POPULAR SUMMARY

Mean ages of stratospheric air derived from in situ observations of CO_2, CH_4, and N_2O

Carbon dioxide concentrations at the Earth's surface show a long-term increase due to fossil fuel combustion. In addition, carbon dioxide varies seasonally because it is removed from the atmosphere during the growing season by photosynthetic plants. Seasonal differences depend on the type and amount of vegetation and on other factors, such as temperature, rainfall, and the length of the day. The seasonal cycle and long-term increase propagate from the surface to high altitudes, eventually reaching the stratosphere. Measurements of carbon dioxide can therefore be used to study the rate at which air moves throughout the atmosphere.

Data from instruments flown on board the NASA ER-2 aircraft and high-altitude balloons have been used to create a map of the average age of stratospheric air, which provides information about how long pollutants will remain in the atmosphere. The data were collected from 1992 through 1998 with nearly pole-to-pole coverage, including all seasons except Southern Hemisphere summer. The resulting comprehensive record of stratospheric carbon dioxide concentrations is unprecedented and extremely precise. The instruments can measure a change in the carbon dioxide concentration of one part in ten million (or 0.00001 percent). The distribution of the average age of stratospheric air will serve as a critical test for models used to understand the response of the stratospheric ozone layer to natural and anthropogenic perturbations, such as volcanic eruptions, the buildup and subsequent gradual decrease of chlorofluorocarbons (CFCs), or emissions from high-flying aircraft like the Concorde. This dataset provides a benchmark for measuring future changes in the stratospheric circulation that might result from climate change or other processes.

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Mean ages of stratospheric air derived from in situ observations of CO_2, CH_4, and N_2O

A. E. Andrews,[1,2] K. A. Boering,[3] B. C. Daube,[1] S. C. Wofsy,[1] M. Loewenstein,[4] H. Jost,[4,5] J. R. Podolske,[4] C. R. Webster,[6] R. L. Herman,[6] D. C. Scott,[6] G. J. Flesch,[6] E. J. Moyer,[6,7] J. W. Elkins,[8] G. S. Dutton,[8] D. F. Hurst,[8] F. L. Moore,[8] E. A. Ray,[8] P. A. Romashkin,[8] and S. E. Strahan[9]

Abstract. Accurate mean ages for stratospheric air have been derived from a spatially and temporally comprehensive set of in situ observations of CO_2, CH_4, and N_2O obtained from 1992 to 1998 from the NASA ER-2 aircraft and balloon flights. Errors associated with the tropospheric CO_2 seasonal cycle and interannual variations in the CO_2 growth rate are < 0.5 year throughout the stratosphere and < 0.3 year for air older than 2 years (N_2O < 275 ppbv), indicating that the age spectra are broad enough to attenuate these influences over the time period covered by these observations. The distribution of mean age with latitude and altitude provides detailed, quantitative information about the general circulation of the stratosphere. At 20 km, sharp meridional gradients in the mean age are observed across the subtropics. Between 20 and 30 km, the average difference in mean age between the tropics and midlatitudes is ~2 years, with slightly smaller differences at higher and lower altitudes. The mean age in the midlatitude middle stratosphere (~25-32 km) is relatively constant with respect to altitude at 5 ± 0.5 years. Comparison with earlier balloon observations of CO_2 dating back to the 1970s indicates that the mean age of air in this region has remained within ±1 year of its current value over the last 25 years. A climatology of mean age is derived from the observed compact relationship between mean age and N_2O. These characteristics of the distribution of mean age in the stratosphere will serve as critically needed diagnostics for models of stratospheric transport.

1. Introduction

Transport of trace species into and within the stratosphere must be accurately represented in models of the stratospheric ozone layer in order to reliably simulate the atmosphere's response to natural and anthropogenic perturbations. Air enters the stratosphere primarily through the tropical tropopause, rises to higher altitudes, then moves poleward and descends at middle and high latitudes, eventually returning to the troposphere [e.g., *Brewer*, 1949; *Dobson*, 1956; *Holton et al.*, 1995]. However, many details of the circulation, such as the altitude dependence of horizontal transport rates and the relative importance of advective and diffusive processes, are still not well quantified, and inadequate representation of constituent transport is perhaps the largest single source of uncertainty in current models of the ozone layer [*Kawa et al.*, 1999].

The "mean age" of stratospheric air has become an important diagnostic for evaluating transport simulations in models of the stratosphere. A stratospheric air parcel may be considered to be comprised of infinitesimal fluid elements with diverse transport histories since crossing the tropical tropopause [*Kida*, 1983; *Hall and Plumb*, 1994]. The statistical distribution of transit times for the fluid elements in the parcel is called the "age spectrum," equivalent to the Green's function between

the boundary at the tropical tropopause and the interior of the stratosphere, and the mean age corresponds to the first moment of this distribution [*Hall and Plumb*, 1994]. Thus the mean age of the parcel is the average transit time from the tropical tropopause, calculated over the ensemble of fluid elements comprising the parcel.

For an inert tracer with a linearly increasing source, the mean age at a given point in the stratosphere would be equivalent to the elapsed time between the occurrence of a particular mixing ratio at the tropical tropopause and the occurrence of the same mixing ratio at the point in the stratosphere [*Hall and Plumb*, 1994]. Several studies have shown that mean ages can be estimated from observations of nearly linearly increasing tracers such as CO_2 [e.g., *Bischof et al.*, 1980, 1985; *Schmidt and Khedim*, 1991; *Nakazawa et al.*, 1995; *Boering et al.*, 1996; *Strunk et al.*, 2000] or SF_6 [e.g., *Maiss et al.*, 1996; *Harnisch et al.*, 1996; *Volk et al.*, 1997; *Strunk et al.*, 2000]. The recent NASA Models and Measurements II (MMII) study revealed a large discrepancy between mean ages predicted by the majority of two-dimensional (2-D) and three-dimensional (3-D) models of the atmosphere and those derived from observations of SF_6 and CO_2, with most models significantly underestimating mean ages compared to observations [*Park et al.*, 1999; *Hall et al.*, 1999]. Several studies have investigated factors controlling mean age in these models and the implications for predicting the stratospheric response to natural or anthropogenic perturbations [e.g., *Bacmeister et al.*, 1998; *Fleming et al.*, 1999; *Li and Waugh*, 1999; *Hall and Waugh*, 2000; *Fleming et al.*, 2001; *Jones et al.*, 2001]. However, uncertainties regarding the nature and significance of the discrepancy between modeled and tracer-based mean ages remain.

Boering et al. [1996] noted that mean age is mathematically equivalent to a conserved tracer with a uniform stratospheric source of 1 yr/yr and may therefore be viewed as an approximate surrogate for exhaust that would be emitted by stratospheric aircraft. Although emissions from any future stratospheric aircraft are likely to be concentrated in the lower stratosphere along certain flight corridors, rather than to be emitted homogeneously throughout the stratosphere, mean age is more representative of aircraft exhaust than most other common tracers of stratospheric transport (e.g., N_2O, CH_4, and the CFCs), which are characterized by tropospheric sources and stratospheric sinks. *Hall and Waugh* [2000] used a simple model to further explore the relationship between mean age and the residence time of stratospheric pollutants and found that mean age and residence time were correlated, although the correlation was imperfect. In particular, the stratospheric residence time was quite sensitive to varying the height of the mid-latitude tropopause, while mean age was largely unaffected.

The results of MMII showed that models with systematically young mean ages tended to have more N_2O and less NO_y and Cl_y than those with older mean ages, raising concern that models which underestimate mean age may also underestimate the impact of chemical perturbations to the stratosphere, such

as an increase in NO_y resulting from a fleet of stratospheric aircraft [*Park et al.*, 1999; *Hall et al.*, 1999]. *Li and Waugh* [1999] obtained similar results using a 2-D model to explore the sensitivity of mean age and long-lived tracers to variations in the transport parameters.

Recently, *Fleming et al.* [2001] compared results from the 1995 and 1999 versions of the NASA Goddard Space Flight Center 2-D model and showed that mean ages in the 1999 version agree much better with mean ages derived from observations. The total ozone simulations for both versions were in reasonably good agreement with each other and with data from the Total Ozone Mapping Spectrometer, but the modeled ozone loss resulting from a perturbation due to exhaust from stratospheric aircraft was a factor of 2.4 larger in the 1999 version, illustrating that simulations of inert tracers can reveal important model transport deficiencies that are not apparent in simulations of chemically active species.

In this paper, we present stratospheric mean ages derived from the extensive set of in situ observations of stratospheric CO_2, CH_4, and N_2O obtained from 1992 to 1998 using the NASA ER-2 aircraft and high-altitude balloons. This work is intended to provide accurate nearly global distributions of stratospheric mean age. Errors in the derived mean ages associated with the seasonal cycle in CO_2 mixing ratios in air entering the stratosphere and with interannual variations in the tropospheric CO_2 growth rate are analyzed. The associated errors are shown to be insignificant for air with N_2O mixing ratios < 275 ppbv, corresponding to mean ages > ~1.9 years. For air with N_2O > 275 ppbv, for which errors in mean age due to seasonal and interannual variations in CO_2 are significant, we use the empirical age spectra derived from CO_2 observations by *Andrews et al.* [1999, 2001] to obtain accurate values for mean age. These mean ages from CO_2 agree with mean ages derived from simultaneous measurements of SF_6 to within 20% and are also consistent with mean ages derived from earlier measurements of both CO_2 and SF_6 in whole air samples obtained using balloon-borne cryosamplers. Finally, a comparison of published CO_2 mixing ratios measured in the midlatitude middle stratosphere since the mid-1970s shows that the mean age in this region has been relatively constant over the past 25 years.

2. Observations

The measurements used in this analysis were obtained on flights of the NASA ER-2 aircraft and high-altitude balloons. The ER-2 measurement campaigns occurred from 1992 to 1998 and included the Stratospheric Photochemistry and Dynamics Expedition (SPADE), the Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA), Stratospheric Tracers of Atmospheric Transport (STRAT), Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS), and a short test flight series in November 1998. The balloon flights were conducted during the Observations of

the Middle Stratosphere (OMS) experiment, which consisted of deployments from Fort Sumner, New Mexico (35°N); Juazeiro do Norte, Ceara, Brazil (7°S); and Fairbanks, Alaska (65°N). The maximum altitude of the ER-2 aircraft is ~21 km, while the balloons typically reached altitudes of ~32 km. Detailed descriptions of the dates and latitude ranges for each deployment are given in Table 1 for the ER-2 deployments and in Table 2 for the balloon flights. This set of data presents a uniquely comprehensive picture of stratospheric composition in time and space, allowing the analysis of mean age to account for spatial, seasonal, and interannual variations that could not be addressed using previously available data.

Mixing ratios of CO_2 were measured by nondispersive infrared absorption by two separate instruments, one on each platform. The design of the balloon CO_2 analyzer was based on that of the ER-2 instrument, with modifications allowing it to operate at much higher altitudes (B. C. Daube et al., A high-precision fast-response airborne CO_2 analyzer for in situ sampling from the surface to the middle stratosphere, submitted to *Journal of Atmospheric Oceanic Technology*, 2001) (hereinafter referred to as (Daube et al., submitted manuscript, 2001)). Note that two of the balloon flights, on September 21, 1996 and June 30, 1997, were nearly spatially and temporally coincident with ER-2 flights. Data from these flights indicated excellent agreement between the balloon and ER-2 instruments. The June 1997 flight showed that the balloon and ER-2 CO_2 instruments agreed to within 0.1 ppmv.

Both CO_2 instruments are calibrated in flight, giving a long-term precision better than 0.1 ppmv from 1992 to 1998 for all deployments except the September and December 1996 deployments of the STRAT experiment, when degradation of a component in the detector led to slightly reduced precision of ~0.15 ppmv. The calibration standards are traceable to standards held by the Scripps Institute of Oceanography (SIO) and to a second set of standards calibrated by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostic Laboratory (NOAA/CMDL). Stratospheric data have been reported on the SIO X95 mole fraction scale. We have participated in two round robin intercomparisons organized by the World Meteorological Organization, so the data can be related to that from the other participating institutions [*Francey*, 1997]. The NOAA/CMDL scale differs by up to 0.2 ppmv from the SIO X95 scale for the relevant range of CO_2 mixing ratios, with the SIO X95 scale having higher values. However, the maximum difference between the SIO X95 and NOAA/CMDL scales is equivalent to a 0.1 year difference in mean age and will be neglected for this analysis.

In the stratosphere, CO_2 is conserved, apart from a small source from CH_4 oxidation. Measurements of CH_4 are available on both platforms and are used to correct for stratospheric production of CO_2, by assuming that the difference between observed CH_4 and the tropospheric value (~1.725 ppmv for this time period) corresponds to the amount of CO_2 produced. CH_4 was measured by the Aircraft Laser Infrared Absorption Spectrometer (ALIAS) on the ER-2 with a stated accuracy of 5%

[*Webster et al.*, 1994]. Since CH_4 data are not available for all flights, we use an average relationship between ALIAS CH_4 and N_2O measurements from the Airborne Tunable Laser Absorption Spectrometer (ATLAS) on the ER-2 (see below):

$$CH_4 = 0.56 + 0.002287\ N_2O + 4.6 \times 10^{-6} N_2O^2, \qquad (1)$$

where CH_4 is given in ppmv and N_2O is in ppbv. For flights where CH_4 data are available, differences between measured CH_4 and the value predicted by (1) are negligible in terms of the CO_2 source correction. Therefore for simplicity we use (1) and measured N_2O to correct for the stratospheric production of CO_2 from CH_4 for all ER-2 flights. Equation (1) is robust over the 6 year time period of the measurements used in this analysis despite increases in the tropospheric mixing ratios of both N_2O and CH_4 during this time, because the growth rates of both species from 1992 to 1998 are relatively small. Note that for other aspects of this analysis, N_2O mixing ratios have been corrected for growth, as described below.

