Implications of ice core smoothing for inferring CO_2 flux variability

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[1] Ice core records are commonly used to infer information about past variability of CO_2 fluxes. Because of processes involved in enclosing this air in ice, ice core records are a smoothed representation of the actual past atmospheric variations. As such, there is a limit to how much information ice core measurements can contain about flux variability on short timescales. With a numerical model of the firn processes we quantify this smoothing and describe how it can be reproduced with pulse response functions. We generate and make available pulse response functions for CO_2 at the DE08 site on Law Dome, Antarctica. We discuss implications of the smoothing for inferring CO_2 flux variability from the Law Dome ice core record. In particular we look at results from an intercomparison of terrestrial biosphere models over the twentieth century and show how much of the CO_2 variability would be reflected in the Law Dome ice core record. We also smooth atmospheric $\delta^{13}CO_2$ from a study that compared fixed and varying isotopic discrimination. We find that the impact of changing discrimination, shown previously to be large on interannual timescales, is small on the decadal scales accessible from ice core records. *INDEX TERMS:* 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 1610 Global Change: Atmosphere (0315, 0325); 1615 Global Change: Biogeochemical processes (4805); *KEYWORDS:* ice core, firn, carbon cycle, terrestrial, carbon dioxide

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1. Introduction

[2] Variations in net CO_2 fluxes between the atmosphere, oceans and the terrestrial biosphere can be inferred from atmospheric CO_2 concentration measurements. Reliable direct measurements of atmospheric CO_2 began in 1958. Insight into atmospheric CO_2 prior to direct atmospheric measurements comes from proxy records, mainly measurements of CO_2 in air extracted from polar ice. However, ice core CO_2 records are a smoothed representation of the actual atmospheric variations. An important question is how much of the information about atmospheric CO_2 variability and the net fluxes is suppressed by the smoothing.

[3] The way in which air is trapped into the bubbles in ice influences the trapped concentration. Briefly, the main processes involved are (1) diffusion through the firn layer (the porous layer of unconsolidated snow containing channels of air still in contact with the surface) and (2) the gradual trapping of air into bubbles in ice in the lock-in zone [*Schwander et al.*, 1988; *Schwander*, 1989]. These processes have a smoothing effect on the record and high frequency variations are lost. Using a numerical model of firn diffusion and bubble trapping [*Schwander et al.*, 1988; *Trudinger et al.*, 1997, 2002b], we can quantify how atmospheric variations are lost, and what information can be inferred meaningfully from an ice core record.

[4] The CO_2 and $\delta^{13}CO_2$ ice core records from Law Dome in Antarctica [*Etheridge et al.*, 1996; *Francey et al.*, 1999] offer the best opportunity to reconstruct atmospheric variability, as they have the highest time resolution of the published ice core records. They have been used in inversion calculations, where net fluxes are estimated based on variations in CO_2 [*Joos et al.*, 1999; *Trudinger et al.*, 2002a]. The derivative of the CO_2 ice core record determines the fluxes, thus the results of these inversions are sensitive to the smoothing. With more and more calculations of carbon exchange for the last 100 years using global process models [e.g., *Dai and Fung*, 1993; *Cox et al.*, 2000; *McGuire et al.*, 2001; *Berthelot et al.*, 2002], ice core records may also be used for verification of the results

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(when the models are forced by observed climate). Some account needs to be taken of the smoothing in the ice core record, and we illustrate this here with a pulse response function representation of the firn model.

[5] The layout of this paper is as follows. In section 2 we describe use of the age distributions for smoothing data. We then consider two applications of the age distributions to carbon cycle questions. In section 3 we smooth the results of four terrestrial biosphere models from the *McGuire et al.* [2001] CCMLP 'Grand Slam' model intercomparison, and in section 4 we smooth $\delta^{13}CO_2$ from fluxes by *Scholze et al.* [2003] to comment on how much climate-driven variations in discrimination can be reflected in the ice core record. Section 5 summarizes the main results.

