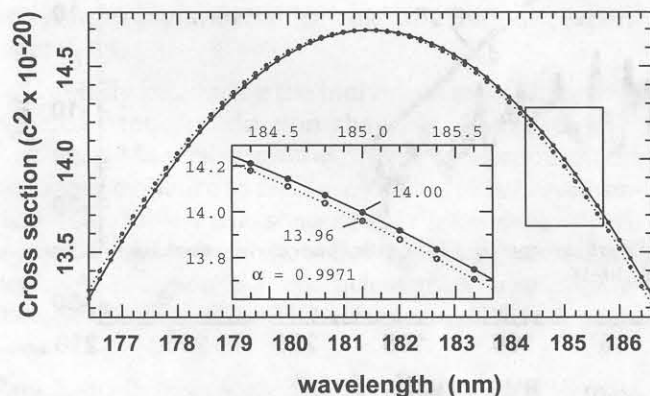


Figure 3. Representation of the theoretical shift in cross section with ^{18}O substitution according to Yung and Miller [1997]. The inset plot is a detail of the highlighted section between 184 and 187 nm.

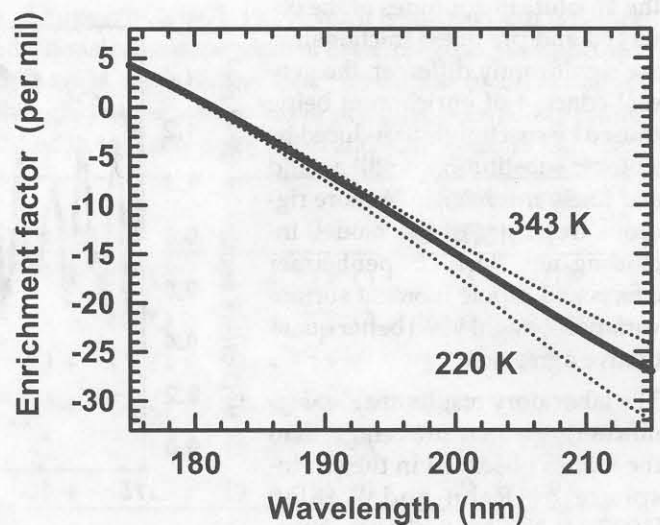


Figure 4. Theoretical wavelength dependence of the photolytic fractionation of N_2^{18}O as predicted according to Yung and Miller [1997]. Solid curve calculated at 300 K, dashed curves calculated at temperatures indicated.

tive at shorter wavelengths, passes through zero at the cross section maximum, and gets progressively more negative with increasing wavelength.

Similar constructs can be developed for each of the remaining isotopic species, all of which exhibit similar behavior with varying magnitude. However, the asymmetry of nitrous oxide leads to complications in the ^{15}N analyses because the two isotopomers, $^{14}\text{N}^{15}\text{NO}$ and $^{15}\text{N}^{14}\text{NO}$, have different predicted blue shifts. Yung and Miller [1997] account for this complexity by averaging the predicted enrichment of the two ^{15}N species. If the averaged ^{15}N value and the ^{18}O value are taken as a ratio $\epsilon_{^{15}\text{N}}/\epsilon_{^{18}\text{O}}$, a fairly uniform value between 1.1 and 1.2 is calculated over all wavelengths. This is in good agreement with the ratio observed in the stratosphere by Rahn and Wahlen [1997] where

$$\frac{\epsilon_{^{15}\text{N}}}{\epsilon_{^{18}\text{O}}} = \frac{-14.5}{-12.9} = 1.12$$

In reality, the situation is complicated even further by vibrational structure in the absorption continuum. If we apply the same treatment as described above to the cross section curves of Selwyn and Johnston [1981], we see that there are multiple curve crossings causing ϵ_λ to change sign several times over the cross section spectrum (Figure 5). Included in Figure 5 are the results of Rahn *et al.* [1998] for laser induced photolysis at two discrete wavelengths. The results compare favorably with the predicted ϵ_λ value at 193 nm but the data of Selwyn and Johnston [1981] do not extend to wavelengths greater than 197 nm making a comparison of the 207 nm data impossible.

The results shown in Figure 5 are approximately double that predicted by the theory of Yung and Miller [1997]. While the absolute magnitudes of the observed and predicted fractionation are significantly different, the general concept of enrichment being caused by spectral shifts induced by isotopic substitution is still a valid and likely mechanism. A more rigorous treatment of the model, including non-Born-Oppenheimer effects and dipole moment surface variations, might yield better quantitative agreement.

The laboratory results are also significantly greater, on average, than the values observed in the stratosphere by Rahn and Wahlen [1997]. It has been shown, however, that the standard Rayleigh fractionation model scales with $(\alpha^{1/2} - 1)$ rather than $(\alpha - 1)$ in a

purely diffusive regime [Eriksson, 1965]. If the integrated fractionation factors under stratospheric conditions can be determined, this result may prove useful in models dealing with stratospheric transport processes and troposphere/stratosphere exchange.

Conclusions

Since photolysis is the most important sink of atmospheric nitrous oxide, any attempts at constructing a global N_2O budget incorporating isotopic results must take into account this photolytic fractionation. In order to determine the integrated stratospheric fractionation, enrichment factors at high spectral resolution will have to be determined and convolved with models of stratospheric actinic flux. This will be an essential parameter if we are to advance our understanding of the global nitrous oxide isotopic budget and could also provide a new tool for examining issues of troposphere/stratosphere exchange.

Fractionation associated with the minor sink, reaction with excited atomic oxygen, must also be taken into account. The fractionation due to this reaction has been determined for the oxygen species, ^{17}O and ^{18}O , and has been shown to be mass dependent with $\epsilon_{^{18}\text{O}} = -6 \pm 1\%$ [Johnston *et al.*, 1995]. The fractionation due to photooxidation for the N species has yet to be determined. Finally, we note that the asymmetry of N_2O presents a unique opportunity to investigate an additional set of parameters with which we can constrain the N_2O budget. The fractionation for the two ^{15}N isotopomers is predicted to be significantly different according to the theory of Yung and Miller [1997], and should be detectable with advanced optical techniques. It will be interesting to determine someday if the biologically mediated source terms have unique ^{15}N position signatures as well.

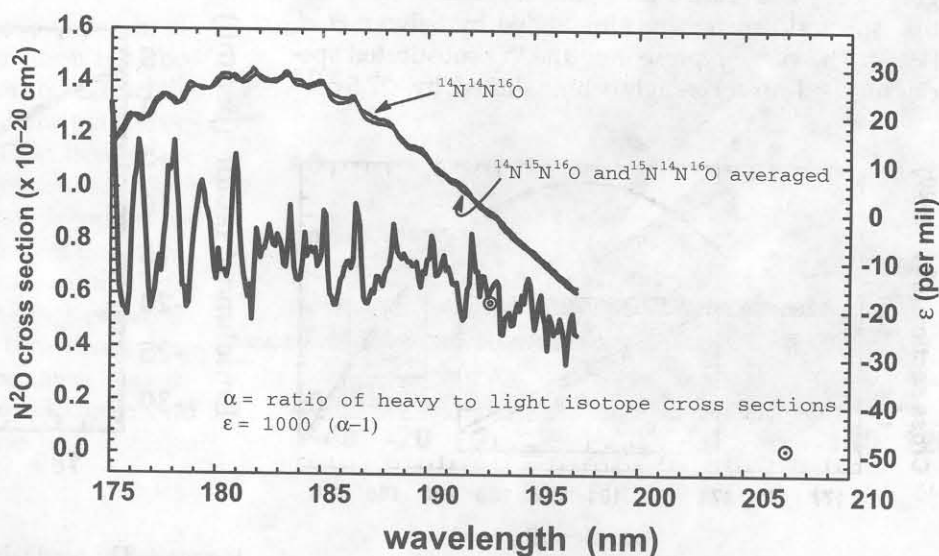


Figure 5. Top two curves show absorption cross sections for the N_2O species as indicated (reproduced from Selwyn and Johnston, 1981). Bottom curve indicates the spectral enrichment factor calculated as described in the text. The two symbols at 193 and 207 nm are the laboratory results from Rahn *et al.* [1998].