On the balloon flights, CH_4 was measured by the Airborne Laser Infrared Absorption Spectrometer (ALIAS-II) [*Scott et al.*, 1999] with a measurement accuracy of 5%. CH_4 data from ALIAS-II are not available for the November 11, 1997, flight from Juazeiro do Norte, Brazil (7°S). For this flight, methane mixing ratios were estimated using N_2O data from the Argus instrument (see below) and the tropical CH_4:N_2O relationship determined from the Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) [*Michelsen et al.*, 1998]. Several filaments of air which appeared to have been recently transported from midlatitudes were observed during this flight [*Jost et al.*, 1998], for which the midlatitude CH_4:N_2O relationship from ATMOS may provide more accurate estimates of CH_4. However, the difference for the CO_2 correction between the tropical and midlatitude CH_4:N_2O correlations from ATMOS is negligible for this analysis (< 0.15 ppmv) for the relevant range of N_2O mixing ratios.

N_2O was measured on the ER-2 by the ATLAS instrument as described by *Podolske and Loewenstein* [1993] and on the OMS balloon gondola by ALIAS-II and Argus [*Jost et al.*, 1998]. The measurement accuracy for ATLAS and Argus is 2.5%, while that for ALIAS and ALIAS-II is 5%. We corrected for growth in the tropospheric mixing ratio of N_2O from 1992 to 1997 by scaling data from each flight by a factor of $1.0020^{(1997-t)}$, where t is the flight date in years, following *Strahan et al.* [1999]. This factor corresponds to an average trend of 0.2% per year.

SF_6 and CFC-11 were measured by gas chromatography by the four channel Airborne Chromatograph for Atmospheric Trace Species (ACATS-IV) on the ER-2 [*Elkins et al.*, 1996; *Romashkin et al.*, 2001] and by the Lightweight Airborne Chromatography Experiment during the balloon flights [*Ray et al.*, 1999]. The accuracy of the measurements typically ranges from 1 to 4% depending on the species and the flight [*Ray et al.*, 1999].

3. Analysis

Detailed knowledge of the stratospheric boundary condition for CO_2 (i.e., the CO_2 mixing ratio in air entering the stratosphere) is required to calculate mean age from observations of stratospheric CO_2 mixing ratios. Newly stratospheric air encountered by the ER-2 was identified by near-tropospheric N_2O mixing ratios (~310 ppbv), high CO (30 to 50 ppbv), low H_2O (< ~6 ppmv), and potential temperature ≥ 390 K. (In this analysis, we consider only the "stratospheric overworld," as discussed by *Holton et al.* [1995], where isentropes are contained completely within the stratosphere.) Air with these characteristics was frequently sampled by the ER-2 near the tropical tropopause and at higher latitudes in filaments of air recently transported from the tropics. A continuous representation for the observed boundary condition was derived (Figure 1a), assuming that the seasonal cycle is invariant and that the long-term trend can be represented by the deseasonalized (12-month running mean) average of surface data from Mauna Loa (19°N) and Samoa (14°S) delayed by 2 months, as shown by *Boering et al.* [1996]; see *Andrews et al.* [1999] for additional details. Note that the deseasonalized average of data from Mauna Loa and Samoa represents the global surface mean given by *Conway et al.* [1994] to a very good approximation.

The elapsed time since the CO_2 mixing ratio observed in an air parcel (corrected for CH_4 oxidation) last occurred at the tropical tropopause provides a simple estimate of the mean age Γ. For clarity, estimates of the mean age derived in this manner will be called CO_2 lag times Γ_{LAG}. Initially, we will ignore seasonal and interannual variations in CO_2 and calculate Γ_{LAG} using a linear fit to the long-term trend in CO_2 mixing ratios from 1980 to 1998:

$$\Gamma_{LAG} = t - (1749.88 + 0.68241(CO_2 - (1.725 - CH_4))). \quad (2)$$

Here, t is the date of the observation in years, CO_2 and CH_4 are in units of ppmv, and the mean time to add 1 ppmv CO_2 is 0.68241 year (corresponding to a growth rate of 1.47 ppmv yr^{-1}). Note that since we do not have direct observations of the stratospheric boundary condition prior to November 1992, we must assume that the relationship between the stratospheric boundary condition and surface station data has not changed significantly since 1980. Published observations of stratospheric CO_2 from balloons since the 1970s indicate that this assumption is valid (see sedfoihd.fa8).of increase of CO_2 were constant at 1.47 ppmv yr^{-1} and there were no seasonal cycle, Γ_{LAG} would exactly equal the mean age. However, the rate of increase of CO_2 has varied considerably over the last two decades [*Keeling et al.*, 1995], as can be seen by comparing the long-term trend derived from surface data with the linear fit used to calculate Γ_{LAG} (Figure 1a). In fact, the growth rate of the deseasonalized (12-month running average) continuous stratospheric boundary condition varies from 0.5 to >3 ppmv yr^{-1} over this time period (Figure 1b). Furthermore, there is a strong seasonal cycle in

CO_2 mixing ratios in air entering the stratosphere, with a peak-to-peak amplitude of ~3.2 ppmv.

Both the seasonal cycle and interannual variations in the growth rate are potentially large enough to cause substantial error in estimates of mean age from Γ_{LAG}, as noted in a modeling study by *Hall and Prather* [1993]. For example, air with a true mean age of 0 year on July 1, 1992, would have a CO_2 mixing ratio of 357.35 ppmv, according to our continuous representation of the CO_2 stratospheric boundary condition. However, (2) would give a value of -1.2 year for Γ_{LAG}. Similarly, Γ_{LAG} for air with a true mean age of 0 year on July 1, 1993, (CO_2 = 357.85 ppmv) would be -0.6 year. If the CO_2 growth rate were constant at 1.47 ppmv yr^{-1}, Γ_{LAG} would equal -1.1 year for air with a true mean age of 0 year on July 1 of any year, since that is the date of the seasonal maximum in CO_2 mixing ratios and the peak-to-peak amplitude of the seasonal cycle is ~3.2 ppmv.

As air moves through the stratosphere, air parcels with differing transit times since crossing the tropical tropopause mix, and the effects of seasonal and interannual variations in CO_2 on mean age are attenuated. The amount of attenuation depends on the width of the age spectrum [*Hall and Plumb*, 1994; *Andrews et al.*, 1999, 2001]. The examples above for air with a true mean age of 0 year represent a special case, where the age spectrum is a delta function with a spectral width of 0 year.

We have shown elsewhere that for air younger than ~3 years the comprehensive data set for CO_2 from 1992 to 1998 provides sufficient information to derive detailed empirical age spectra [*Andrews et al.*, 1999, 2001]. The seasonal cycle and growth rate changes were used in those analyses to estimate the width and shape of the age spectrum. We can thus use the first moment of the derived age spectra to provide accurate estimates of Γ as a function of N_2O for air younger than 3 years. As shown in section 4.1, mean ages calculated from the age spectra are in good agreement with CO_2 lag times averaged over the 1992-1998 data sets for latitudes with frequent coverage.

Little is known, however, about the age spectral width for older air, and it is not immediately obvious that using a single average growth rate from 1980 to 1998 will provide accurate estimates of the mean age. The growth rate calculated over various averaging periods is shown in Figure 1b. For example, in mid-1995 the "instantaneous" growth rate of the deseasonalized CO_2 boundary condition is 2.2 ppmv yr^{-1}, while the average calculated over the preceding 5 year period (mid-1991 to mid-1995) is only 1.1 ppmv yr^{-1}. These values bracket the long-term average growth rate of 1.47 ppmv yr^{-1}. For a 5 ppmv lag in CO_2 relative to the boundary condition, the mean age corresponding to these growth rates would be 2.3, 4.5, and 3.4 years, respectively. Intuitively, an average growth rate computed over a shorter (longer) interval seems more appropriate for determining mean ages for younger (older) air, but implementing such a strategy is complicated. Fortunately, our analysis shows that errors associated with the propagation of

seasonal and interannual variations in tropospheric CO_2 into the stratosphere are small (<0.3 year) for air with Γ > ~2 years, suggesting that the stratospheric age spectra are sufficiently wide to attenuate CO_2 fluctuations around the long-term trend during the period over which the sampled air entered the stratosphere.

Figure 2 illustrates another potential complication for deriving stratospheric mean ages from measurements of CO_2. CO_2 mixing ratios in air extracted from ice cores [*Etheridge et al.*, 1996] provide a measure of atmospheric CO_2 levels prior to 1958, when the first routine measurements of atmospheric CO_2 were begun [*Keeling and Whorf*, 1994]. These data indicate a dramatic change in the CO_2 growth rate between 1960 and 1980 (Figure 2a). In order to investigate whether such a change in the slope of the CO_2 boundary condition could significantly affect the mean age calculation, theoretical age spectra with a mean age of 5 years and varying width (Figure 2b) were convolved with a boundary condition comprised of the long-term trend shown in Figure 2a plus a seasonally varying component (as in Figure 1).

As shown in Figures 2c and 2d, age spectra with long exponentially decaying tails pick up enough very old air to produce significant deviations from the CO_2 time series that would result from a constant growth rate. However, after 1984 the calculated mean ages are within 0.5 year of the true mean age for all but the widest test spectrum, which has a modal time (time of maximum probability) of 0.3 year and a tail so long that 13% of the air has been in the stratosphere more than 10 years (6% for more than 20 years). This anomalous age spectrum would require rapid transport of a large amount of air from the troposphere to the measurement location. However, mean ages of 5 years were found only for midlatitude and high-latitude balloon flights above 25 km and at ER-2 altitudes in filaments of air that had descended in the polar vortices. Large-scale transport of air from the tropical tropopause to altitudes >25 km on timescales of a few months is not consistent with current understanding of stratospheric transport. Thus a change in slope of the CO_2 stratospheric boundary condition prior to 1980 is unlikely to cause large errors in mean age estimates from measurements made from 1992 to 1998. For spectra with $\Delta^2/\Gamma \leq 5$ years, errors in the calculated mean age are < 10%. Note that before 1980, the change in the CO_2 growth rate is evident in the calculated CO_2 time series even for relatively narrow age spectra. This should be considered when comparing recent measurements with earlier stratospheric CO_2 data, as in section 4.3.2. Tests using age spectra with mean ages of 4 and 7 years yielded similar results.

4. Results and Discussion

4.1. Results From the ER-2 Aircraft Data

Boering et al. [1994, 1996] showed that, below 21 km, stratospheric CO_2 and N_2O are compactly related over a wide range of latitudes. N_2O is photolyzed rapidly at high altitudes but has a relatively long lifetime (years) below ~30 km. Thus,

on average, N_2O mixing ratios decrease with altitude throughout the stratosphere. There are significant motions of air associated with planetary scale waves that displace tracer isopleths vertically but do not affect relationships among long-lived tracers [Ehhalt et al., 1983]. To remove this source of apparent variance, we use N_2O as a convenient vertical coordinate for analysis of CO_2 data. The spatial distribution of mean age is then obtained using mean distributions of N_2O with potential temperature and equivalent latitude [Strahan et al., 1999]. Equivalent latitude is a coordinate based on potential vorticity, which is nearly conserved on timescales typical of reversible wave transport [e.g., Nash et al., 1996]. By analyzing the CO_2 data using Γ_{LAG}, we can explore the consistency of the relationship between CO_2 and N_2O from deployment to deployment and from year to year, which is otherwise complicated by the long-term increase in CO_2 mixing ratios.

Figure 3 shows Γ_{LAG} plotted as a function of N_2O for all of the ER-2 data collected from 1992 to 1998. The data span latitudes from 70°S to the North Pole with data in both hemispheres for all seasons except Southern Hemisphere summer. N_2O data were corrected for tropospheric growth over this period as described above. The 1σ uncertainty on the average Γ_{LAG} is < 0.3 year for air with 70 ppbv $\leq N_2O \leq 275$ ppbv. The small standard deviation in Γ_{LAG} for a given value of N_2O provides evidence that age spectra in the lower stratosphere are wide enough to dampen seasonal variations and fluctuations in the CO_2 growth rate that occurred over the time period that the sampled air entered the stratosphere. Air with $N_2O = 275$ ppbv has a mean age of 2.0 years, corresponding to a CO_2 difference of 2.94 ppmv relative to the boundary condition, assuming a growth rate of 1.47 ppmv yr^{-1}. The observed 1σ variation of ~0.3 year in the calculated mean age corresponds to a variance in the average CO_2 growth rate of ± 0.2 ppmv yr^{-1}. This represents an upper limit, neglecting uncertainty in the measured CO_2 and N_2O mixing ratios. For older air, with larger CO_2 differences and smaller uncertainty in Γ_{LAG} (< 0.2 year), the CO_2 growth rate is even more tightly constrained. Air with $\Gamma_{LAG} = 5$ years ($N_2O = 110$ ppbv) reflects a nearly invariant average CO_2 growth rate of 1.47 ± 0.05 ppmv yr^{-1}. Uncertainty in Γ_{LAG} increases for $N_2O < 80$ ppbv, but these values represent relatively few data points, which were obtained in filaments of polar vortex air that had mixed to varying degrees with air from midlatitudes.