2. Age Distributions

[6] Air in a sample of ice does not correspond to a single time in the past, but is a mix of air parcels that left the atmosphere over a range of times. This can be characterized by the age distribution, which gives the contribution at each depth of the atmospheric concentration at different times in the past [*Rommelaere et al.*, 1997; *Trudinger et al.*, 2002b]. We determine the age distributions from the response of the firn model to an atmospheric pulse in CO_2 concentration. Because the firn model is linear, and the transport processes are taken as independent of time, the age distributions can be used instead of the firn model to calculate concentrations in the firn or ice due to an atmospheric time series.

[7] The solid line in Figure 1 shows the age distribution for ice at the DE08-2 site on Law Dome, calculated with the firn model of *Trudinger et al.* [1997]. The firn model was calibrated by tuning the diffusivity profile to obtain best fits to measurements of a number of gases in the DE08-2 firn. The age distributions would also apply for the nearby DE08 site with similar site properties. The dashed line shows how this age distribution compares with a 10-year running mean. The ice core age distribution is wider than the 10-year running mean, and nonsymmetric. The age distribution is plotted relative to the mean age of the air [*Trudinger et al.*, 2002b]. As air in the firn layer is still in contact with the atmosphere, the age spread varies with depth through the firn. However, below the lock-in zone (where diffusion ceases), the age distribution retains the same shape, with the mean age increasing with depth, as trapped air is advected downwards with the ice. The CO_2 age distribution in the ice at DE08 has a spectral width [*Trudinger et al.*, 2002b] of 4.7 years.

[8] The Law Dome CO_2 ice core record [*Etheridge et al.*, 1996] also consists of measurements from another site, DSS, with lower accumulation. The DSS measurements mainly cover the earlier part of the record. The diffusion profile at DSS has not been well characterized, as firn air was not collected from the site, but based on $\Delta^{14}CO_2$ ice core measurements, the age distribution at DSS is almost certainly wider than at DE08. Age distributions for other sites require a firn model calibrated for the site. The snow accumulation rate largely determines the age spread from bubble close-off, with higher accumulation rate sites having narrower age distributions than low accumulation rate sites. The accumulation rate at DE08 is very high, and it may be that DE08 is close to the limit of the narrowest age distributions for sites that are suitable for CO_2 measurements [*Etheridge et al.*, 1996].

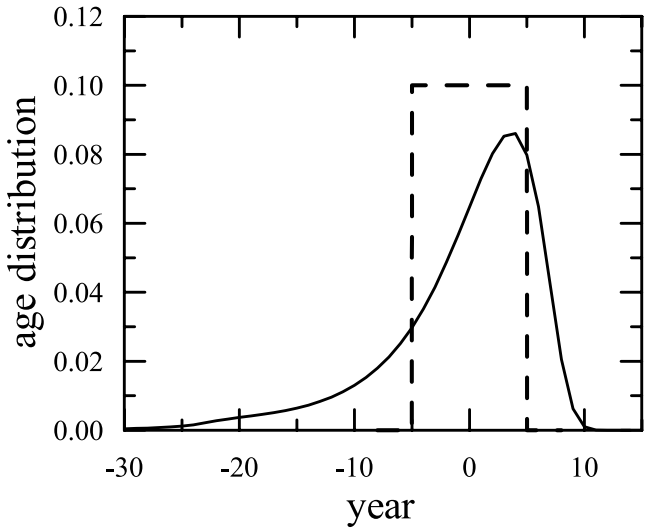

Figure 1. Age distribution for CO_2 in ice at DE08 on Law Dome (solid line) from the firn model of *Trudinger et al.* [1997]. The dashed line depicts the 10-year running mean.

[9] The smoothed concentration, $C_s(t)$, can be calculated from a time series of annual atmospheric concentration, $C(t)$, using

$$C_s(t_k) = \sum_{i=-40}^{14} R(i)C(t_{k+i}) \quad (1)$$

where $R(i)$ is the age distribution, defined for $-40 < i < 14$.