The application of stable sulfur isotopes to atmospheric studies

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Introduction

There are four naturally occurring stable isotopes of sulfur ^{32}S , ^{33}S , ^{34}S and ^{36}S with approximate abundances of 95.02, 0.75, 4.21 and 0.02%, respectively [MacNamara and Thode, 1950]. Isotopic variations are almost always considered in terms of the ratio of the two most abundant isotopes $^{34}\text{S}/^{32}\text{S}$. Isotope effects are usually small and fractional differences in isotope ratios (δ values) are normally expressed in parts per thousand (‰) relative to a standard:

$$\delta^{34}\text{S} = \left[\frac{\left(\frac{^{34}\text{S}}{^{32}\text{S}} \right)_{\text{sample}}}{\left(\frac{^{34}\text{S}}{^{32}\text{S}} \right)_{\text{standard}}} - 1 \right] \times 1000$$

The generally accepted standard is a meteoritic iron sulfide, the Canyon Diablo Troilite. There is evidence that the ratio of $^{34}\text{S}/^{32}\text{S}$ in this type of meteorite is the primordial value for sulfur on earth, and is therefore a natural baseline to which terrestrial variations can be related.

The $^{34}\text{S}/^{32}\text{S}$ ratio is measured by stable isotope mass spectrometry most commonly using sulfur dioxide, although sulfur hexafluoride is sometimes used. Traditional off-line preparation methods for sulfur dioxide are time consuming and require rather large amounts of sulfur ($\sim 300\mu\text{g S}$), which have placed limitations on their usefulness for atmospheric samples. However, recent use of an elemental analyser coupled to a mass spectrometer (e.g., Giesemann *et al.*, 1994, Patris *et al.*, 1998) is reducing both sample size (to $\sim 20\mu\text{g S}$) and preparation times, although some loss of precision is a potential problem.

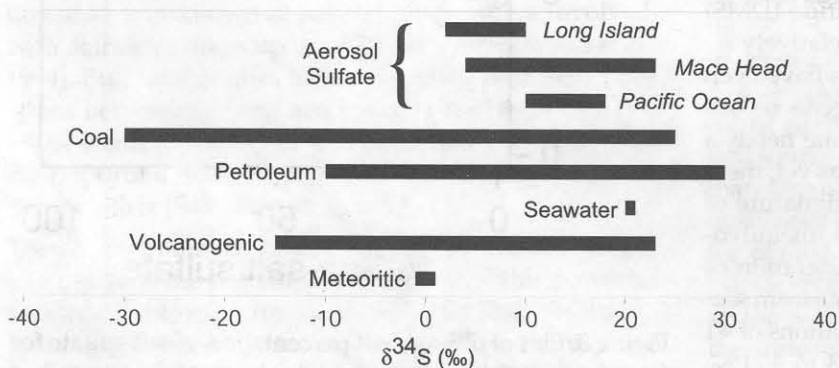


Figure 1. Variations of $\delta^{34}\text{S}$ values for different sources of sulfur to the atmosphere (after Thode, 1991), and some measurements from atmospheric aerosol samples. [Long Island: Newman and Forrest, 1991; Mace Head: McArdle and Liss, 1995; Pacific Ocean: Calhoun *et al.*, 1995].

Sources of sulfur to the atmosphere have a wide range in $\delta^{34}\text{S}$ values and this is reflected in the $\delta^{34}\text{S}$ of sulfur sampled in the atmosphere (Figure 1). Although the range of $\delta^{34}\text{S}$ values found for samples of fossil fuels is large, the range of $\delta^{34}\text{S}$ observed in the flue gases of fuels actually combusted can be very much smaller. For example Newman and Forrest [1991] found a range in $\delta^{34}\text{S}$ values of only -4 to $+8\text{‰}$ for flue gases from coal and oil fired power plants in the northeastern USA.

In addition, the ratio of the two isotopes can be altered (fractionated) during biological, physical and chemical transformations due to the difference in mass between the isotopes. In a unidirectional chemical reaction a kinetic isotope effect occurs when the lighter isotope reacts faster, so at any instant in time the products will be lighter than the reactants. However, if all the reactants are transformed there will be no overall fractionation between reactants and products. Fractionation during equilibrium reactions may lead to an enrichment in the products of either the heavier or lighter isotope.

A process by which sulfur isotopes are commonly altered in nature is by biological transformation of the sulfur, either by oxidation or reduction. There are two biochemical pathways to sulfate reduction: assimilatory sulfate reduction, which is thought to result in little or no isotopic fractionation, and dissimilatory sulfate reduction usually associated with large fractionations. Bacterial oxidation of reduced inorganic sulfur compounds can also result in significant fractionations.

Applications

Sulfur isotopes can be used to trace the emissions of point sources if they have sufficiently different $\delta^{34}\text{S}$ values compared to environmental receptors. For example, the emissions from sour gas processing plants in Canada are significantly enriched in ^{34}S and have provided an effective tool for tracing the fate of these emissions in surrounding ecosystems [Krouse, 1991].

On a larger scale sulfur isotopes can be used to look at historical changes in the amount of sulfur from human sources that has been taken up into the terrestrial biosphere and soil. Figure 2 shows data from a study by Zhao *et al.* [1998] of soil and herbage samples collected in the UK over the past 140 years. The variations in sulfur content of the plants reflect changing anthropogenic emissions of SO_2 in the UK. The $\delta^{34}\text{S}$ of the plants has an opposite trend indicating that the additional sulfur has a low $\delta^{34}\text{S}$, consistent with that expected from the combustion of coal. The authors estimate that anthropogenic S contributed up to 50% of the herbage uptake at the peak of SO_2 emissions (in the early 1970s).

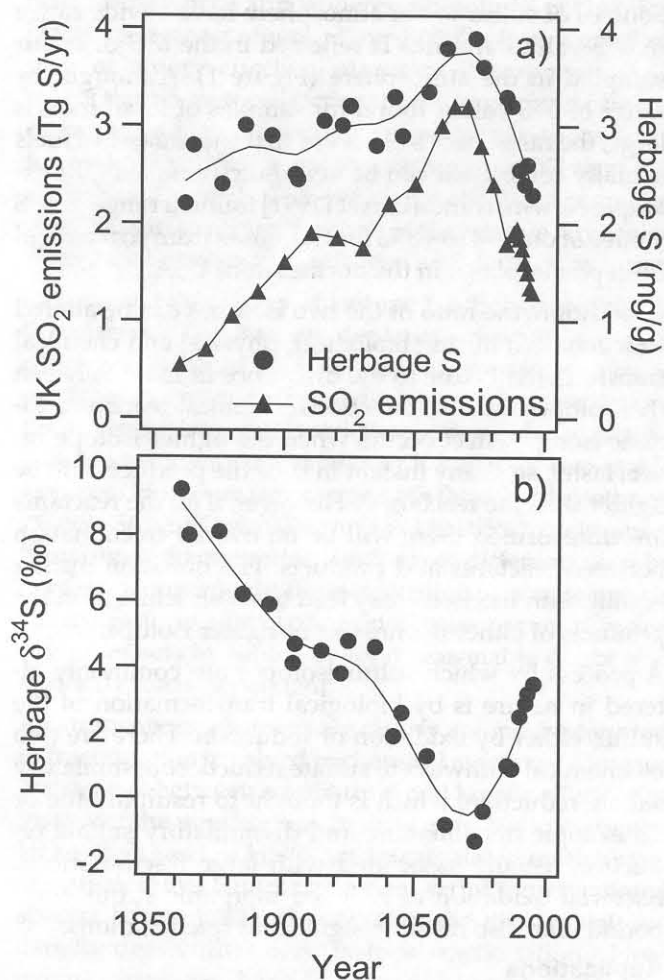


Figure 2 (a). Sulfur content in grassland plants and UK sulfur dioxide emissions from 1860 to 1996. (b) Herbage $\delta^{34}\text{S}$ variations from 1860 to 1996 [from Zhao *et al.*, 1998].

Isotopic signatures can also be used for quantitative source apportionment if the isotopic compositions of atmospheric sulfur from different sources are known and are sufficiently different from each other. Perhaps one of the most interesting applications of sulfur isotopes is for assessing the magnitude of the marine biogenic component (i.e., from the oxidation of dimethylsulfide (DMS) produced by phytoplankton) in remote and relatively remote locations, where anthropogenic sources have been well mixed resulting in a reasonably homogeneous anthropogenic $\delta^{34}\text{S}$ value. In order to do this one needs a $\delta^{34}\text{S}$ value for DMS derived sulfur. However, as yet, there are no direct measurements of the isotopic signature of DMS in the atmosphere or of sulfate that is unequivocally derived from DMS. A theoretical consideration of the production pathway for atmospheric sulfate from seawater via oxidation of DMS suggests fractionations of +1 to -7‰ relative to seawater, i.e., $\delta^{34}\text{S}$ of +13 to +21‰. [Calhoun *et al.*, 1991]. This is consistent with $\delta^{34}\text{S}$ values observed in atmospheric samples from remote locations.