Figure 4a shows Γ_{LAG} plotted as a function of N_2O for data collected from the ER-2 aircraft within 2.5° of the NASA Ames Research Center in Moffett Field, California (37.4°N) from 1992 to 1998 during each of the four seasons. Note that there is very little seasonal variation in this relationship for 200 ppbv $< N_2O < 275$ ppbv. The corresponding standard deviations indicate that interannual variations are also small (Figure 4b). For air with $N_2O > 275$ ppbv (corresponding to altitudes $< ~19$ km at this latitude), the influence of the CO_2 seasonal cycle propagating from the troposphere via the tropical stratosphere is evident: artificially young (old) mean ages are calculated in summer (winter) when the observed CO_2 con-

centration in the extratropical stratosphere is at its maximum (minimum). *Andrews et al.* [2001] showed that the CO_2 seasonal cycle is still discernible for air with $N_2O = 275$ ppbv but that the peak-to-peak amplitude is reduced to 0.8 ppmv, corresponding to small errors in the mean age ($< \pm 0.3$ year). The seasonal variations in Γ observed for air with $N_2O < 200$ ppbv are apparently due not to the propagation of tropospheric seasonal variations, but rather to the mixing of remnants of the polar vortex with air from lower latitudes during spring [*Waugh et al.*, 1997].

When averaged over all seasons and years, the relationship between Γ_{LAG} and N_2O is remarkably invariant over a large range of latitudes (Figure 4c). Nevertheless, estimates of the mean age from Γ_{LAG} for a particular flight are subject to significant error for air with $N_2O > 275$ ppbv due to seasonal and interannual variations in CO_2 mixing ratios propagating from the tropical tropopause, as evidenced by the sharp increase in the standard deviation of the average Γ_{LAG} at all latitudes (Figure 4d). For the individual deployments, typical (Northern Hemisphere) NH midlatitude CO_2 standard deviations in a 10 ppbv N_2O bin centered at 295 ppbv were < 0.4 ppmv [*Andrews et al.*, 2001], corresponding to uncertainties in Γ_{LAG} of < 0.3 year. Thus the increased standard deviations seen in Figures 4b and 4d are not explained by increased measurement uncertainty at high values of N_2O.

A method for estimating Γ for a particular flight that is not sensitive to errors associated with seasonal and interannual variations in CO_2 mixing ratios is highly desirable. *Andrews et al.* [2001] showed that for NH midlatitudes, empirical age spectra can be derived from the time series of CO_2 observations for air with $N_2O \geq 235$ ppbv, where seasonal and interannual oscillations in CO_2 propagating from the troposphere provide information about transport processes occurring on multiple timescales. They found that the data are consistent with a seasonally invariant relationship between mean age and N_2O. This relationship is essentially equivalent to the cubic fit to the averaged Γ_{LAG}:N_2O correlation shown in Figure 3, within ± 0.05 year.

Thus for observations at NH midlatitudes we can apply the relationship between mean age from the empirical age spectra Γ_{SPEC} and N_2O to estimate mean ages from measured N_2O for air with $N_2O > 275$ ppbv, thereby avoiding complications caused by the seasonal cycle and variability in the CO_2 growth rate. For N_2O data with uncertainty $\leq 2.5\%$, this method provides mean ages with an uncertainty of < 0.5 year. Figure 4c suggests that the average Γ_{SPEC}:N_2O relationship provides mean ages with errors of < 0.5 year regardless of latitude at ER-2 altitudes. (Whether this result extends to higher altitudes is considered in section 4.2.)

To further explore whether the relationship between Γ_{SPEC} and N_2O derived from midlatitude data applies in the tropics, we compare to mean ages from tropical age spectra derived by *Andrews et al.* [1999] (Figure 5). Mean ages from the tropical age spectra agree to within 0.3 year with those predicted by applying the midlatitude Γ_{SPEC}:N_2O relationship to tropical

N_2O data, except in NH late winter/early spring, when the mean ages from the tropical age spectrum analysis are youngest. The observed tropical N_2O mixing ratios were slightly lower in March 1994 and February 1996 than at other times of year, which should correspond to older air according to the relationship between Γ_{SPEC} and N_2O derived for midlatitudes. As noted by *Andrews et al.* [1999], the seasonality in the derived tropical age spectra relies heavily on the results for a single profile (February 1996). However, the variations in the tropical N_2O mixing ratios are of the order of the accuracy of the ATLAS instrument, so it is not clear whether the apparent differences in the seasonal mean ages are significant. In any case, the maximum error incurred by applying the midlatitude $\Gamma_{SPEC}{:}N_2O$ relationship in the tropics is 0.5 year. Although this amounts to a difference of nearly 100% for these young ages, knowledge of the tropical mean age to better than 0.5 year places a tight constraint on models of the stratospheric circulation.

We showed above that Γ_{LAG} provides a precise estimate of the mean age for air with $N_2O < 275$ ppbv and that we can use the relationship between Γ_{SPEC} and N_2O derived for midlatitudes to estimate mean age for air with $N_2O > 275$ ppbv, regardless of latitude. While this approach produces the correct average distribution of mean age, it creates a small discontinuity in the mean age at $N_2O = 275$ ppbv for most flights. To avoid this, we introduce the following functional form for Γ, with a smooth transition from Γ_{SPEC} to Γ_{LAG}:

$$\Gamma = \Gamma_{LAG} = t - (1749.88 + 0.68241(CO_2 - (1.725 - CH_4)))$$
$$N_2O < 235 \text{ ppbv}$$

$$\Gamma = 0.025(275 - N_2O)\Gamma_{LAG} + (1 - 0.025(275 - N_2O))\,\Gamma_{SPEC}$$
$$235 \text{ ppbv} \leq N_2O \leq 275 \text{ ppbv}$$

$$\Gamma = \Gamma_{SPEC} = 0.0566(313 - N_2O) - 0.000195(313 - N_2O)^2$$
$$N_2O > 275 \text{ ppbv}. \tag{3}$$

Here the units of CO_2 and CH_4 are ppmv, and N_2O has units of ppbv. Equation (3) produces a smooth profile of mean age for each flight. Errors associated with the persistence of seasonal and interannual variations in the growth rate of CO_2 are < 0.5 year. In the following discussion the symbol Γ refers to mean ages calculated using (3).

Figure 6a shows the latitudinal distribution of Γ at 20 ± 0.5 km, corresponding to the cruise altitude of the ER-2 aircraft. The shaded symbols represent 10-s averages of the data along the flight track, and the large solid symbols with error bars represent the median value in overlapping 5° latitude bins. Note the large meridional gradients in the subtropics of both hemispheres. Similar gradients have been observed for other tracers, for example, NO_y/O_3 [*Murphy et al.*, 1993]. This feature is a sensitive indicator of meridional exchange between the tropics and higher latitudes [*Plumb*, 1996] that most models of the stratosphere currently fail to simulate [*Park et al.*, 1999; *Hall et al.*, 1999].

The latitudinal variation of Γ is compared in Figure 6b with that calculated by simply averaging Γ_{LAG}. Since NH data are available for many seasons over a period of several years, Γ and Γ_{LAG} produce nearly identical results, as expected based on Figures 3 and 4. There is good agreement between Γ and Γ_{LAG} for the middle and high latitudes of both hemispheres, which implies that the corresponding age spectra are sufficiently broad to dampen the effects of seasonal and interannual variations in CO_2 during the time period over which the data were acquired.

In the southern tropics and subtropics, however, Γ_{LAG} is as much as 0.8 year older than Γ. The reason for this difference is twofold. First, we do not have Southern Hemisphere (SH) data for December - February (Figure 6c), the time of seasonal maximum in CO_2 concentrations in the tropics at 20 km. The seasonal maximum in CO_2 corresponds to artificially young ages, and since these data are lacking, the average is skewed toward older ages. Second, as discussed above, interannual variations in the CO_2 growth rate propagating into the stratosphere can cause significant (for air with $N_2O > 275$ ppbv) bias in Γ_{LAG}, which is calculated assuming a linear growth rate. The SH data shown in Figure 6a were acquired from March to October 1994; thus the data from the equator to 20"S, with values for Γ of 1 ± 0.5 year, represent air that entered the stratosphere between early 1993 and early 1994. According to Figure 1, the annual mean (i.e., deseasonalized) CO_2 mixing ratios in air entering the stratosphere were lower than the linear fit used to calculate Γ_{LAG} (equation (2)) by 0.25 to 1 ppmv throughout this time period, which corresponds to a bias toward older ages of 0.1 - 0.7 year and is therefore consistent with the size of the observed discrepancy. Based on the NH data, Γ and Γ_{LAG} should converge if more seasons and years are sampled in the SH stratosphere.

The only significant seasonal variation in the average Γ at 20 km is found in the NH subtropics where mean ages during December-February are older by ~1 year than for March-August and older by ~2 years than for September-November (Figure 6c). There is also some variation in the SH subtropics, but the data for this region are temporally too sparse to interpret, as discussed above. Subtropical variations in mean age may be associated with the seasonal migration of the boundary of the tropical upwelling region. Using observations of the distribution of stratospheric aerosols, *Grant et al.* [1996] found that the northern boundary of the tropics did not extend north of 20°N from November to March 1991, while there were frequent excursions farther north during the rest of the year. A mean age maximum during NH winter is consistent with this migration. Note that we would also expect to see significant seasonal variations at high latitudes associated with the polar vortices, but this analysis does not include data for the south polar region during southern summer or for the north polar regions during northern winter.

In order to obtain further information about the spatial distribution of mean age, we used the polynomial relationship between average Γ_{LAG} and N_2O shown in Figure 3 to generate

distributions of mean age as a function of equivalent latitude and potential temperature, by mapping this relationship onto the seasonally resolved N_2O climatology of *Strahan et al.* [1999] (Figure 7). This function gives values of Γ that are within 10% of the value calculated using (3) for all but 2% of the individual measurements and that are within 15% of the value calculated using (3) for all but 0.2% of the data. The resulting distributions provide a comprehensive picture of mean age in the lower stratosphere that can easily be compared with output from numerical models. Contours of mean age are relatively symmetric about the equator during NH spring, and old air descending in the polar vortex can be seen during winters in both hemispheres. Note that our analysis did not include any data north of ~60°N for the December-February period, but high-latitude winter data were included in the N_2O climatology from earlier deployments. Thus we have assumed that the Γ:N_2O relationship is valid in the polar vortex at these altitudes. Data obtained in the 1999/2000 Arctic vortex during the Sage III Ozone Loss and Validation Experiment (SOLVE) indicates that this is valid.

4.2. Extension to Higher Altitudes

The OMS flights produced a unique set of in situ observations of CO_2, N_2O, CH_4, O_3, H_2O, SF_6, CFC-11, CFC-12, and Halon-1211 up to 32 km. Data were obtained in the tropics and at NH middle and high latitudes from 1996 to 1998 during several seasons. In this section, vertical profiles of mean age are presented for each of the balloon flights and the relationships between mean age and N_2O and CFC-11 above ER-2 altitudes are explored.

We first consider whether (3) can be used to obtain mean ages for the balloon profiles. This should not present a problem at middle and high latitudes, since air with N_2O > 275 ppbv was not encountered above 21 km, the maximum altitude of the ER-2. However, in the tropics, air with N_2O > 275 ppbv was sampled up to 23 km. Figures 8a and 8b show Γ_{LAG} as a function of N_2O for each extratropical and tropical balloon flight. Average relationships between Γ_{LAG} and N_2O for the tropics and extratropics were produced from the OMS data by calculating the average relationship for each flight, then averaging the results according to latitude (Figure 8c). The February and November results were weighted equally in determining the average tropical relationship. The polynomial relationship derived from ER-2 data is shown for comparison in Figures 8a and 8c. The "reference correlation" of *Strunk et al.* [2000], derived from CO_2 and N_2O data in whole air samples from 10 middle and high-latitude balloon flights, is also shown in Figure 8a; agreement is relatively good, although we obtain ages that are 10-20% older than their reference correlation for air with 275 ppbv > N_2O > 175 ppbv. Part of the discrepancy may be due to the fact that Strunk et al. calculate mean age relative to the surface rather than the tropical tropopause, but this should amount to a difference of only 2 months and would appear as an offset over the entire range of N_2O values.

For air with N_2O > 275 ppbv, the agreement between the average relationship from the ER-2 data and the average Γ_{LAG} for both the tropical and the extratropical balloon flights is somewhat surprising, given the limited number of balloon profiles. Errors in the averaged Γ_{LAG} resulting from seasonal and interannual variations in CO_2 are fortuitously negligible for the tropical balloon flights due to fortunate timing. For example, the age spectrum analysis of the tropical ER-2 data [*Andrews et al.*, 1999] shows that the vertically propagating CO_2 seasonal cycle in February is roughly 180° out of phase with respect to November below 460 K, so we expect that errors in Γ_{LAG} associated with the persistence of the seasonal cycle will largely cancel when data from these months are averaged. At higher potential temperatures, error due to the seasonal cycle would be < 0.4 year, even if there were no cancellation, because the peak-to-peak amplitude is small [*Andrews et al.*, 1999]. Also from 1995 to 1998 the long-term trend in CO_2 mixing ratios entering the stratosphere is nearly indistinguishable from the linear fit used to calculate Γ_{LAG}. Thus for a "young" air parcel that does not contain a large amount of air that entered the stratosphere prior to 1995, errors due to interannual variation in the CO_2 growth rate are small for all of the OMS flights. Older air parcels are likely to have wide enough age spectra to dampen errors due to fluctuations in the CO_2 growth rate. We therefore conclude that it is legitimate to use (3) to generate smooth profiles of mean age for each of the OMS balloon flights to date. Note, however, that uncertainty in Γ depends on the accuracy of available N_2O data. Uncertainty in individual values of Γ for OMS flights can be as large as ± 1 year because available N_2O data typically has an estimated accuracy of 5%.