[10] It is also possible to smooth atmospheric $\delta^{13}CO_2$ to be comparable with the $\delta^{13}CO_2$ ice core record [*Francey et al.*, 1999], where $\delta^{13}CO_2$ is defined as

$$\delta^{13}C = \left[\left(^{13}C/^{12}C\right)_{sample}/\left(^{13}C/^{12}C\right)_{standard} - 1\right] \times 1000 \quad (2)$$

in per mil. We calculate $^{13}CO_2$ concentration from the CO_2 concentration and $\delta^{13}C$, then smooth the CO_2 and $^{13}CO_2$ separately before recombining them to get the smoothed $\delta^{13}C$. This is somewhat complicated because diffusion in the firn causes a fractionation of $\delta^{13}C$. We discuss this in more detail in the Appendix.

[11] The age distributions for CO_2 and $^{13}CO_2$ ice core measurements at DE08 on Law Dome are available at ftp://gaspublic:gaspublic@ftp.dar.csiro.au/data/guesslab/DE08. With these age distributions, it is possible to smooth time series of atmospheric CO_2 or $\delta^{13}CO_2$ so that they have comparable smoothing to the DE08 ice core record. Apart from smoothing concentrations in a forward sense, the age distributions can be used for inversions of firn or ice core measurements to deduce atmospheric records and uncertainties [*Trudinger et al.*, 2002b; *Sturrock et al.*, 2002]. As age distributions provide a compact representation of the smoothing on ice core measurements, it would be useful if they were more widely used and made available for other sites. Age distributions could be applied in a range of issues