A study of aerosol samples collected at Mace Head on the west coast of Eire and Ny Ålesund, Spitsbergen sug-

gested that the signature of sulfate derived from DMS is probably at the higher end of the predicted range [McArdle and Liss, 1995]. At the latitudes of the sampling sites in that study DMS production is strongly seasonal with little being produced during the winter, confirmed by the very low observed MSA (methanesulfonic acid, another oxidation product of DMS) concentrations compared with the spring and summer months. It was assumed that winter samples contained no DMS derived sulfur but were a mixture of sea-salt sulfate and terrestrial (mostly anthropogenic) sulfate. The contribution of

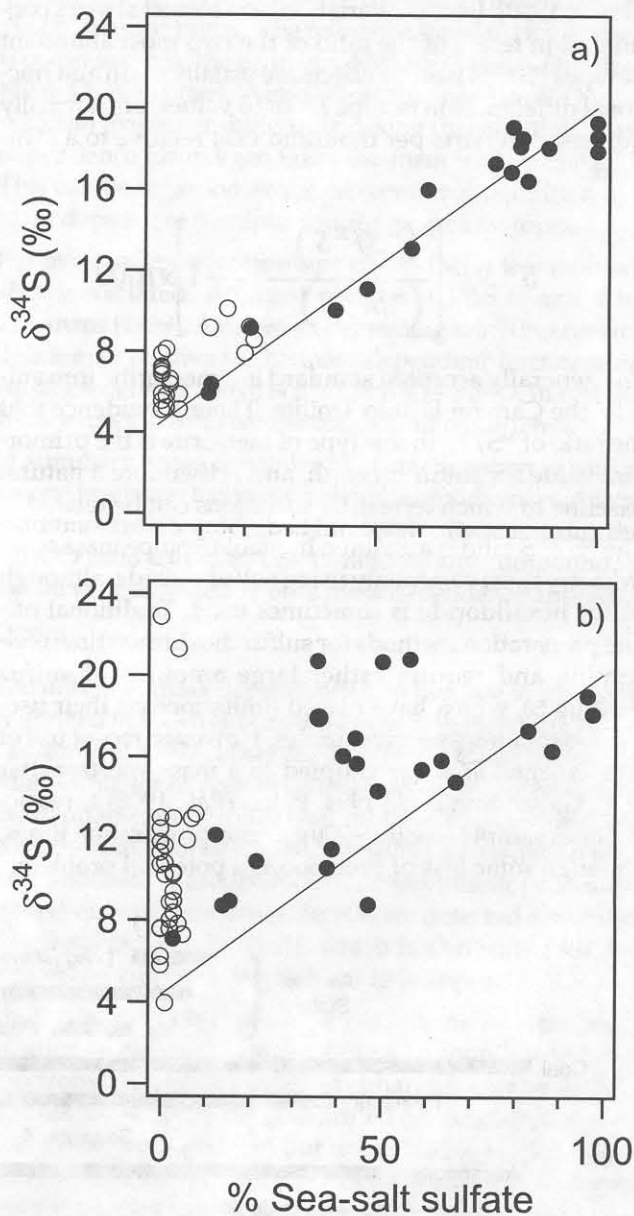


Figure 3. Plot of $\delta^{34}\text{S}$ against percentage sea-salt sulfate for (a) winter and (b) summer aerosol samples collected at Mace Head (solid dots) and Ny Ålesund (open circles). The linear regression line is for the Mace Head winter data and has intercepts of +4.4 and +20.1‰ at 0 and 100 % sea-salt sulfate, respectively (from McArdle and Liss, 1995).

sea-salt sulfate can be calculated assuming that sodium is a conservative tracer for oceanic sulfate. Figures 3 (a) and (b) show $\delta^{34}\text{S}$ values plotted against % sea-salt sulfate for winter and summer. In winter the data are distributed along a two-source mixing line, with the spread giving an indication of the variability in the terrestrial signature at these two sites.

In summer the distribution of data is very different with points lying well above the winter mixing line. This indicates the presence of an isotopically heavy source of sulfur during the summer which was assumed to be derived from the oxidation of DMS with an estimated $\delta^{34}\text{S}$ of +22‰. In this study the biogenic sulfur was found to make up ~30% of the sampled sulfur for the spring and summer months. An isotopic study of aerosol sulfate at Alert, Canadian Arctic also found biogenic contributions of 25-30% during the summer [Li and Barrie, 1993].

In studies such as this the terrestrial/anthropogenic signature needs to be constrained as tightly as possible for each location as biogenic contributions are often relatively small, particularly in the Northern Hemisphere. However, there seems to be rather little variation in $\delta^{34}\text{S}$ values across Europe and N. America with remarkably consistent terrestrial $\delta^{34}\text{S}$ values found in other studies around the N. Atlantic [e.g., McArdle *et al.*, 1998, Wadleigh *et al.*, 1996, Newman and Forrest, 1991, for sites in Wales, Nova Scotia and Long Island, respectively].

A number of studies have utilized isotopic fractionations to examine atmospheric processes, for example determining the relative importance of homogeneous (gas phase) versus heterogeneous (aqueous phase, in cloud droplets or on the surface of wet aerosols) oxidation of sulfur dioxide. The fractionation associated with a homogeneous oxidation pathway is a kinetic effect whereby the lighter isotope reacts faster, resulting in sulfate isotopically lighter than the initial SO_2 . Estimates of this fractionation range from 4 to 9‰ lighter [Saltzman *et al.*, 1983; Tanaka *et al.*, 1994]. The heterogeneous pathway, on the other hand, is expected to result in sulfate isotopically heavier than the SO_2 . However, the exact value of the total fractionation is unknown as several reactions are involved, with sulfate perhaps up to 16.5‰ heavier [Tanaka *et al.*, 1994]. But, field studies have only found small fractionations between gas and aerosol or rain in the range 0 to +4‰, leading authors to postulate that both processes are important, with one fractionation tending to cancel out the other [Saltzman *et al.*, 1983].

The development of new methods that reduce sample size expands the potential applications of this powerful technique, allowing for example better time resolution of samples, especially for remote southern hemisphere locations and ice cores. Also, there are good possibilities of combining stable isotope measurements of sulfur with those of other elements, such as oxygen or nitrogen, to provide more information about sources and environmental processes.

Anomalous (or Not Strictly Mass Dependent) Isotope Variations Observed in Important Atmospheric Trace Gases

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Introduction

This article is a synopsis of the recently discovered mass-independent isotope effects in atmospheric trace gases. What was once believed to be an exception measured in meteoritic material appears to be a surprisingly common effect in the atmosphere which enhances the usefulness of isotope analysis in atmospheric chemistry studies.

Variations in stable isotope ratios in the environment have generally been well understood and put to good use. However, the atmosphere appears to be the scene for a host of isotope effects that we do not yet understand. The prime example is ozone, whose anomalous enrichment has repeatedly defied correct interpretation. Gas phase reactions in the atmosphere appear to lead rather frequently to anomalous or "mass independent fractionation" (MIF). These anomalies offer the opportunity to advance the science of atmospheric chemistry and to relate its findings to fundamental atomic and molecular processes.

Isotope fractionation

The generally small environmental variations in the isotope ratios of the light elements—i.e., mainly H, C, N, O, and S—have been measured extensively and have at times provided unrivaled data; for example, information about past climate derived from $^{18}\text{O}/^{16}\text{O}$ ratio measurements on ice cores and on carbonates from sediment cores. Atmospheric studies also benefit from stable isotope variations. An illustration is the ongoing decline of the $^{13}\text{C}/^{12}\text{C}$ ratio of atmospheric carbon dioxide, largely in consequence of the increasing fraction of fossil fuel-derived carbon dioxide. This isotope effect is thus directly related to the isotopic composition of an important source of the gas. Fossil fuels have about 2% less ^{13}C than atmospheric carbon dioxide. This in itself is obviously not a source effect (ambient CO_2 is the carbon source for plants), but rather an isotope fractionation effect of photosynthesis. Plants favor $^{12}\text{CO}_2$ slightly over $^{13}\text{CO}_2$, so the assimilated carbon is depleted in ^{13}C relative to the atmosphere. In isotope applications of interest to atmospheric chemistry, source signatures and fractionation effects in chemical reactions are both relevant.