The ER-2 and OMS data demonstrate that the relationship between Γ and N_2O is remarkably invariant over a wide range of latitudes and altitudes. In contrast, there is significant latitudinal variation in the relationship between Γ and CFC-11 (Figure 8d). The existence of a compact relationship between two species with different chemical lifetimes provides information about transport timescales [*Plumb and Ko*, 1992]. Evidently, at ER-2 and OMS altitudes, horizontal exchange across the subtropics occurs rapidly compared to the lifetime of N_2O (a few years at 30 km), but photochemical loss is faster than meridional transport for CFC-11, which has a lifetime of a few months at these altitudes. We would expect the invariance of the relationship between Γ and N_2O to break down where the lifetime of N_2O becomes very short, for example, at higher altitudes in the tropics. The ability to simulate relationships among tracers with varying lifetimes is a key test of transport parameterizations in models of the stratosphere.

Mean ages calculated using (3) are shown versus potential temperature in Plate 1 for the OMS flights. Tropical ages are ~2 years younger than extratropical ages on the same isentrope over most of the potential temperature range. *Neu and Plumb* [1999] showed that in a simple model this difference is a fundamental property of the circulation that depends primarily on the vertical velocity in the tropics. These results represent the

first observations of the mean age difference between the inner tropics and midlatitudes above ~20 km. Evidence of large-scale mixing events can also be seen in the mean age profiles in Plate 1. As discussed below, remnants of the 1996/1997 Arctic polar vortex are evident in the June 1997 profile from Fairbanks, Alaska (65°N) near 520 and 625 K. Filaments of extratropical air appear in both of the November 1997 profiles from Juazeiro do Norte, Brazil (7°S), indicating that air at that latitude was not completely isolated from midlatitudes at that time.

The May 1998 OMS flight from Fort Sumner, New Mexico (35°N) is characterized by a region of nearly constant mean age above ~550 K (~22.5 km). SF_6 data from the September 1996 flight indicate a similar feature above ~650 K (~26 km). Unfortunately, there are no CO_2 data available above 640 K (~25.5 km) for that flight. A region of nearly constant mean age is present in almost every midlatitude balloon profile of CO_2 and SF_6 to date, starting between 20 and 26 km and extending to the maximum altitude of the profile (~32 km), with typical mean ages of 4-6 years in this region [*Bischof et al.*, 1980, 1985; *Schmidt and Khedim*, 1991; *Nakazawa et al.*, 1995; *Harnisch et al.* 1998]. We present a detailed comparison of these measurements and consider implications for models of transport in section 4.3.2.

Although the relationship between Γ and N_2O has been shown to be remarkably compact, careful examination of data from the nearly coincident balloon and ER-2 flights of June 30, 1997, reveals subtle but significant differences in the $N_2O{:}\Gamma$ relationship at ER-2 altitudes versus higher altitudes (Plate 2). Using data from ATMOS, *Michelsen et al.* [1998] suggested that distinct relationships between mixing ratios of N_2O and CH_4 can be used to identify air with tropical, midlatitude, or polar vortex character. *Herman et al.* [1998] showed that the $N_2O{:}CH_4$ relationships observed during these OMS flights are in good agreement with the ATMOS relationships and that air with both midlatitude and vortex character was sampled during the June 30, 1997, balloon flight. Air characterized by the "vortex-like" $N_2O{:}CH_4$ relationship corresponds to distinct features in the tracer profiles, the sharp minima in CO_2 (maxima in mean age) at ~520 K and 640 K (Plate 2a). The presence of such sharp features was a surprise given that the vortex had broken up several months earlier. Note that the ER-2 only sampled air with low N_2O values in the vortex remnants, while the balloon sampled air with low N_2O both in the vortex remnants and aloft. From 10 km to the maximum altitude of the ER-2, the median difference between the ER-2 and balloon CO_2 data was 0.04 ppmv, well within the combined uncertainties of the instruments (Daube et al., submitted manuscript, 2001).

The relationship between CO_2 and N_2O for this flight is shown in Plate 2b for air with $\Gamma > 3.5$ years ($CO_2 > 358$ ppmv). Balloon data classified as "midlatitude-like" exhibit a slightly sigmoidal (S-shaped) correlation, while the correlations corresponding to the vortex remnants are significantly straightened. One interpretation of the data in Plate 2b

is that the correlations for the vortex remnants reflect downwelling of midlatitude-like air from high altitudes in the polar vortex followed by mixing with midlatitude air at lower altitudes, either as midlatitude air was entrained into the vortex [*Plumb et al.*, 2000] or after the vortex had broken up [e.g., *Waugh*, 1997], resulting in a straightening of the relationship across the "concave down" portion of the high-altitude correlation. However, data from the April 26, 1997, ER-2 flight are included in Plate 2b to show that the correlations in the vortex remnants in July could also be interpreted as a straightening of the relationships across the "concave up" correlation observed near the edge of the polar vortex in April. For comparison, Plate 2c shows the relationship between Γ and N_2O for the same data. Because mean age is not conserved in the stratosphere (having a uniform source of 1 yr/yr), in general it is more appropriate to examine particular mixing events using CO_2 corrected for CH_4 oxidation, which is conserved. Accounting for the source of mean age would be equivalent to adding 0.18 year to the mean ages for April 1997 in Plate 2c.

4.3. Comparison With Other Estimates of Mean Age

4.3.1. Mean ages from simultaneous measurements of SF_6.
We first consider mean ages derived from measurements of SF_6 obtained concurrently with the CO_2 data used in this analysis. Figure 9 shows a scatterplot of all the mean ages derived from CO_2 and SF_6 measurements obtained using the ER-2 aircraft (~3000 points). Mean age estimates are derived from stratospheric SF_6 mixing ratios using the expressions of *Volk et al.* [1997]. The boundary condition is the global mean surface time series of SF_6 [*Geller et al.*, 1997] with an imposed delay of 0.8 year representing the transit time for surface air to reach the tropical tropopause. The delay time is chosen to give the best agreement with measured tropical tropopause concentrations where available.

There is excellent agreement between the CO_2 and SF_6 estimates for mean ages up to ~3 years, while for older air the SF_6 ages are ~ 20% older. Results are similar for OMS data, with mean ages derived from SF_6 10-20% older than the corresponding mean ages from CO_2 [see *Park et al.*, 1999; *Hall et al.*, 1999]. *Strunk et al.* [2000] reported somewhat better agreement (± 0.5 year, ~10%) between mean ages derived from SF_6 and CO_2 in whole air samples obtained during balloon flights at midlatitudes and high latitudes referenced to the surface rather than the tropical tropopause.

There are several possible explanations for differences between mean ages derived from SF_6 and CO_2. The growth rate for SF_6 is slightly nonlinear, and a correction factor based on the width of age spectra in the lower stratosphere from models was applied to calculate the SF_6 ages [*Volk et al.*, 1997]. Errors in the correction could lead to a systematic bias that would be largest for old ages. Note that *Volk et al.* [1997] claimed only that the correction was valid for the lower stratosphere (< 21 km), although here and in the work of *Strunk et al.* [2000] the correction was applied to balloon data obtained up to ~30 km. Also uncertainty in the stratospheric boundary

condition for SF_6 gives rise to uncertainty of the order of ± 0.5 year in derived mean ages. Finally, there is the possibility that mesospheric loss of SF_6 leads to artificially old mean ages from SF_6 observations [*Hall and Waugh*, 1998]. Some evidence for the latter theory is found in the data from the June 30, 1997, OMS flight from Fairbanks, Alaska (65°N). Mean ages from CO_2 were oldest at the top of the profile, while mean ages from SF_6 were significantly older in remnants of the polar vortex [see *Hall et al.*, 1999, Figure 5], consistent with the idea that SF_6 is destroyed at high altitudes. A similar anomalous discrepancy between mean ages from SF_6 and CO_2 in whole air sampled during a balloon flight over southern France on June 23, 1997, has been attributed to mesospheric loss of SF_6 [*Strunk et al.*, 2000]. Preliminary analysis of data from the 1999/2000 Arctic vortex during the SOLVE campaign also indicates substantial mesospheric loss of SF_6 (F. L. Moore, manuscript in preparation, 2001).

4.3.2. Comparison with previous measurements of CO_2 in the middle stratosphere. *Schmidt and Khedim* [1991] compiled a list of CO_2 measurements from balloon-borne cryo-samplers through 1990 that includes 21 flights at middle or high latitudes in the Northern Hemisphere. All of these profiles were characterized by a region of nearly constant CO_2 mixing ratio at the top of the profile. They reported an average mean age corresponding to this region of 5.6 ± 1.1 years, in good agreement with the mean ages from the OMS flights over Fort Sumner, New Mexico (35°N) and Fairbanks, Alaska (65°N), although with relatively large uncertainty. A time series of the average mixing ratio corresponding to the region of near-constant CO_2 for each of the profiles given by *Schmidt and Khedim* [1991] is shown in Figure 10 along with CO_2 data from the same region for OMS flights presented here. Data from *Nakazawa et al.* [1995] and *Harnisch et al.* [1998] are also shown.

The data presented in Figure 10 have not been corrected for stratospheric CO_2 production by CH_4 oxidation. During OMS, CH_4 in the midlatitude middle stratosphere was ~1000 ppbv on average, and the tropospheric value was ~1725 ppbv. Thus the correction applied to the CO_2 data would be 1.725 – 1.000 = 0.725 ppmv, or 42% of the tropospheric CH_4 mixing ratio, and neglecting to account for stratospheric CO_2 production by CH_4 oxidation would result in mean ages that are too young by approximately (0.725 ppmv)/(1.47 ppmv yr^{-1}) = 0.5 year. In 1975 the tropospheric CH_4 mixing ratio was ~1440 ppbv, implying a correction to the midlatitude middle stratospheric CO_2 data of 0.60 ppmv, according to the relationship between midstratospheric and tropospheric CH_4 observed during OMS. Differences in the CO_2 correction due to the tropospheric trend in CH_4 over this time period are therefore likely to be < 0.2 ppmv, unless the rate of stratospheric CH_4 oxidation has changed substantially since 1975.

When corrected for CH_4 oxidation, the CO_2 data from the extratropical OMS flights correspond to a lag time with respect to the stratospheric boundary condition of 5.0 ± 0.5 years. This value is notably consistent with the *Nakazawa et al.*

[1995] data obtained from 1985 to 1991 and with the *Bischof et al.* [1985] and *Volz et al.* [1981] data obtained from 1976 to 1984 (as reported by *Schmidt and Khedim* [1991]), although in general the earlier data have larger uncertanties. Data for the OMS flight of September 21, 1996, are not included since there are no CO_2 data above ~25 km for that flight, but analysis of concurrent observations of SF_6 indicates that the mid-stratospheric mean age is similar to that obtained for the May 18, 1998, flight. For the OMS and *Nakazawa et al.* [1995] data, the error bars represent the standard deviation of the CO_2 mixing ratio in the near constant region. For OMS the measurement precision is 0.1 ppmv, corresponding to the size of the symbols in Figure 10b. Error bars for *Volz et a.l* [1981] and *Bischof et al.* [1985] are as given by *Schmidt and Khedim* [1991].

The data reported by *Schmidt and Khedim* [1991] and by *Harnisch et al.* [1998] have considerably more scatter than the other data sets. The error bars in Figure 10b on the Schmidt and Khedim data are as given in that study, but a later paper by that group [*Strunk et al.*, 2000] stated that the precision on the earlier measurements was ±1 ppmv. Schmidt and Khedim attributed the variability in their calculated ages to real changes in the large-scale stratospheric circulation, but that interpretation seems inconsistent with the observations of *Nakazawa et al.* [1995] during the same time period, which show little variability.

The CO_2 values shown for *Harnisch et al.* [1998] were obtained by averaging their midlatitude data for altitudes greater than 20 km, and the error bars represent 1 standard deviation of the mean. Their stated measurement precision is ± 0.2 ppmv. Interestingly, they report mean ages from SF_6 for both of these flights that are consistent with the 5.0 ± 0.5 year mean ages implied by the ensemble of CO_2 data. Moreover, while their SF_6 profiles are characterized by a smooth decrease with a region of near-constant mixing ratio at the top of the profile, like the CO_2 and SF_6 profiles discussed above, their CO_2 profiles are noisy. They also reported N_2O mixing ratios, which facilitates comparison of their observations from 1993 and 1995 at 20 km (215 ± 5 pbbv N_2O for both flights) with CO_2 data from the ER-2 from 1992 to 1998 and from the OMS balloon flights (Figure 11). The height of the symbols reflects the 1σ standard deviation in the average of the ER-2 and OMS CO_2 data. The ER-2 and OMS data show a linear increase with time on the 215 ppbv N_2O isopleth, consistent with the average tropospheric trend, but *Harnisch et al.* [1998] observed a decrease in corresponding CO_2 mixing ratios between 1993 and 1995. This decrease is even larger at other altitudes (1-2 ppmv), despite very similar N_2O profiles for the two flights. It is difficult to imagine a plausible transport scenario capable of explaining these discrepancies. *Strunk et al.* [2000] reported good agreement between mean ages calculated from SF_6 and CO_2 in whole air samples from the Arctic and midlatitude stratosphere and argued that the CO_2 mixing ratios reported by *Harnisch et al.* [1998] may have been affected by contamination or sample degradation.