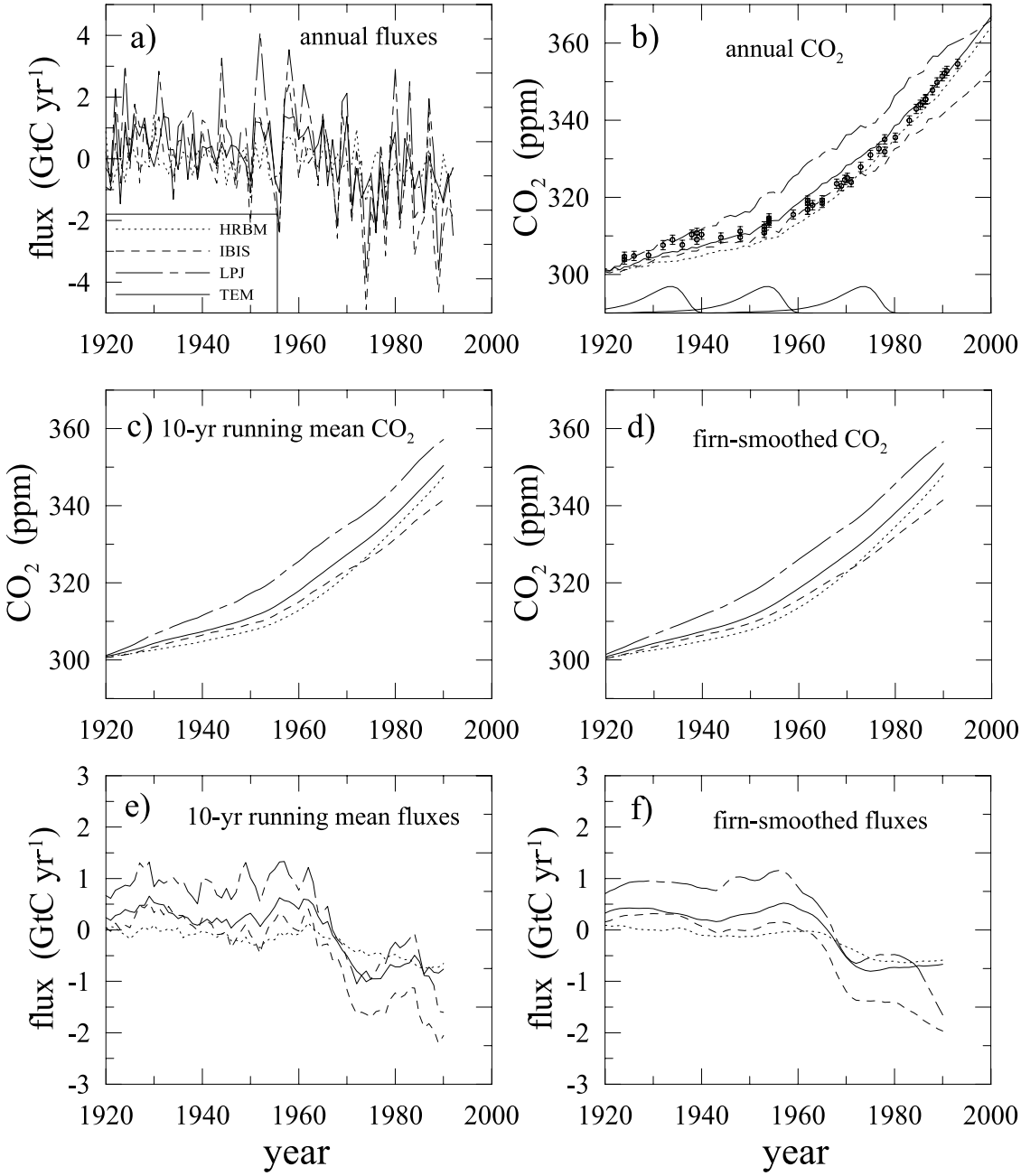

Figure 2. a) Net terrestrial fluxes from the model intercomparison by *McGuire et al.* [2001], driven by atmospheric CO_2, climate, and cropland establishment and abandonment. (b) CO_2 concentration calculated by running these terrestrial fluxes in a carbon cycle model that consists of a mixed layer pulse response function representation of the box diffusion model from *Joos et al.* [1996]. Also shown are the DE08 and DE08-2 CO_2 ice core measurements from *Etheridge et al.* [1996] (circles), with the error bars showing their 1σ uncertainties (1.2 ppm). The curves near the lower axis show the DE08 age distribution for mean ages of 1930, 1950, and 1970. (c) Annual concentrations from the carbon cycle model smoothed with a 10-year running mean. (d) Annual concentrations from the carbon cycle model smoothed with the DE08 age distributions. (e) Fluxes generated from the derivative of the 10-year running mean smoothed concentrations, minus (10-year) smoothed fossil fuel and oceanic fluxes. (f) Fluxes generated from the derivative of the firn-smoothed concentrations, minus (firn-smoothed) fossil fuel and oceanic fluxes.

where ice core records are used, provided the smoothing can be modeled and either remains constant or varies with depth in a known way. Characterising air age distributions in the firn layer is more complicated than in the ice, because smoothing varies with depth through the firn, so different distributions represent different depths. Determining air age distributions for ice cores over periods of fast climatic variations, such as deglaciation, would require knowledge