Many processes in nature can cause isotope fractionation: diffusion, gravitation, thermal diffusion, phase transi-

tions, escape from atmospheres, photolysis, or chemical reactions, among others. Kaye [1987] offers a good review of isotope effects in planetary atmospheres. As a rule of thumb, isotope fractionation is larger for the lighter elements and thus, the greatest isotope variations occur for hydrogen. HH reacts 65% faster with OH than HD [Ehhalt *et al.*, 1989]. This very large effect can be understood qualitatively on the basis of the relative large mass difference between the hydrogen and deuterium atoms.

Generally, two classes of isotope fractionation are distinguished. The isotopic depletion of water vapor in contact with liquid water is a good example of a classic equilibrium isotope effect, which is purely mass dependent. For hydrogen this strict mass dependence is difficult to verify experimentally as it has only two stable isotopes. However, for oxygen with three stable isotopes, ^{16}O (99.756%), ^{17}O (0.038%) and ^{18}O (0.205%), the proportionality of fractionation with mass difference can be verified accurately. In the evaporation of water vapor, a kinetic isotope effect based on differences in diffusion velocities sets in, which beyond reasonable doubt also is strictly mass dependent.

As atmospheric chemists we clearly are most interested in fractionation involved in chemical reactions. Here we distinguish between equilibrium and kinetic effects. For instance, the equilibrium hydrogen isotopic exchange $\text{HD} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{HDO}$ can be calculated on the basis of statistical mechanics using data about the vibrational spectra [Urey, 1947]. However, in the atmosphere we usually deal with kinetic isotope fractionation. Here calculations are based on transition state theory [Bigeleisen and Wolfsberg, 1958], where a transition complex is considered. Various degrees of refinement have been developed to calculate fractionation factors that are in agreement with measured data. A successful *ab initio* calculation of the isotope effects in the $\text{CH}_4 + \text{Cl}$ reaction has recently been published [Roberto-Neto *et al.*, 1998], giving results that agree with careful observations [Saueressig *et al.*, 1995, 1996], which show large fractionation factors of $\approx 7\%$ for carbon and $\approx 60\%$ for hydrogen.

For decades after the experimental and theoretical frontier research by Urey, Bigeleisen, Craig, Nier, Keeling, Clayton, Epstein, Baertschi, Wolfsberg and others, it was believed that we understood all observed isotope effects. At this stage you may not be surprised to read that most naturally occurring isotope effects are mass dependent. But how do we know whether an isotope effect is mass dependent, and how is this defined?

Acceptance of the near universal applicability of mass dependence in isotope fractionation appears to have been guided by the success of theoretical models of fractionation processes. The mass dependence of isotope fractionation in chemical reactions according to transition state calculations and equilibrium calculations is mainly the result of differences in the normal vibrational frequencies for the individual isotopic species [Kaye, 1987]. Be-

cause the vibrational frequencies of a chemical bond depend on the masses of the atoms that form the bond, the heavy isotopes are usually more tightly bound, which leads to fractionation in chemical reactions. For multi-isotope systems like oxygen, and for small isotopic variations, it has been shown that such mass dependent fractionation processes produce shifts in the $^{17}\text{O}/^{16}\text{O}$ ratio which are half the size of the accompanying $^{18}\text{O}/^{16}\text{O}$ variations [Matuhisa *et al.*, 1978; Hulston and Thode, 1965].

We now introduce the common delta notation for representing the "small" natural isotope variations, e.g., $\delta^{18}\text{O} = [^{18}\text{R}_{\text{sample}}/^{18}\text{R}_{\text{standard}} - 1] \times 1000$ in which ^{18}R denotes the $^{18}\text{O}/^{16}\text{O}$ atomic ratios. The reference standard for oxygen is ocean water in the form of V-SMOW (Vienna-Standard Mean Ocean Water). Atmospheric oxygen has $\delta^{18}\text{O}_{\text{V-SMOW}} = 23.5\text{‰}$ (parts per thousand). Using this notation, mass dependence for oxygen takes the form $\delta^{17}\text{O} \approx 0.5 * \delta^{18}\text{O}$. This can be regarded as the conventional definition of a mass dependent fractionation for oxygen isotopes.

For mass independent isotope effects (MIF) this relationship is violated. A recent review of MIF is given by Thiemens [1999]. A means of expressing the ^{17}O excess (or deficiency) relative to the mass dependent fractionation equation defined above is $\Delta^{17}\text{O} = \delta^{17}\text{O} - r \delta^{18}\text{O}$, in which r is the expected ratio for the compound considered.

In summary, mass dependence of fractionation exists on several levels and has many well understood causes. Again, this is most easily confirmed for oxygen. By measuring the $^{17}\text{O}/^{16}\text{O}$ ratio and the $^{18}\text{O}/^{16}\text{O}$ ratio of any compound, it can be verified whether pure mass dependence applies.

Ozone

The notion of mass dependence had become thoroughly engrained in the environmental isotope community when Clayton *et al.* [1973] observed deviations from this simple relationship for oxygen in certain meteoritic material. Understandably, they concluded that the anomalous composition could not be due to a chemical fractionation process, and instead ascribed it to nucleosynthetic processes. However, no anomalous effects were detected for sulfur [Hulston and Thode, 1965], which is also suited for detecting deviations as it has 4 stable isotopes.

Mauersberger [1981] measured the ozone isotopic composition in the stratosphere using a balloon-borne mass spectrometer. The discovery of enhancements up to 40% in mass 50—i.e., the ^{18}O -substituted ozone isotopomer—was extensively debated but not explained. The violation of mass dependence for oxygen in such a simple laboratory experiment as the production of ozone by an electrical discharge changed conventional thinking about isotope effects [Thiemens and Heidenreich, 1983]. The surprising fact is that ^{18}O and ^{17}O are enriched in the ozone product approximately equally, rather than in a 2 : 1 ratio. This led to the concept of mass independent (or non-mass dependent) fractionation in chemical reactions. Since then numerous investigations firmly es-

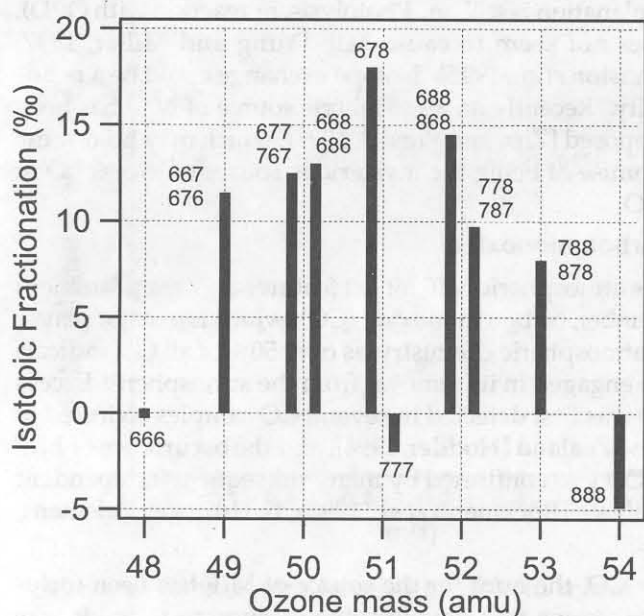


Figure 1. The distribution of ozone isotopomers measured by using enriched mixtures. The asymmetric molecules are formed preferentially. Numbers next to bars indicate molecular composition, e.g., "667" = ¹⁶O¹⁶O¹⁷O.

tablished that both stratospheric and tropospheric ozone exhibit MIF [Schueler *et al.*, 1990; Johnston and Thiemens, 1997; Krankowsky *et al.*, 1995].

It has taken years to unravel the secrets of the anomalous isotope fractionation of ozone, perhaps the most extensively studied reactive atmospheric trace gas. In regard to molecular symmetry, ¹⁷O and ¹⁸O in an ozone molecule are identical (they are simply different from the abundant ¹⁶O isotope); consequently, several theories of symmetry selection in the ozone formation process were proposed. Figure 1 shows the now famous picture of the strange isotopic mix of ozone produced from enriched oxygen mixtures, with illusive preferences for asymmetric configurations. However, theories based on symmetry have been challenged by the latest experimental data.

By carefully measuring the individual rate constants of selected ozone production channels, Anderson *et al.* [1997] and Mauersberger *et al.* [1999] have produced the necessary evidence to pin down the origin of ozone enrichment. Table 1 lists some of their interesting experimental results, which show that certain reaction channels have enormous rate coefficient advantages. For instance, ¹⁶O reacts with ¹⁸O¹⁸O a staggering 50% faster than does ¹⁸O.