The consistency between our results and those of *Nakazawa et al.* [1995], *Bischof et al.* [1980, 1985], and *Volz et al.* [1981] suggests that the mean residence time of air in the middle stratosphere has remained within 1 year of its current value over the past 25 years. However, as noted above, we would expect CO_2 mixing ratios to have been influenced by the dramatic change in the CO_2 growth rate that occurred between 1960 and 1980. Figure 2d indicates that air with a mean age of 5 years would have CO_2 mixing ratios at least 1.5 ppmv higher than predicted for a constant CO_2 growth rate, if the real age spectrum resembles any of the test spectra. The fact that CO_2 mixing ratios were not measurably elevated in the early flights relative to the long-term trend suggests that the age spectrum for this region is rather narrow, although it is possible that transport rates have changed over this period in such a way as to mask a change in the slope of the CO_2 time series. The ability of models to reproduce the midlatitude midstratospheric CO_2 time series will provide a useful diagnostic. This analysis illustrates the potential value of a time series of high-accuracy CO_2 measurements as an indicator of changes in the circulation. In addition, future changes in the CO_2 growth rate may allow more detailed information about the age spectrum to be inferred from observations.

The repeated observation of a region characterized by near-constant mean age in the midlatitude stratosphere also has implications for understanding the general circulation of the stratosphere. *Bischof et al.* [1985] found that profiles with this shape could not be reproduced using a simple time-dependent one-dimensional diffusion model and suggested that the shape may result from tropical upwelling followed by poleward transport in the middle and upper tropical stratosphere. *Nakazawa et al.* [1995] noted that the profiles are consistent with more rapid poleward motion near the tropopause than at higher altitudes, a transport scenario that has also been invoked to explain numerous observations from satellites, balloons, and aircraft over the last decade.

The shape of the midlatitude CO_2 profiles, as well as the observed mean ages in the midlatitude middle stratosphere, provide corroborative evidence for the validity of the bimodal age spectra derived for the midlatitude lower stratosphere from this time series of CO_2 observations by *Andrews et al.* [2001]. The younger peak in their derived age spectra (corresponding to air younger than 1 year) was thought to represent air transported quasihorizontally from the tropical stratosphere, while the older peak (consisting of air that has been in the stratosphere for 4 to 6 years) represents air descended from higher altitudes. The mean ages observed from 25 to 32 km during the OMS flights at middle and high latitudes of 5 ± 0.5 years are consistent with that region being the source of the air comprising the older peak in the bimodal age spectra derived for lower altitudes. The separation of the two peaks in the age spectra requires a significant altitude region above 20 km where meridional transport is slow relative to higher and lower altitudes, consistent with the idea of a subtropical "barrier" to horizontal mixing [e.g., *Plumb*, 1996].

5. Conclusions

We have derived accurate mean ages for stratospheric air from a comprehensive set of in situ observations of CO_2, CH_4, and N_2O obtained from 1992 to 1998 from aircraft and balloon flights. Detailed analysis of the uncertainty in the derived mean ages was possible because of the depth of the underlying dataset, characterized by extensive latitudinal coverage and frequent sampling. Errors associated with the seasonal cycle in CO_2 mixing ratios and interannual variation in the CO_2 growth rate are < 0.5 year throughout the stratosphere (for Γ defined by (3) or for averaged Γ_{LAG} values) and < 0.3 year for air with $N_2O < 275$ ppbv (for any Γ for a given $CO_2{:}N_2O$ measurement). We conclude that stratospheric age spectra are broad enough to attenuate the effects of the seasonal cycle and fluctuations in the CO_2 growth rate over the time period during which the sampled air entered the stratosphere.

A remarkably compact relationship exists between measured N_2O and mean ages derived from CO_2 that is independent of latitude. In contrast, the relationship between CFC-11 and mean age exhibits substantial latitudinal variation. These relationships give insight into timescales for exchange of air between the tropics and higher latitudes. The robust relationship between mean age and N_2O allows a climatology of mean age to be derived from even more extensive observations of N_2O during this period.

The climatology of mean age can be used to evaluate transport in models used to assess the impact of anthropogenic perturbations on stratospheric ozone concentrations. The distribution of mean age with latitude and altitude provides detailed quantitative information about the general circulation of the stratosphere. At 20 km, sharp meridional gradients in the mean age are observed in the subtropics, further confirming earlier observations that exchange between the tropics and higher latitudes is significantly inhibited [e.g., *Randel et al.*, 1993; *Murphy et al.*, 1993; *Volk et al.*, 1996; *Plumb*, 1996]. Between 20 and 30 km the average difference in mean age between the tropics and midlatitudes is ~2 years, with slightly smaller differences at higher and lower altitudes.

Vertical profiles of CO_2 mixing ratios at midlatitudes are characterized by a rapid decrease from the tropopause to a region of near-constant mixing ratio in the middle stratosphere (~25-32 km), corresponding to mean ages of 5 ± 0.5 years, notably similar to the mean age of the older peak in the bimodal age spectra derived for the midlatitude lower stratosphere of *Andrews et al.* [2001]. This shape is consistent with the view that the meridional exchange is most rapid near the tropopause, with limited exchange from 20 to 30 km. Comparison of CO_2 measurements obtained in the midlatitude middle stratosphere since the mid-1970s with our balloon data shows that the mean age of air in this region has been relatively constant over the last 25 years, suggesting that continued monitoring of CO_2 at high altitudes could provide a baseline against which to measure changes in the stratospheric circulation.

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A. E. Andrews, Code 916, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA. (andrews@code916.gsfc.nasa.gov)

K. A. Boering, Departments of Chemistry and of Earth and Planetary Science, University of California, Berkeley, CA 94720, USA.

B. C. Daube and S. C. Wofsy, Department of Earth and Planetary Sciences and the Division of Engineering and Applied Sciences, 20 Oxford St., Harvard University, Cambridge, MA 02138, USA.

G. S. Dutton, J. W. Elkins, D. F. Hurst, F. L. Moore, E. A. Ray, and P. A. Romashkin, Climate Monitoring and Diagnostics Laboratory, NOAA, Boulder, CO 80303-3328, USA.

G. J. Flesch, R. L. Herman, D. C. Scott, and C. R. Webster, Jet Propulsion Laboratory, Mail Stop 183-401, 4800 Oak Grove Drive, Pasadena, CA 91109, USA.

H. Jost, M. Loewenstein and J. R. Podolske, NASA Ames Research Center, Mailstop 245-5, Moffett Field, CA 94035, USA.

E. J. Moyer, Department of Chemistry, 12 Oxford St., Harvard University, Cambridge, MA 02138, USA.

S. E. Strahan, NASA Goddard Space Flight Center, Code 910.3, Greenbelt, MD 20771, USA.

[1]Department of Earth and Planetary Sciences and the Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, USA.

[2]Now at NASA Goddard Space Flight Center, Greenbelt, Maryland, USA.

[3]Departments of Chemistry and of Earth and Planetary Science, University of California, Berkeley, California, USA.

[4]NASA Ames Research Center, Moffett Field, California, USA.

[5]Also at Bay Area Environmental Research Institute, San Francisco, California, USA.

[6]NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, USA.

[7]Now at Department of Chemistry and Biochemistry, Harvard University, Cambridge, Massachusetts, USA.

[8]NOAA Climate Monitoring and Diagnostics Laboratory, Boulder, Colorado, USA.

[9]General Sciences Corporation, Beltsville, Maryland, USA.

Table 1. ER-2 Field Deployments

Field Campaign	Deployment Site(s)	Dates	Latitude Range
SPADE	Moffett Field, California	Nov. 9 - 21, 1992	20°N - 40°N
	Moffett Field, California	April 19 to May 18, 1993	14°N - 60°N
	Moffett Field, California	Oct. 20 – 25, 1993	14°N - 60°N
ASHOE/MAESA	Moffett Field, California	Feb. 2 – 19, 1994	35°N - 61°N
	Moffett Field, California	March 18 to April 15, 1994	68°S - 38°N
	Barber's Point, Hawaii		
	Nadi, Fiji		
	Christchurch, New Zealand		
	Christchurch, New Zealand	May 24 to June 8, 1994	69°S - 20°S
	Christchurch, New Zealand	July 25 to Aug. 10, 1994	69°S - 19°S
	Christchurch, New Zealand	Oct. 3 to Nov. 4, 1994	70°S - 60°N
STRAT	Moffett Field, California	May 1 - 18, 1995	14°N - 62°N
	Moffett Field, California	Oct. 18 to Nov. 9, 1995	2°S - 59°N
	Barber's Point, Hawaii		
	Moffett Field, California	Jan. 23 to Feb. 15, 1996	2°S - 53°N
	Barber's Point, Hawaii		
	Moffett Field, California	July 16 to Aug. 10, 1996	2°S - 61°N
	Barber's Point, Hawaii		
	Moffett Field, California	Sept. 12 – 21, 1996	14°N - 61°N
	Moffett Field, California	Dec. 2 - 19, 1996	2°S - 61°N
	Barber's Point, Hawaii		
POLARIS	Moffett Field, California	April 17 to May 13, 1997	14°N - 90°N
	Fairbanks, Alaska		
	Fairbanks, Alaska	June 22 to July 10, 1997	45°N - 90°N
	Fairbanks, Alaska	Sept. 3 - 25, 1997	2°S - 90°N
	Barber's Point, Hawaii		
Flights-of-opportunity	Edwards, California	Nov. 10 – 15, 1998	11°N - 37°N

Table 2. Observations of the Middle Stratosphere (OMS)

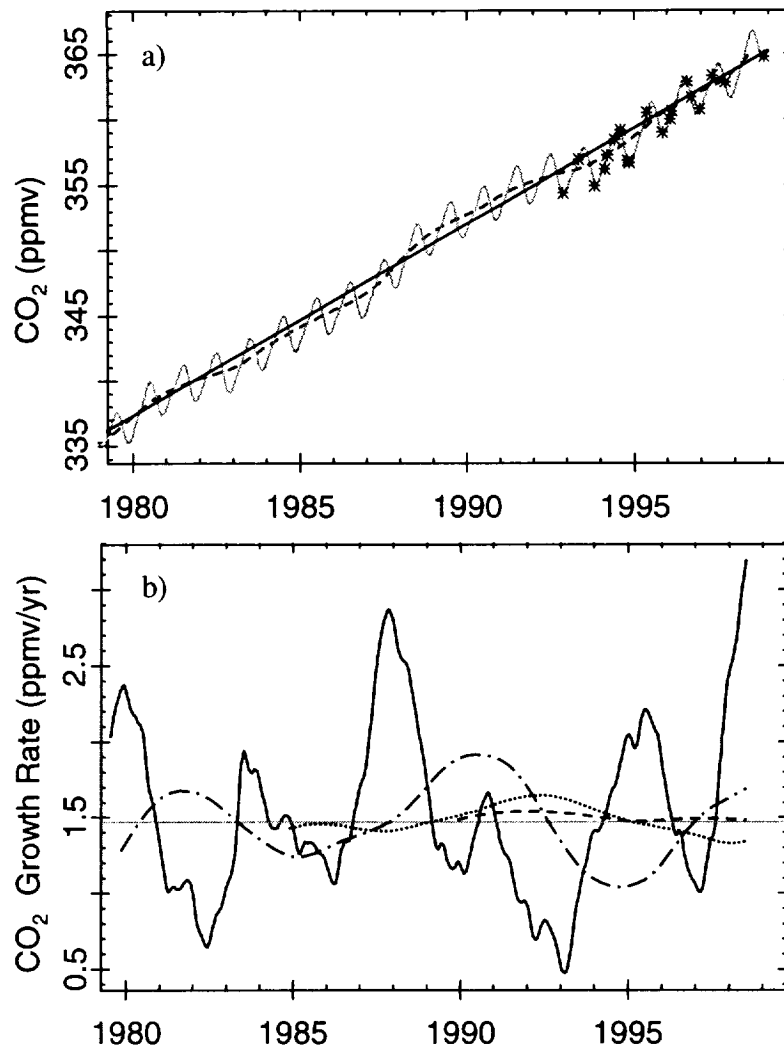| Deployment Site	Dates	Latitude	Altitude Range for CO_2 (km)
Fort Sumner, New Mexico	Sept. 21, 1996	35°N	9 – 26
Juazeiro do Norte, Brazil	Feb. 14, 1997	7°S	9 – 28
Fairbanks, Alaska	June 30, 1997	65°N	9 – 32
Juazeiro do Norte, Brazil	Nov. 11 and 20, 1997	7°S	9 – 32
Fort Sumner, New Mexico	May 18, 1998	35°N	9 – 32