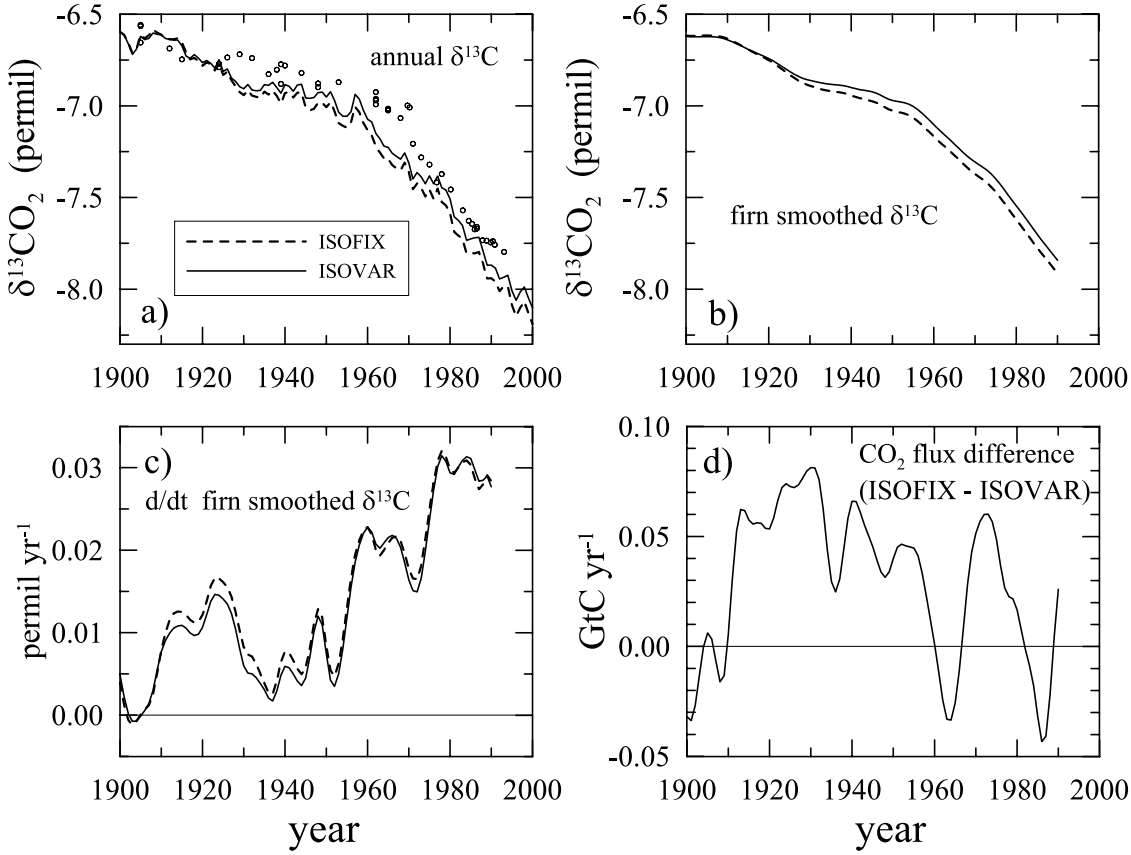

Figure 3. (a) Atmospheric $\delta^{13}C$ from the carbon cycle model using the CO_2 and ^{13}C fluxes from *Scholze et al.* [2003]. The dashed line shows the case with constant isotopic discrimination (ISOFIX) and the solid line varying discrimination (ISOVAR). (b) $\delta^{13}C$ for the two cases (ISOFIX and ISOVAR) smoothed with the DE08 ice core age distributions. (c) Derivatives of the firn-smoothed $\delta^{13}C$. (d) Estimate of the error in an inversion calculation that would be caused by neglecting variations in the isotopic discrimination.

of variations in smoothing due to temperature and accumulation rate changes, and the age distributions would probably vary with depth.

3. Example A: CCMLP Fluxes

[12] *McGuire et al.* [2001] presented net CO_2 terrestrial fluxes from four terrestrial biosphere models (HRBM, IBIS, LPJ and TEM) for the period 1920 to 1992, driven by observed CO_2, climate and cropland establishment and abandonment. *McGuire et al.* [2001] showed the 10-year running means of these fluxes. With the age distributions for DE08, we can smooth the fluxes in a way comparable to the Law Dome ice core record, to see (1) how much of the variability predicted by the terrestrial models would have been preserved in the ice at Law Dome and (2) whether the outputs of the models are actually different when smoothed by the firn processes.

[13] We ran the CO_2 fluxes from the four terrestrial models (Figure 2a) in a carbon cycle model with one atmospheric reservoir, mixed layer pulse response functions of a box diffusion model to characterize ocean uptake [*Joos et al.*, 1996], and a source due to fossil fuel burning [*Marland et al.*, 1999]. The calculated atmospheric CO_2 for the four models is shown in Figure 2b. The Law Dome ice core measurements are shown by the symbols, with 1 σ uncertainties shown by the error bars. To give an indication of the width of the age distribution relative to the data spacing, the curves along the lower axis show the age distribution centered on 1930, 1950 and 1970. The four CO_2 curves are smoothed by 10-year running means in Figure 2c and by convolution with the DE08 age distribution in Figure 2d. The 'smoothed terrestrial fluxes' (Figure 2e and 2f) are calculated by taking the derivatives of these curves, and subtracting the smoothed fossil and ocean fluxes. This is similar to how fluxes would be inferred from ice core measurements in a deconvolution calculation.

[14] The 10-year running mean of the fluxes, as presented by *McGuire et al.* [2001], looks very much like the 10-year running mean fluxes calculated from the derivative of concentration from the carbon cycle model (Figure 2e). This is as expected [*Enting*, 1999], and means that we can recover the smoothed fluxes from the smoothed concentration measurements. We can now test the effect of the ice core smoothing by applying the same algorithm to the atmospheric concentration record convolved with the age distribution. This procedure produces a flux record even smoother than the 10-year running mean of the original

fluxes. While much of the interannual variability has gone, there is still significant decadal variability in the firn-smoothed fluxes.