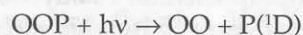
Paradoxically, the results shown in Table 1 suggest mass dependence after all. The fastest reaction occurs for the heaviest isotopomer with the lightest atom, the slowest rate constants for the heaviest atom reacting with the lightest molecule. It seems clear now that the anomalous

fractionation in ozone formation is not caused by a "mass independent" symmetry selection processes, but rather by some unknown parameter in the three body collision process that depends strongly on the masses of the atoms and molecules involved. New theories for explaining the odd behavior of ozone are cheerfully in development.

Now let us revisit the conventional, well-behaved mass dependence. As noted above, small fractionations in ¹⁷O are half as large as the accompanying variations in ¹⁸O. Is this strictly 0.500? No, the exact ratio between $\delta^{17}\text{O}$ and concomitant $\delta^{18}\text{O}$ variations depends on the nature of the fractionation process and on the molecular masses involved [Matsuhisa, 1978]. For diffusion, which is easy to handle mathematically with the diffusion speed being inversely proportional to the square root of the masses, the ratios range from 0.523 for atomic oxygen to 0.500 for very heavy molecules.

Carbon dioxide

After ozone, it was found that carbon dioxide in the stratosphere exhibits MIF [Thiemens *et al.*, 1995, Gamo *et al.*, 1989]. A chemical mechanism was proposed by Yung *et al.* [1991], who showed that the observed ¹⁷O excess in CO₂ could be explained by transfer of the enrichment present in ozone to CO₂ via the excited oxygen radical O(¹D):



where P denotes the rare isotopes ¹⁸O or ¹⁷O and the asterisk an excited intermediate complex.

Refinements were later proposed by Barth and Zahn [1997] and Yung *et al.* [1997]. However, it is still not clear whether additional mass dependent or even mass independent fractionations occur in the CO₃* formation or breakup, although the mechanism has in principle been firmly established in the laboratory [Wen and Thiemens, 1993].

Reaction	Relative rate coefficient
¹⁶ O + ¹⁸ O ¹⁸ O / ¹⁶ O + ¹⁶ O ¹⁶ O	1.53 ± 0.03
¹⁸ O + ¹⁶ O ¹⁶ O / ¹⁸ O + ¹⁸ O ¹⁸ O	0.90 ± 0.03
¹⁶ O + ¹⁷ O ¹⁷ O / ¹⁶ O + ¹⁶ O ¹⁶ O	1.23 ± 0.03
¹⁷ O + ¹⁶ O ¹⁶ O / ¹⁷ O + ¹⁷ O ¹⁶ O	1.01 ± 0.05
¹⁸ O + ¹⁷ O ¹⁷ O / ¹⁸ O + ¹⁸ O ¹⁸ O	1.00 ± 0.06
¹⁷ O + ¹⁸ O ¹⁸ O / ¹⁷ O + ¹⁷ O ¹⁷ O	1.29 ± 0.07

Table 1: Measured relative rate coefficients of six individual ozone formation channels, compared to the homonuclear rate constants for formation of ¹⁶O¹⁶O¹⁶O, ¹⁷O¹⁷O¹⁷O and ¹⁸O¹⁸O¹⁸O, which are approximately equal [Mauersberger *et al.*, 1999].

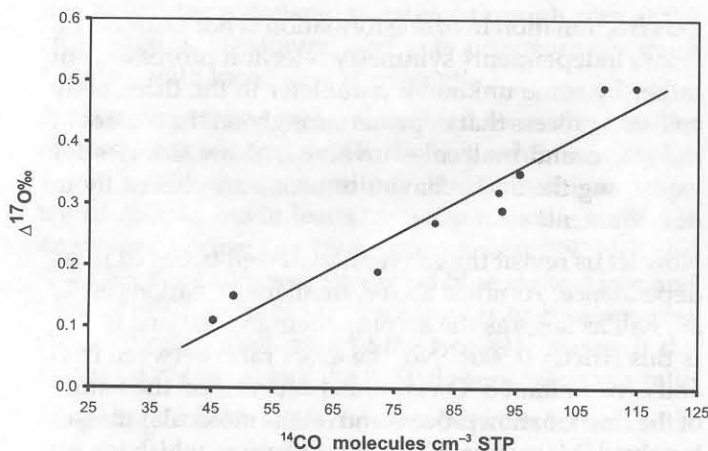


Figure 2. The correlation in the lowermost stratosphere between the two independent variables ^{14}CO and $\Delta^{17}\text{O}$ in CO_2 . Note that the vertical scale is only 0.6‰. Despite that, the correlation is excellent.

This all made CO_2 , which had been of little interest to atmospheric chemists due to its lack of reactivity in the lower regions, suddenly a molecule of some importance: MIF in CO_2 is a marker of its exposure to $\text{O}(^1\text{D})$. The predominantly stratospheric signal is diluted when CO_2 is transferred into the troposphere and finally washed out over a period of several years by isotopic exchange with the large reservoir of soil, leaf, and ocean water. Thus, the ^{17}O excess in CO_2 determined on stratospheric air samples correlates well with another stratospheric tracer, ^{14}CO , as displayed in Figure 2. Figure 3 shows the mass dependent fractionation line, and the typical ^{17}O and ^{18}O values for important gases and V-SMOW.

This is good news for atmospheric research, although the experimental determination is elaborate. One has to collect air samples and extract the CO_2 . A further problem arises with the mass spectrometric measurement. When CO_2 is analyzed in an isotope ratio mass spectrometer, masses 44, 45 and 46 are collected. This gives two isotope ratios only, whereas there are three unknown ratios: i.e., $^{13}\text{C}/^{12}\text{C}$, $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$. A way around this is to convert the CO_2 to O_2 by using aggressive reagents like BrF_5 . This process is time consuming and can be hazardous. New experimental methods are being developed [Brenninkmeijer and Röckmann, 1998]. Spectroscopic methods may also be promising.

Nitrous oxide

Remarkably, MIF is not restricted to CO_2 and ozone alone. Cliff and Thiemens [1997] have shown that atmospheric N_2O has a small excess of ^{17}O . In view of the uncertainties in the budget of N_2O , this is a welcome fact of nature, yet the race for finding an

explanation is still on. Photolysis, or reaction with $\text{O}(^1\text{D})$, does not seem to cause MIF [Yung and Miller, 1997; Johnston *et al.*, 1995]. Isotope exchange could be a possibility. Recently an atmospheric source of N_2O has been proposed [Zipf and Prasad, 1998], which may hold some promise of being the mysterious source of excess ^{17}O in N_2O .

Carbon monoxide

The atmospheric MIF hit list features another prominent member, carbon monoxide (CO), which is a major player in atmospheric chemistry, as over 50% of all OH radicals are engaged in its removal from the atmosphere. Excess ^{17}O was first detected in several CO samples collected in New Zealand [Hodder, 1994], and the occurrence of MIF in CO was confirmed by many subsequent independent analyses [Röckmann *et al.*, 1998a, b; Huff and Thiemens, 1998].

For CO , the hunt for the source of MIF has been fortunate, so we will devote some discussion to it. It was shown that the ozonolysis of unsaturated hydrocarbons like isoprene, β -pinene and ethene does produce CO , the oxygen of which is derived from ozone with its excess ^{17}O [Röckmann *et al.*, 1998a]. However, the ozonolysis source could not adequately explain the atmospheric values. Subsequent research showed that the important reaction $\text{CO} + \text{OH}$ introduces MIF in the remaining CO . More precisely, CO that has not reacted gains a small excess of ^{17}O [Röckmann *et al.*, 1998b].