Figure 1. (a) Stratospheric boundary condition for CO_2: symbols represent observations of CO_2 in air entering the stratosphere; the light curve is a continuous representation assuming a constant seasonal cycle and that the long-term trend can be represented using the dashed curve, which is the 12-month running mean of the average of surface station data from Mauna Loa, Hawaii (19°N) and American Samoa (14°S) [*Conway et al.*, 1994, updated] delayed by 2 months. The solid line is a linear fit to the long-term trend with a slope of 1.47 ppmv yr^{-1}; see text for details. (b) The derivative of the long-term trend (solid curve) shown along with the average growth rate calculated over the preceding 5 year (dot-dashed), 10 year (dotted), and 15 year (dashed) periods. The horizontal line denotes the average growth rate from 1980 to 1998 of 1.47 ppmv yr^{-1}.
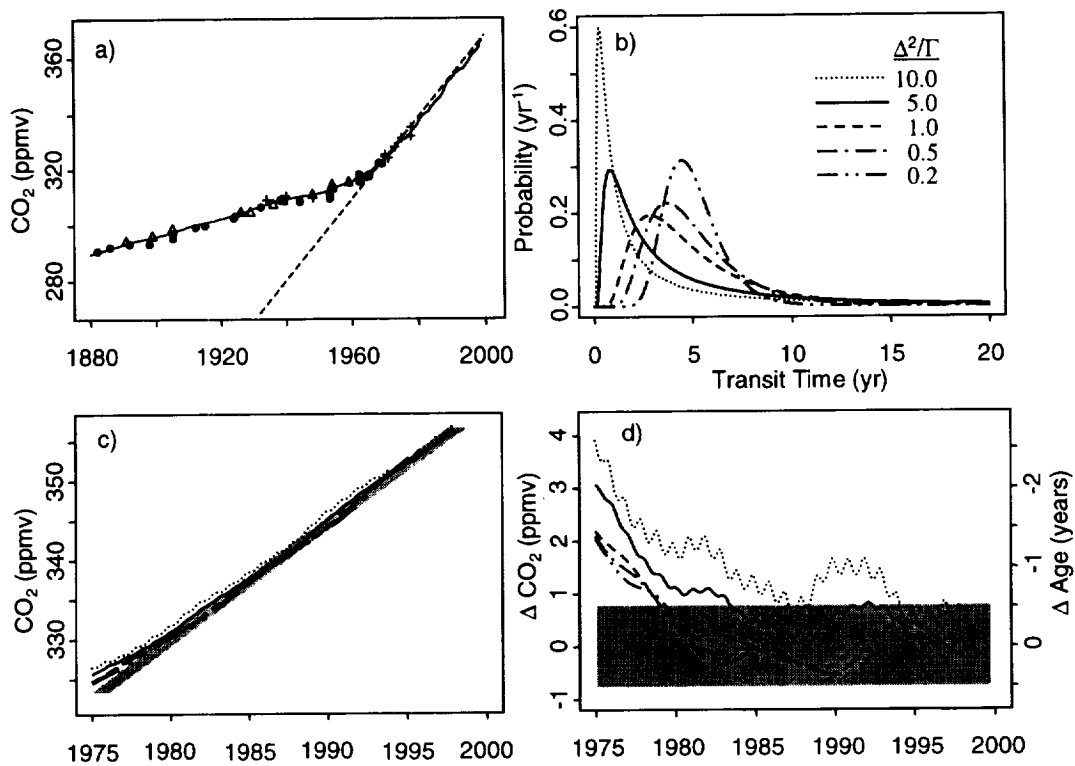
Figure 2. (a) The deseasonalized CO_2 boundary condition since 1880, derived for three periods as described below. Period 1974-1999, from surface data for Mauna Loa, HI and American Samoa, as described in the caption for Figure 1; period 1958-1974, based on annual mean CO_2 mixing ratios measured at Mauna Loa from 1958 to 1974 scaled to match the later years using overlapping data acquired from 1974 to 1993 [*Keeling and Whorf*, 1994]; period 1880-1958, using data from Antarctic Law Dome ice cores [*Etheridge et al.*, 1996]. Symbols denote cores DE08 (triangles), DE08-2 (pluses), and DSS (solid circles). The dashed line is a linear fit to the boundary condition for 1980 to 1998 (same as the solid line in Figure 1a). (b) Test age spectra with mean age = 5 years. Spectra have the functional form of the analytic solution to the Green's function for the 1-D advection-diffusion equation [*Hall and Plumb*, 1994; *Andrews et al.*, 1999, 2001], which has been shown to fit age spectra from more complicated models of the stratosphere reasonably well. (c) CO_2 time series generated by convolving the boundary condition shown in Figure 2a plus a seasonally varying component (as in Figure 1a) with the age spectra shown in Figure 2b. (d) CO_2 time series from Figure 2c detrended by subtracting the linear fit to the CO_2 boundary condition from 1980 to 1998 (dashed line in Figure 2a) delayed by 5 years. This represents the differences between CO_2 evolution predicted using the long-term trend in Figure 2a and that which would occur if the CO_2 growth rate were constant at 1.47 ppmv yr^{-1} with no seasonal cycle.
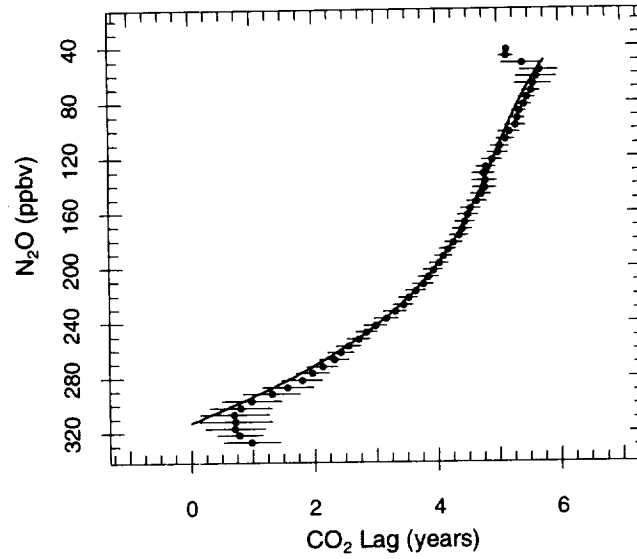
Figure 3. Average Γ_{LAG} (from (2)) versus N_2O from the entire ER-2 data set, spanning latitudes from 70°S to the North Pole with data in all seasons except Southern Hemisphere summer. N_2O measurements are from the ATLAS instrument and have been normalized to the 1997 tropospheric value following *Strahan et al.* [1999]. The solid circles represent the median value of Γ_{LAG} in overlapping 10 ppbv bins of N_2O. The error bars represent 1 standard deviation. The solid curve is a polynomial fit excluding values corresponding to $N_2O < 50$ ppbv given by $\Gamma_{LAG}(N_2O) = 0.0581(313 - N_2O) - 0.000254(313 - N_2O)^2 + 4.41 \times 10^{-7}(313 - N_2O)^3$, where 313 ppbv is the average tropospheric N_2O mixing ratio for the period from 1992 to 1998. The open triangles represent mean ages for the midlatitude lower stratosphere from the empirical age spectrum analysis of *Andrews et al.* [2001], referred to as Γ_{SPEC} in this paper.
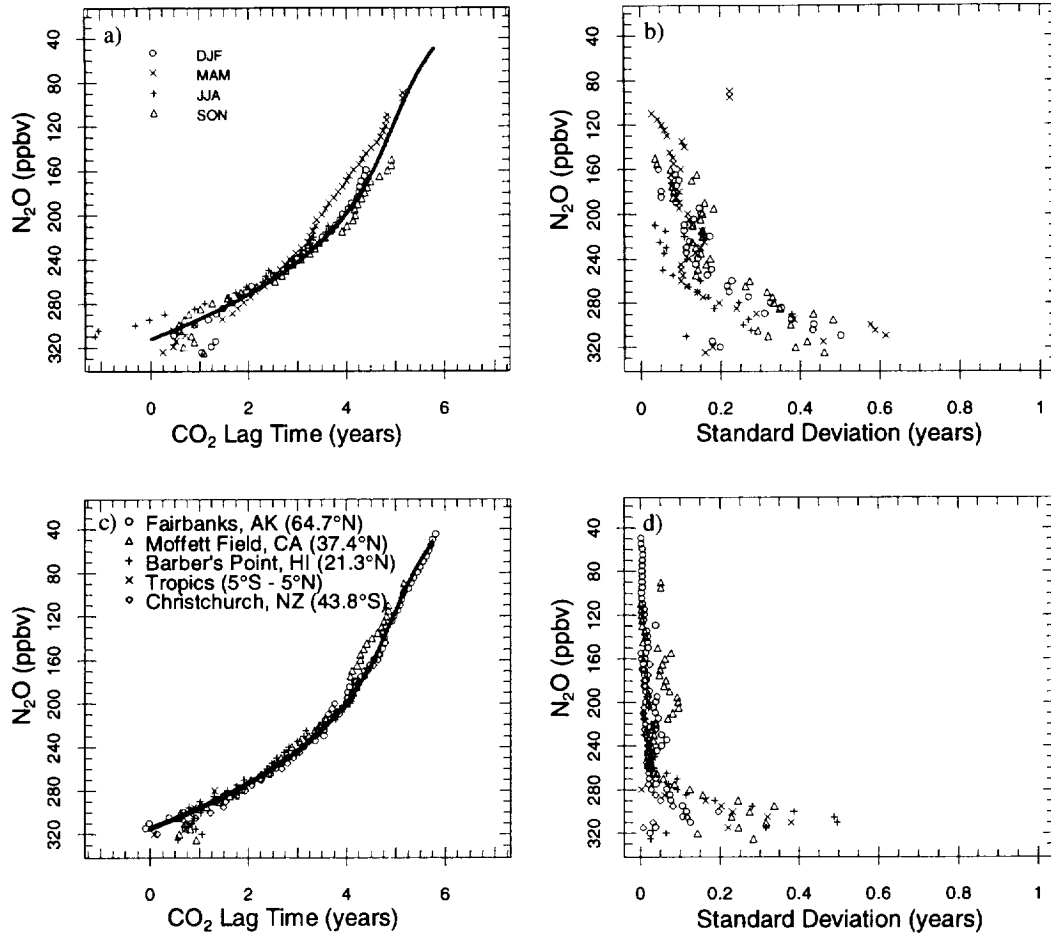
Figure 4. (a) Γ_{LAG} (from (2)) versus N_2O for measurements from the NASA ER-2 aircraft within 2.5° of NASA Ames Research Center in Moffett Field, California (37.4°N), for each of the four seasons. N_2O mixing ratios have been normalized to the 1997 tropospheric value following *Strahan et al.* [1999]. Each symbol represents the median mean age in a 10 ppbv N_2O interval. DJF, December-January-February; MAM, March-April-May; JJA, June-July-August; SON, September-October-November. (b) The corresponding standard deviations. (c) Average Γ_{LAG} as a function of N_2O for measurements from the NASA ER-2 aircraft within 2.5° of airfields where the airplane was based during SPADE, ASHOE/MAESA, STRAT, and POLARIS and for measurements obtained within 5° of the equator. Each symbol represents the median mean age in a 10 ppbv N_2O interval. (d) The corresponding standard deviations. See text for discussion of sampling at each location. The curve shown in Figures 4a and 4c is the cubic fit to mean ages from the entire ER-2 data set, as shown in Figure 3.
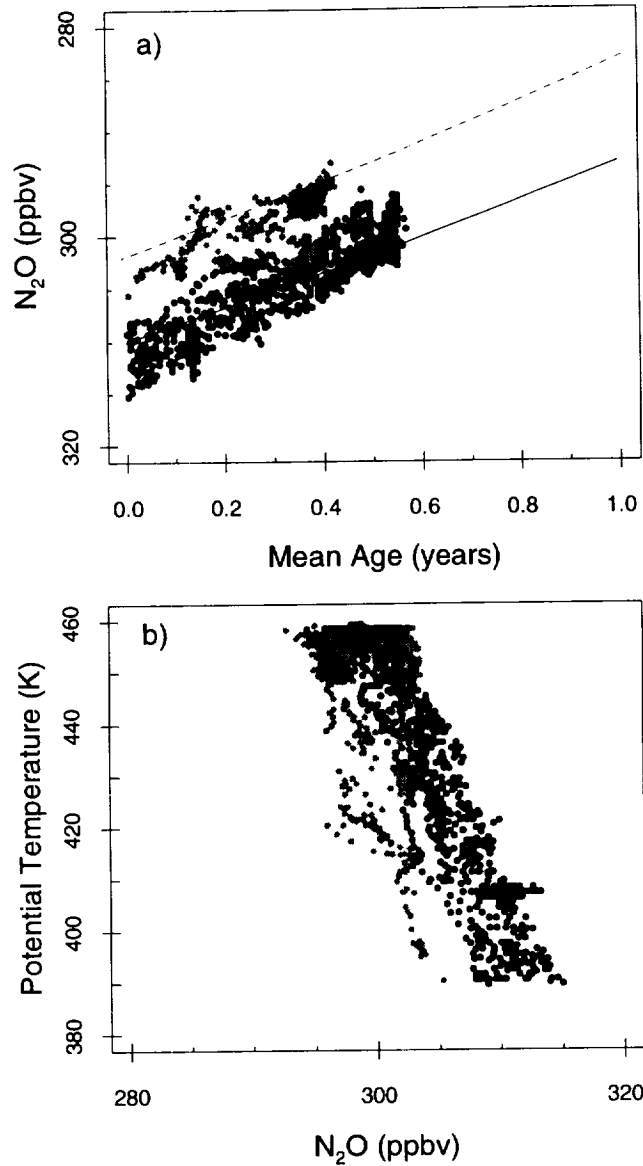
Figure 5. (a) Mean ages from the tropical empirical age spectrum analysis of *Andrews et al.* [1999] for the seven tropical profiles obtained by the ER-2 from 1994 to 1997 plotted versus N_2O measurements from ATLAS. N_2O mixing ratios have been normalized to the 1997 tropospheric value following Strahan et al. [1999]. Shaded symbols denote tropical data obtained in March 1994 and February 1996. The solid symbols represent data from all other flights, which were obtained from NH summer through early winter (July - December). The solid line represents the relationship between N_2O and mean age from the midlatitude empirical age spectrum analysis of *Andrews et al.* [2001]. The tropical age spectra give mean ages for March 1994 and February 1996 that are younger by as much as ~0.5 year than those obtained by applying the Γ_{SPEC}:N_2O relationship derived for midlatitudes (dashed line). (b) N_2O profiles from ATLAS corresponding to the mean ages shown in Figure 5a.