Figure 4 shows the ^{17}O excess in the remaining CO fraction after reaction with OH in He and N_2 as carrier gas

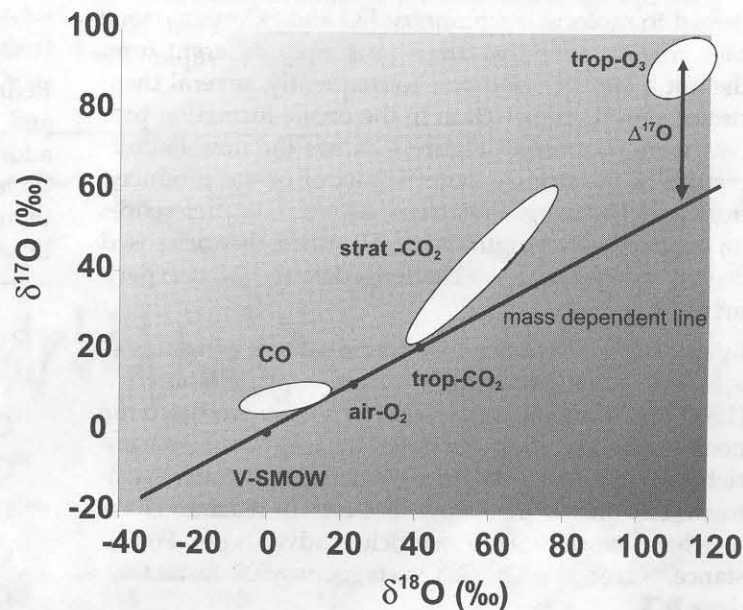
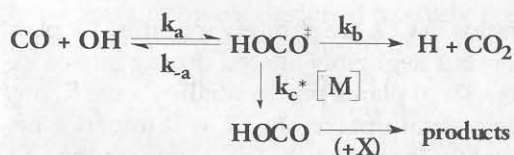


Figure 3. A three-isotope plot showing the mass dependent line and the most important deviations for CO_2 , CO , and tropospheric O_3 . Stratospheric ozone (not shown here) is further enriched.

for different periods of time. The more CO has reacted, the higher is the mass independent component in the remaining CO. Furthermore, the excess ^{17}O increases with increasing total pressure. Referring to the reaction mechanism for $\text{CO} + \text{OH}$ (see below), this suggests an important role of the intermediate HOCO^\ddagger in the fractionation process, although it is difficult to relate the occurrence of MIF to a specific reaction step. Another peculiarity of the reaction is that C^{18}O reacts about 1% faster with OH than C^{16}O , an inverse isotope effect, which is almost independent of pressure. To produce the observed excess ^{17}O enrichment (Figure 4) at all pressures, the rate coefficients of C^{16}O and C^{17}O for reaction with OH must be equal at atmospheric pressure.



The annual cycle of CO (Figure 5) at mid- and high latitudes is strongly driven by the seasonality in OH. This is the cause for the observed anti-correlation between CO mixing ratios and $\Delta^{17}\text{O}$. In summer, with maximum OH, CO decreases rapidly, in phase with the increase in $\Delta^{17}\text{O}$. In winter, the CO inventory is replenished with CO with $\Delta^{17}\text{O}$ values close to zero. Consequently, $\Delta^{17}\text{O}$ declines. A comparison with $\delta^{18}\text{O}$ also shows a strong similarity. The reason for the negative correlation in this case is that the reaction with OH preferentially removes ^{18}O due to the negative kinetic isotope effect [Stevens *et al.*, 1980].

Very large isotope effects have been reported to occur in photochemical reactions by selective ionization, and for certain ion-molecule reactions [Gellene, 1992]. These effects, of course, are of importance for molecular studies. Besides this, the large reaction rate enhancement effects in ozone and the extremely large effects measured by Gellene imply that very small sources of atmospheric trace gases may measurably affect the overall isotopic composition. This may allow the identification of certain sources.

To finish our discussion, we draw attention to some attractive features of MIF. One as

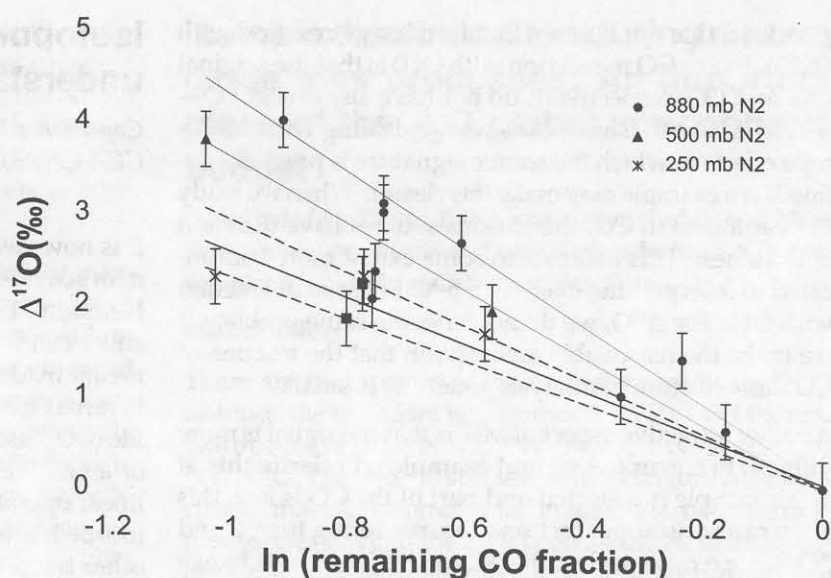


Figure 4. The increase in $\Delta^{17}\text{O}$ of the remaining CO after reaction with OH. With lower pressures, or He as carrier gas, the enrichment is smaller.

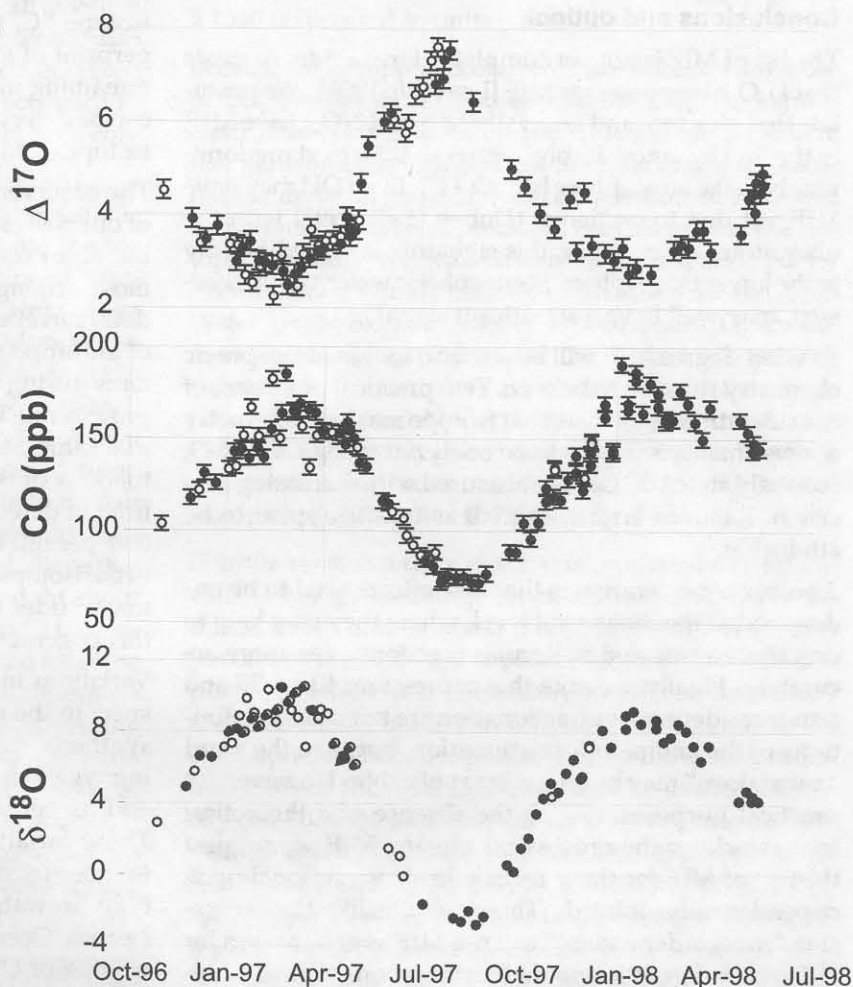


Figure 5. The large annual cycle in CO and its oxygen isotopes measured for surface air in Spitsbergen.

pect (and this applies to CO_2 in exchange reaction with $\text{O}(^1\text{D})$, and to CO in reaction with OH) is that the original CO_2 and CO , respectively, do not have any excess ^{17}O —that is, $\Delta^{17}\text{O} = 0$. This means we are dealing with an isotope effect for which the source signature is precisely defined. An example may make this clearer. When we study ^{18}O variations in CO , the various sources have different $\delta^{18}\text{O}$ values. This makes it to some extent more complicated to interpret the decline in $\delta^{18}\text{O}$ in terms of reaction with OH . For $\Delta^{17}\text{O}$, we do not have the same problem if we make the reasonable assumption that the fraction of CO derived from ozonolysis generally is small.

Another attractive aspect of MIF is that the signal is more difficult to corrupt. A second example will clarify this. If an air sample is collected and part of the CO is lost, this often causes isotope fractionation, rendering the ^{13}C and ^{18}O isotope ratio useless. However, $\Delta^{17}\text{O}$ will not change in this process. Another robust feature of $\Delta^{17}\text{O}$ is that, if the signal is corrupted by dilution or exchange, the end member in the process has nearly always a $\Delta^{17}\text{O}$ value of zero. This facilitates any necessary corrections for dilution and exchange.

Conclusions and outlook

The list of MIF is not yet complete. Firm evidence exists that H_2O_2 also possesses MIF [Lee *et al.*, 1998]. We postulate that NO_2 too (and generally NO_x and NO_y) have MIF, in the first instance simply because it is formed predominantly in the atmosphere by $\text{NO} + \text{O}_3$. Even OH may have MIF, yet due to exchange (Dubey *et al.*, 1997) with the ubiquitous water vapor, this signature is erased rapidly in the lower troposphere. Stratospheric water vapor, however, may well have a significant signal.

To what degree MIF will be a useful tool in atmospheric chemistry remains to be seen. Two practical points are of consideration here: One, that isotope mass spectrometry allows smaller samples to be analyzed using GC-IRMS; secondly, that $\Delta^{17}\text{O}$ can be measured with increasing precision. Random errors as small as 0.03‰ appear to be attainable.

Another consideration is that MIF effects need to be understood at the theoretical level, where they may help to describe atomic and molecular reactions even more accurately. Finally, we note that expressions like MIF and non-mass dependent fractionation are not proper definitions of the anomalous fractionation, but then the word “anomalous” may be no longer applicable. However, for practical purposes, and in the absence of a theoretical framework for the process(es) causing MIF, we suggest the use of MIF for those cases when conventional mass dependence is violated. Those who dislike the expression “mass independent” can use MIF as an acronym for “Missing Information about Fractionation”. For us, however, the main question will be: What can MIF teach us about atmospheric chemistry? The answer is that more work is required!

Isotopomers of CO_2 and their use in understanding the global carbon cycle

Contributed by P. Ciais (*ciais@cea.fr*), LSCE, Unité mixte CEA-CNRS, Gif sur Yvette, France

It is now clear that fossil fuel combustion and other human activities are perturbing the global carbon cycle [e.g., Heimann, 1997]. Today's patterns of carbon sources and sinks can be downscaled from atmospheric measurements made around the world. Usually, the fluxes are inverted from space and time gradients in carbon dioxide (CO_2) using atmospheric transport models. In the case of a passive tracer such as CO_2 , the transport acts as a linear operator between the sources and the modeled atmospheric concentration field. In addition to CO_2 alone, other tracers of the carbon cycle are extremely valuable to improving our estimates of today's carbon sources and sinks.

The $^{13}\text{C}/^{12}\text{C}$ ratios in CO_2 are strongly modified by plant photosynthesis but negligibly altered during air-sea exchange. As terrestrial plants preferentially fix the lighter isotope ^{12}C , terrestrial uptake of CO_2 will impart a fingerprint of slightly increased $^{13}\text{C}/^{12}\text{C}$ ratios on the CO_2 remaining in the atmosphere. Though small, this signal can be detected by ultra-precise measurements of the ^{13}C isotopic composition of CO_2 using mass spectrometry.

The observed meridional gradient of ^{13}C constitutes one of our best clues for understanding the latitudinal distribution of oceanic vs. terrestrial CO_2 fluxes. One of the most striking results that ^{13}C data (and now O_2/N_2 ratio data) unveiled is the existence of a very large repository of anthropogenic CO_2 in Northern Hemisphere ecosystems during the early 1990's when the atmospheric CO_2 growth rate had diminished to only one third of its normal value. Still, the long term trend and interannual fluctuations of ^{13}C at one given monitoring station is at the limit of detection of mass spectrometers, on the order of 0.01 per mil for ^{13}C in CO_2 . Thus, even a very slight bias in the isotopic data would translate into different inferred magnitudes of the global land and ocean uptake of anthropogenic CO_2 .

Variations in the oxygen:nitrogen ratio (O_2/N_2) with respect to the oxygen:argon ratio in air are due to photosynthesis, respiration, and fossil fuel and biomass burning which are directly linked to the global carbon cycle and its perturbation by man [e.g., Keeling *et al.*, 1996]. These variations can be measured by techniques similar to those used for $^{13}\text{C}/^{12}\text{C}$ ratios. Oxygen has a low solubility in water compared to CO_2 and lacks a buffering system. Oceanic productivity as well as mixing or upwelling of O_2 -depleted water imprints a distinct signal on the atmosphere, modulated by air-sea gas exchange. This leads to relatively large annual O_2/N_2 variations in

both hemispheres. The long term trend as well as interannual fluctuations in O_2/N_2 can now be resolved with modern techniques like mass spectrometry. In combination with CO_2 concentration measurements this gives us much information about the global carbon budget, i.e., the so-called "missing sink".

The $^{18}O/^{16}O$ ratio in atmospheric CO_2 has been identified as a unique tracer to constrain separately the gross uptake (photosynthesis) and release (respiration) of carbon by terrestrial biota. CO_2 can exchange an ^{18}O atom with two isotopically distinct water reservoirs: Evaporating leaf water during photosynthesis and soil moisture during respiration. Thus, the $^{18}O/^{16}O$ isotopic composition of CO_2 is controlled indirectly by the $^{18}O/^{16}O$

ratio of water in the biosphere, and thus is linked to the global water cycle. Atmospheric measurements of $^{18}O/^{16}O$ in CO_2 show a pronounced negative latitudinal gradient, which is interpreted as a fingerprint of respiratory CO_2 emissions. The reason ^{18}O in CO_2 is useful is that it relates to the gross fluxes of CO_2 exchanged by land ecosystems (photosynthesis, respiration), rather than to the net fluxes which are constrained by CO_2 , ^{13}C and O_2/N_2 .

In pursuing and improving the atmospheric monitoring of CO_2 and its isotopic composition, there is a crucial need to augment the coverage of poorly known oceanic and continental areas, thus better improving the diagnostic of carbon fluxes at the continental to regional scale.

Announcements

The ACSOE Scientific Symposium

Atmospheric Chemistry Studies in the Oceanic Environment

12–16 July, 1999

University of East Anglia, Norwich

The Symposium marks the end of the 'ACSOE' Thematic Programme of the UK Natural Environment Research Council. ACSOE incorporated important links to IGAC projects: notably MAGE, NARE and ACE-2. Keynote lectures will be given by Dr. Guy Brasseur (NCAR, USA), Professor Barry Huebert (University of Hawaii, USA), and Dr. Frank Raes (JRC, Italy), and overview lectures by Professors Stuart Penkett, Peter Liss (both UEA, UK) and Tom Choularton (UMIST, UK).

There will be a program of invited presentations on the science of ACSOE and related international projects, with dedicated poster sessions in the afternoons.

On the final day there will also be a Special Session on the UK contribution to EUROTRAC-2.

Attendance is open to all, and submission of poster presentations on the general theme of the Symposium are welcomed.

Details and registration forms will be posted on the ACSOE web site at <http://www.uea.ac.uk/~acsoe>, or contact the program manager at w.sturges@uea.ac.uk, (+44-1603) 592018, fax (+44-1603) 452420.

The ACSOE Symposium is sponsored by the NERC, and by the UK EUROTRAC Project Office through a grant from the DETR.

Molina Fellowship in Environmental Science

The Molina Fellowship in Environmental Science was established to bring postdoctoral fellows and young scientists from emerging nations to MIT to pursue studies in environmental sciences. Molina Fellows will then return to their home countries better able to address complex environmental concerns. Professor Mario Molina was awarded the 1995 Nobel Prize in Chemistry for his work on the damaging effects of chlorofluorocarbons on the Earth's protective ozone layer, and used a portion of the prize money to endow the Molina Fellowship. Individuals holding a Ph.D. degree in science or engineering and interested in pursuing work in environmental science are eligible for the one-year Fellowship with an annual stipend of \$35,000.