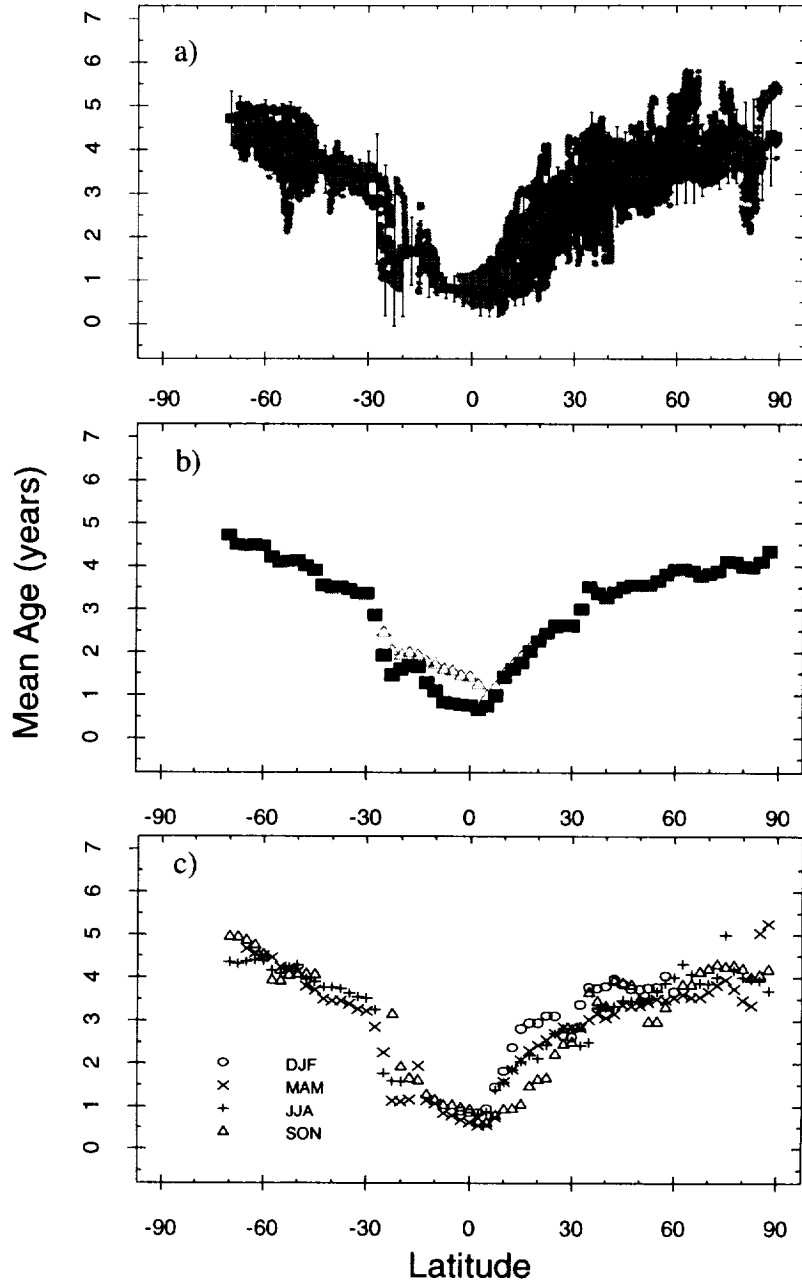**Figure 6.** (a) Variation with latitude of Γ from all ER-2 observations of CO_2 at 20 ± 0.5 km from 1992 to 1998. Shaded symbols represent 10-s average data from each flight. Solid symbols with error bars ($\pm 2\sigma$) represent the average Γ in overlapping 5° latitude bins. (b) Comparison of average latitudinal variation of Γ (calculated using (3), solid circles) and Γ_{LAG} (calculated using (2), open triangles) at 20 ± 0.5 km from 1992 to 1998. (c) Seasonal variation of Γ as a function of latitude.
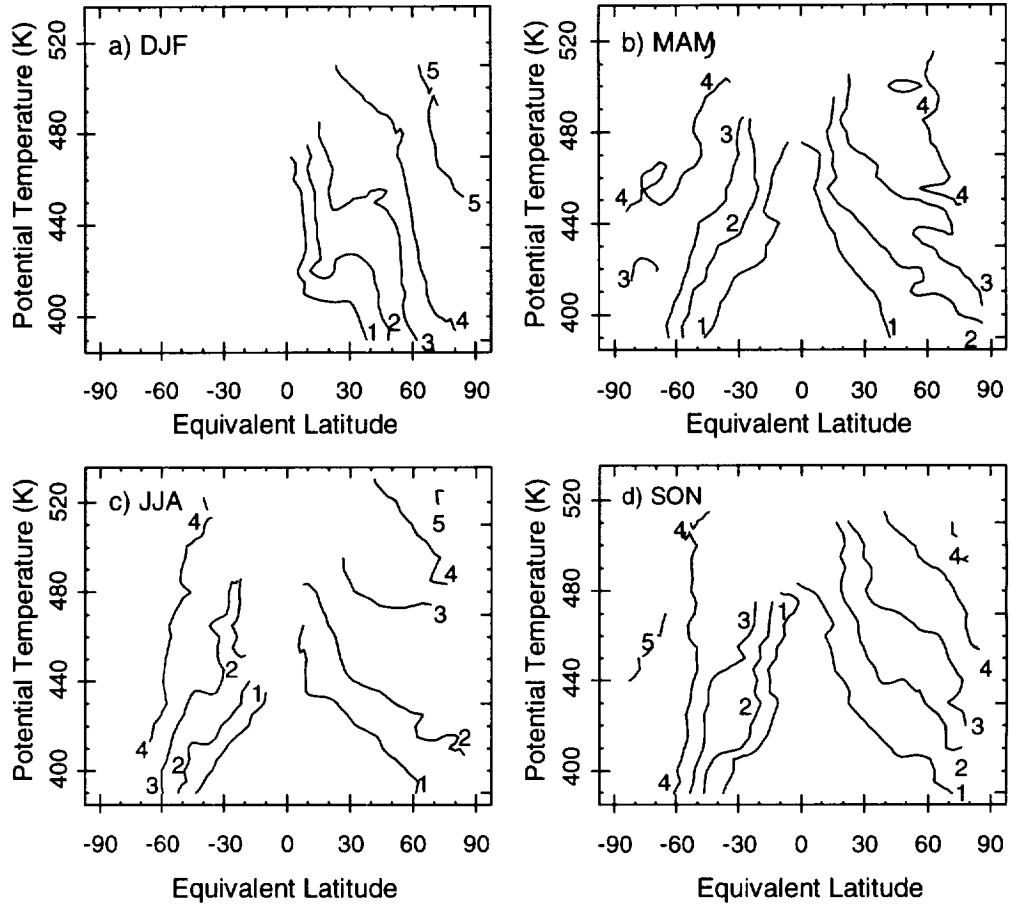
Figure 7. Climatology of Γ obtained by mapping the polynomial Γ:N$_2$O relationship shown in Figure 3a onto the N$_2$O climatology derived by *Strahan et al.* [1999] from in situ measurements of N$_2$O from the NASA ER-2 aircraft. Note that the N$_2$O data are normalized to 1997 levels as described in the section 2.
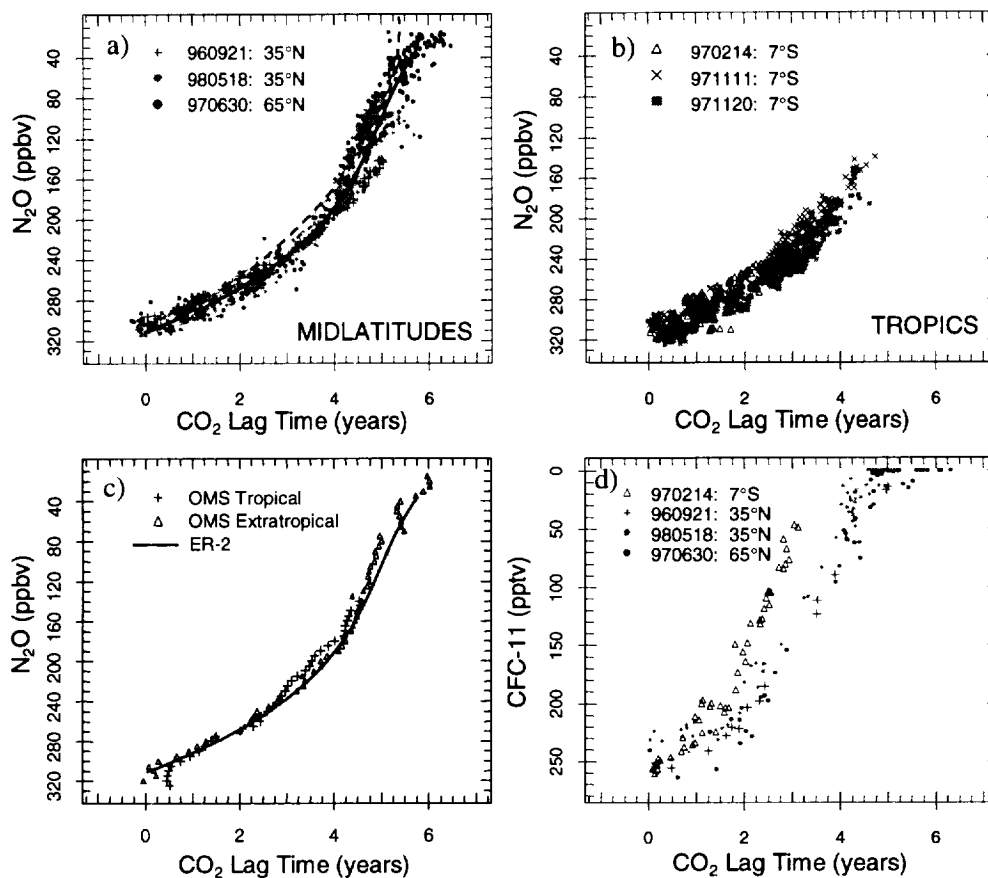
Figure 8. Γ_{LAG} versus N_2O for each of the (a) extratropical and (b) tropical OMS balloon flights; (c) average relationships between Γ_{LAG} and N_2O for the extratropical and tropical flights. N_2O data are from ALIAS-II, except for the November 11, 1997, flight where data are from the Argus instrument. N_2O mixing ratios have been normalized to the 1997 tropospheric value following *Strahan et al.* [1999]. The polynomial fit to the ER-2 data from Figure 3 is shown for comparison. (d) Γ_{LAG} versus CFC-11 for the OMS flights.
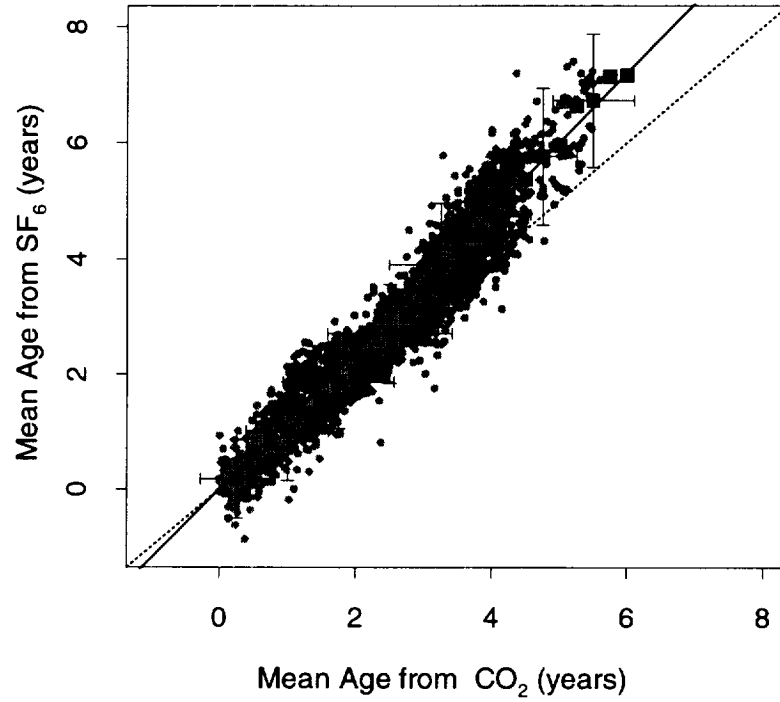
Figure 9. Scatterplot of mean ages derived from SF_6 and CO_2 observations from the NASA ER-2. The dotted line is the 1:1 line, and the solid line is the 1.2:1 line. Shaded symbols represent the 10-s flight data. Solid squares with error bars ($\pm 2\sigma$) denote the average SF_6 age in overlapping 0.5 year intervals of CO_2 age.