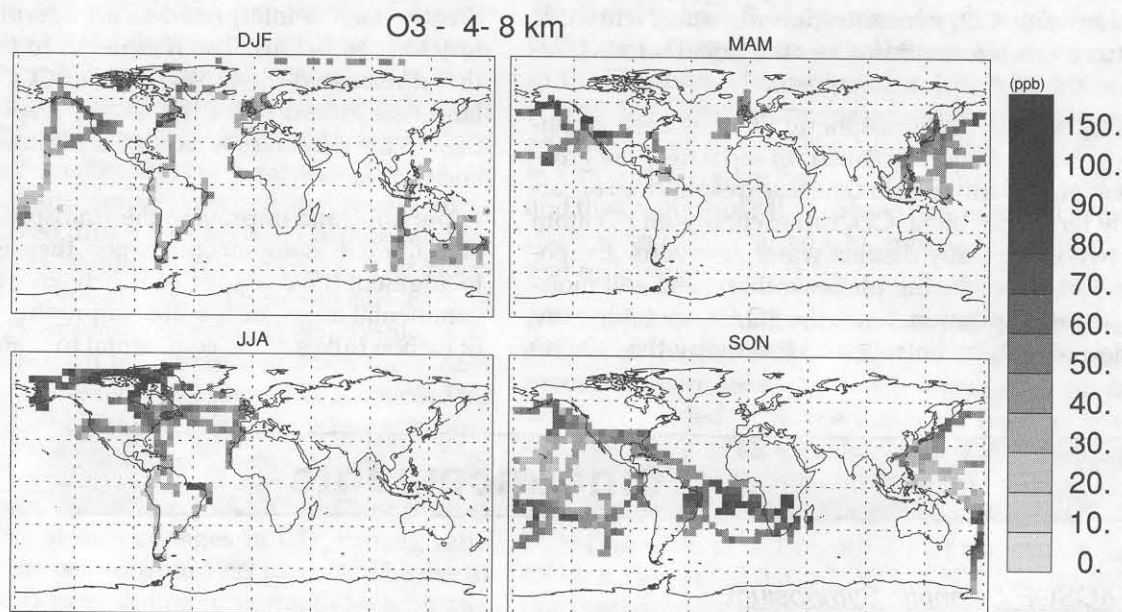
Qualified scientists are encouraged to apply by sending a Curriculum Vitae with a list of publications, names and addresses of three professional references and a brief statement of research interest to the attention of:

Professor Ronald G. Prinn, Head
Dept. Earth, Atmospheric & Planetary Sciences
Bldg. 54-918
Massachusetts Institute of Technology
77 Massachusetts Avenue
Cambridge, MA 02139-4307
USA

In addition, applicants should arrange for the three letters of recommendation to be sent directly by referees to the above address. All materials must be received by May 1, 1999.

Web Site Announcement:

Tropospheric Data Composites



Data 'composites' of tropospheric constituents are now available on the Internet at <http://aoss.engin.umich.edu/SASSarchive/>. Data from numerous aircraft campaigns, as well as ozonesondes and surface measurements, have been gathered together to provide a source of data for the evaluation of models, as well as to provide a global view of our current understanding of the global distributions of these chemical species. The data composites currently include measurements of O₃, CO, NO, NO_x, PAN, HNO₃, H₂O₂, CH₃O₂H, CH₂O, C₃H₆O, C₂H₆ and C₃H₈. We plan to add observations of sulfur compounds (e.g., SO₂, DMS, H₂SO₄) and aerosol number densities and composition (NO₃⁻, SO₄⁼, etc.).

Two forms of data composites are available currently. In the first, the data from each campaign have been averaged into 5° latitude by 5° longitude by 1 km altitude grid boxes. These grid boxes can then be plotted on maps

for a given altitude range, sorted by season, as shown above. Secondly, somewhat larger regions have been chosen from individual aircraft campaigns for examining vertical profiles.

We are also continuously looking for additional data sets to add to the composites, particularly sets that are not already available to the community on a public archive. If you have any data that would be appropriate for this use, please contact us! We look forward to your assistance in making this a valuable resource for the atmospheric science community.

Louisa Emmons (emmons@ucar.edu)

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NCAR, Atmospheric Chemistry Division, Boulder CO

Mary Anne Carroll (mcarroll@umich.edu)

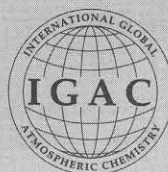
University of Michigan, Dept AOSS, Ann Arbor MI

Sixth Scientific Conference of the International Global Atmospheric Chemistry Project (IGAC)

Bologna, Italy • 13-17 September 1999

Organized by the IGAC Project of IGBP, the European Commission, and
Consiglio Nazionale delle Ricerche-Istituto Fisbat

For complete information, consult the conference
web site at <http://www.fisbat.bo.cnr.it/IGAC99/>.



IGAC Leadership in 1999

Scientists can serve on the IGAC Scientific Steering Committee (SSC) for a maximum of 6 years (except for the Chair who can serve an additional 3 years), so several members rotate off and are replaced by new people each year. As a result of the "refocusing" of IGAC over the past year, many Activity Convenerships have recently changed hands as well. The current SSC membership and Activities and their Conveners are listed below.

IGAC Scientific Steering Committee - 1999

Paulo Artaxo, Brazil	artaxo@if.usp.br
Jariya Boonjawat, Thailand (Vice-Chair)	jariya@start.or.th
Guy P. Brasseur, USA (Chair)	brasseur@ncar.ucar.edu
Ralf Conrad, Germany	conrad@mail.uni-marburg.de
Robert J. Delmas, France	delmas@glaciog.ujf-grenoble.fr
Paul J. Fraser, Australia	paul.fraser@dar.csiro.au
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Neil B.A. Trivett, Canada	neil.trivett@sympatico.ca
Wang Mingxing, China-Beijing	wmx@mail.iap.ac.cn

IGAC Activities and their Conveners as of March 1999

Focus on Biosphere-Atmosphere Interactions

Biosphere-Atmosphere Trace Gas Exchanges (BATREX)

Arvin E. Mosier, USA (mosier@lamar.colostate.edu)*

Heinz-Ulrich Neue, Germany (hneue@bdf.ufz.de)*

Deposition of Biogeochemically Important Trace Species (DEBITS)

Jean-Pierre Lacaux, France (lacjp@aero.obs-mip.fr)

Biomass Burning Experiment (BIBEX)

Johann-Georg Goldammer, Germany

(jggold@sun1.ruf.uni-freiburg.de)

Joyce E. Penner, USA (penner@umich.edu)

Marine Aerosol and Gas Exchange (MAGE)

Barry J. Huebert, USA

(huebert@okika.soest.hawaii.edu)

Focus on Oxidants and Photochemistry

Intercontinental Transport and Chemical Transformations (ITCT)

Hajime Akimoto, Japan

(akimoto@atmchem.rcast.u-tokyo.ac.jp)

Frederick C. Fehsenfeld, USA (fcf@al.noaa.gov)

Stuart A. Penkett, UK (m.penkett@uea.ac.uk)

Sub-Activity: East Asia – North Pacific Regional Experiment (APARE)

Mitsuo Uematsu, Japan (uematsu@ori.u-tokyo.ac.jp)

Sub-Activity: North Atlantic Regional Experiment (NARE)

David D. Parrish, USA (parrish@al.noaa.gov)

Stuart A. Penkett, UK (m.penkett@uea.ac.uk)

Global Tropospheric Ozone Project (GTOP)

Jack Fishman, USA (j.fishman@larc.nasa.gov)*

Shyam Lal, India (shyam@prl.ernet.in)*

Focus on Capacity Building

Atmospheric Chemistry and Environmental Education in Global Change (ACE^{ED})

Jariya Boonjawat, Thailand (jariya@start.or.th)*

Daniel Jaffe, USA (djaffe@u.washington.edu)*

Focus on Atmospheric Aerosols

Aerosol Characterization and Process Studies (ACAPS)

Timothy S. Bates, USA (bates@pmel.noaa.gov)

John L. Gras, Australia (john.gras@dar.csiro.au)

Direct Aerosol Radiative Forcing (DARF)

Vacant

Aerosol-Cloud Interactions (ACI)

Thomas Choularton, UK

(tom.choularton@nessie.mcc.ac.uk)

Dean A. Hegg, USA

(deanhegg@atmos.washington.edu)

Stratospheric and Upper Tropospheric Aerosols (SUTA)

H.-F. Graf, Germany (graf@dkrz.de)

M. Patrick McCormick, USA

(mcc@cs.hamptonu.edu)

Fundamental and Cross-Cutting Activities

Polar Atmospheric and Snow Chemistry (PASC)

Leonard A. Barrie, Canada (len.barrie@ec.gc.ca)

Robert J. Delmas, France

(delmas@glaciog.ujf-grenoble.fr)

Global Emissions Inventory Activity (GEIA)

Derek M. Cunnold, USA (cunnold@eas.gatech.edu)

Jos G.J. Olivier, Netherlands (jos.olivier@rivm.nl)

Global Integration and Modeling (GIM)

Maria Kanakidou, Greece

(mariak@chemistry.uch.gr)

Prasad S. Kasibhatla, USA (psk9@duke.edu)

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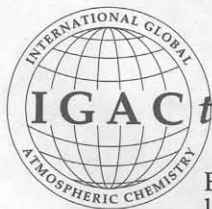
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