a)
- ○ Volz et al., 1981 (44°N)
- + Volz et al., 1981 (52°N)
- ◊ Bischof et al., 1985 (44°N)
- ● Schmidt and Khedim, 1991 (44°N)
- ✳ Nakazawa et al., 1995 (39°N)
- ■ Harnisch et al., 1998 (44°N)
- ▨ Harnisch et al., 1998 (68°N)
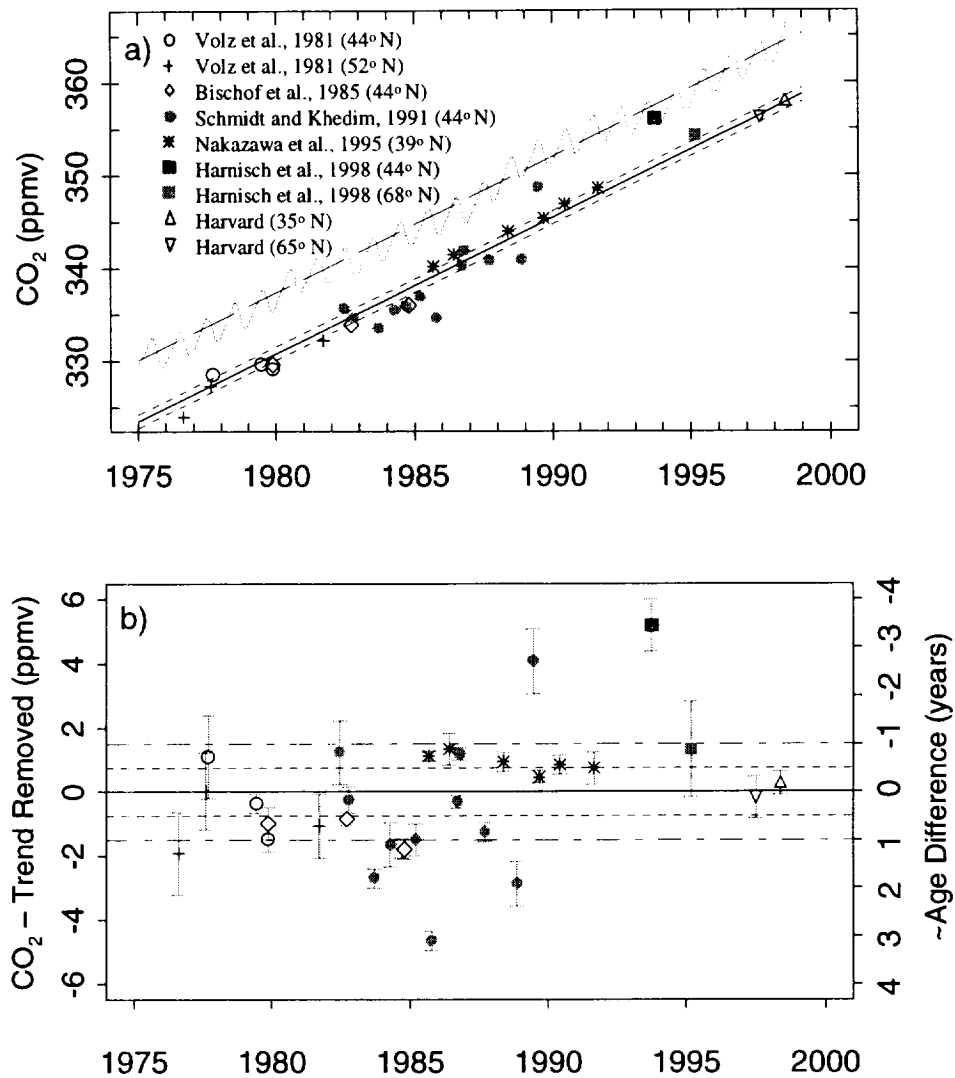- △ Harvard (35°N)
- ▽ Harvard (65°N)

b)

Figure 10. (a) Comparison of CO_2 measurements from the OMS balloon flights with data from balloon-borne cryosamplers for NH midlatitudes. Midlatitude CO_2 profiles are typically characterized by a region of near-constant mixing ratio starting from 20-25 km and extending to the top of the profile (see, e.g., May 1998 profile in Plate 1). Symbols correspond to the average mixing ratio in this region. The shaded line represents our stratospheric boundary condition for CO_2. The long-dashed line is a linear fit to the boundary condition from 1980 to 1998 and the solid line has the same slope but with a delay of 4.5 years. Short-dashed lines correspond to delays of 4 and 5 years. Note that since the data here have not been corrected for CH_4 oxidation, the actual mean age is ~0.5 years older. See text for details. (b) Same data detrended by subtracting the linear fit to the boundary condition delayed by 4.5 years (solid line in Figure 10a).
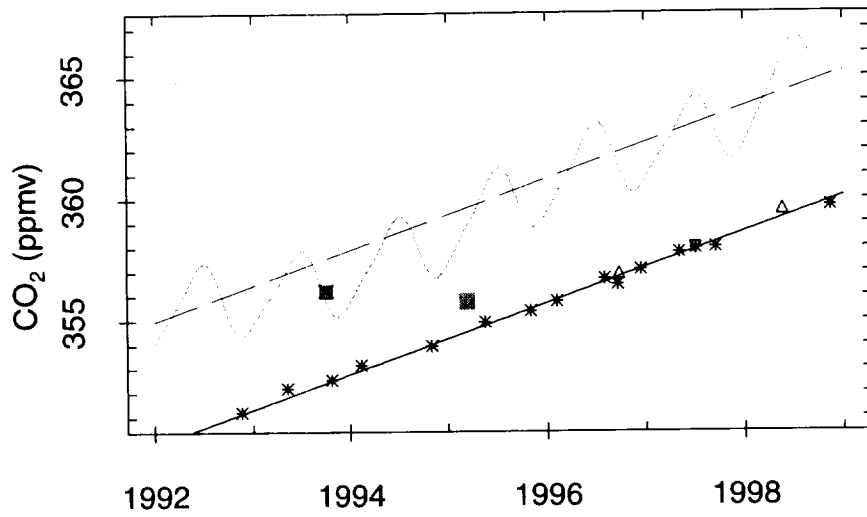
Figure 11. Average CO_2 mixing ratio corresponding to 215 ppbv N_2O as measured on the ER-2 for 1992 - 1998 (asterisks), on the midlatitude OMS balloon flights, and as reported by *Harnisch et al.* [1998] at ~20 km (simultaneous measurements of N_2O were 215 ± 5 ppbv); symbols for the balloon data are the same as in Figure 10. The shaded line and the dashed line are the same as in Figure 10. The solid line has the same slope as the linear fit to the boundary condition but with a delay of 3.5 years.
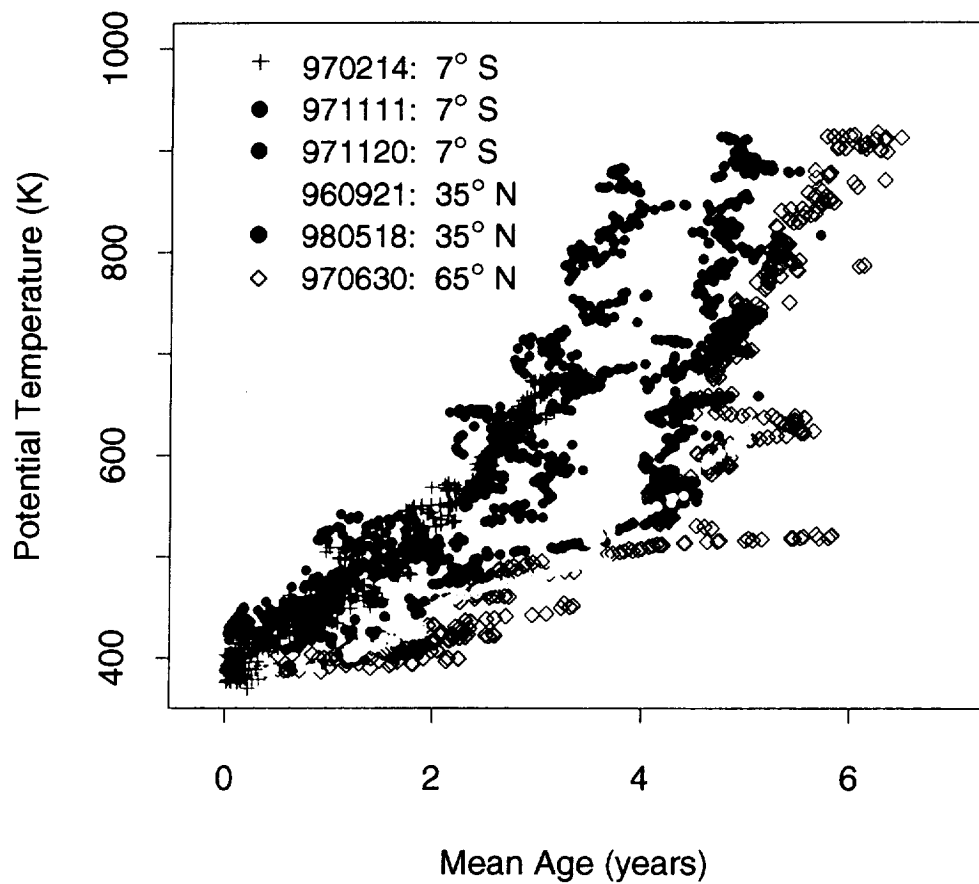
Plate 1. Mean age profiles for each of the OMS balloon flights. The September 1996 and May 1998 flights were from Fort Sumner, New Mexico (34.5°N); the June 1997 flight was from Fairbanks, Alaska (65°N); and the February and November 1997 flights were from Juazeiro do Norte, Brazil (7°S).
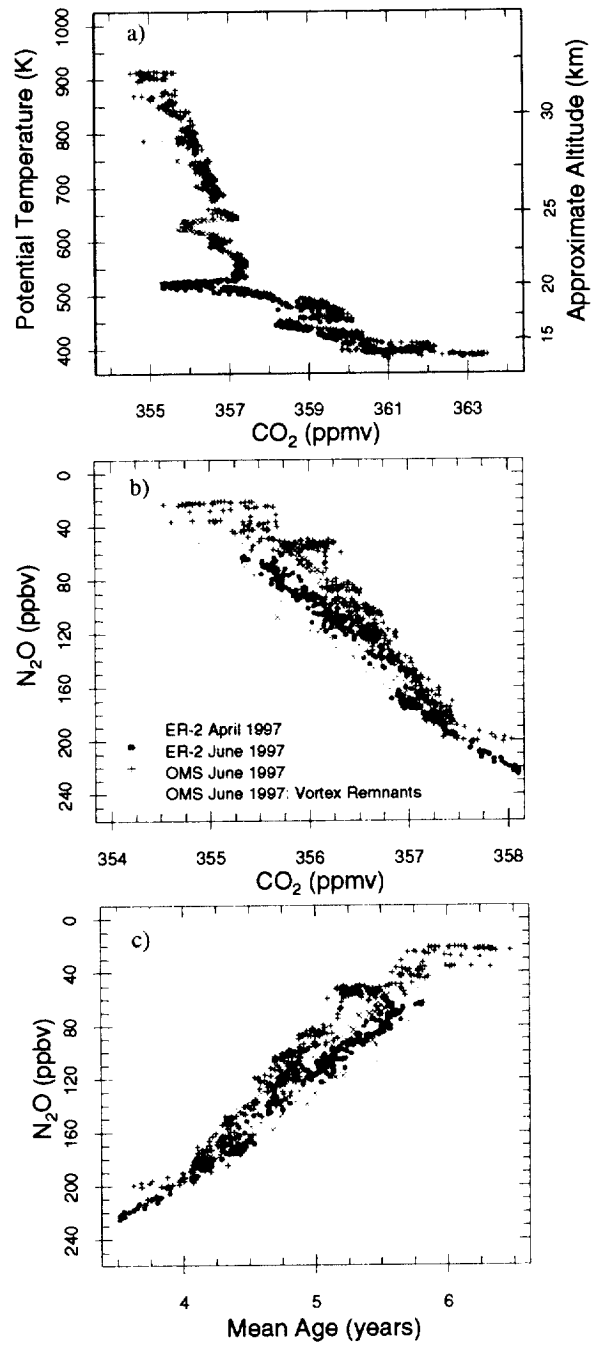
Plate 2. (a) CO_2 profile obtained on June 30, 1997. Magenta crosses represent air with "vortex-like" relationship between CH_4 and N_2O. Data from the ER-2 for the same date are also shown. Approximate pressure altitude is calculated assuming a constant scale height of 7 km. (b) Relationship between CO_2 and N_2O for the same data and for the ER-2 flight of April 26, 1997. (c) Relationship between Γ and N_2O.