[15] Importantly, there are real differences between the fluxes from the four terrestrial models, even when smoothed in the same way as the ice core records. This implies that the Law Dome ice core measurements contain useful information for improving the models' decadal-scale behaviour or their inputs. Inferences from the ice core measurements will relate to the decadal timescale.

4. Example B: Varying Isotopic Discrimination

[16] $\delta^{13}CO_2$ is sometimes used with CO_2 to partition uptake into oceanic and terrestrial components, taking advantage of the different degrees of isotopic discrimination during exchange of CO_2 between the atmosphere, oceans and terrestrial biosphere. The procedure has traditionally involved the assumption of constant discrimination, allowing recovery of terrestrial and oceanic fluxes from the two records [e.g., *Francey et al.*, 1995; *Keeling et al.*, 1995]. *Scholze et al.* [2003] compared the ^{13}C fluxes determined with the global dynamic vegetation model, LPJ, for fixed and varying isotopic discrimination. They found that by not correctly considering variations in discrimination due to climate, net fluxes deduced from the observed CO_2 and $\delta^{13}C$ in an inversion calculation could be up to 0.8 GtC yr^{-1} in error for individual years. We can use the ice core age distributions for CO_2 and $^{13}CO_2$ to smooth time series of atmospheric $\delta^{13}C$ in a realistic way, to determine how much the fixed and varying discrimination cases differ on the decadal timescale recorded in the DE08 ice core records.

[17] We use the same carbon cycle model as in the previous section, but with ^{13}C as well as CO_2. The *Scholze et al.* [2003] terrestrial fluxes start in 1901. We use the two-box biosphere model of *Trudinger et al.* [1999] run from equilibrium in 1800 to determine the terrestrial isotopic disequilibrium fluxes until 1900. We also calculate the oceanic isotopic disequilibrium fluxes with the carbon cycle model. The isotopic ratio of the fossil fuel source is given by *Andres et al.* [2000].

[18] Figure 3a shows the annual atmospheric $\delta^{13}C$ calculated with the carbon cycle model using the fluxes from *Scholze et al.* [2003]. The dashed curve corresponds to fixed isotopic discrimination (ISOFIX) and the solid curve to isotopic discrimination that varies with climate (ISOVAR). The calculated atmospheric $\delta^{13}C$ for both cases are slightly lower than the Law Dome $\delta^{13}C$ ice core record [*Francey et al.*, 1999]. Most likely reasons for this are small errors in the partitioning of CO_2 exchange between oceanic and terrestrial or long-term discrimination, neither of which would have a strong effect on variability on the decadal timescale that is the focus of this study. The $\delta^{13}C$ curves are smoothed using the ice core age distributions as described in the Appendix, and the results are shown in Figure 3b. The derivatives of the smoothed curves are shown in Figure 3c. The difference between the derivatives, multiplied by the amount of CO_2 in the atmosphere and divided by the mean discrimination, is shown in Figure 3d. This quantity gives an estimate of the difference in the net fluxes for an inversion using fixed compared with varying discrimination.

[19] The error introduced into an inversion by not considering varying discrimination, on the timescales that are recorded in the Law Dome ice core record, is less than 0.1 GtC yr^{-1}. This is less than the 0.8 GtC yr^{-1} estimated by *Scholze et al.* [2003] for interannual timescales. It is considerably less than the uncertainty due to a number of different factors in the net fluxes from the double deconvolution calculations by *Joos and Bruno* [1998], *Joos et al.* [1999], and *Trudinger et al.* [2002a].

[20] These results do not contradict the findings of *Scholze et al.* [2003], but show that considering variations in isotopic discrimination on inversion of ice core records is not as important as for the interannual timescale. It would still be desirable to include varying discrimination wherever possible. These results also imply that it would be difficult to constrain varying discrimination with the ice core records.

5. Conclusions

[21] The ice core CO_2 and $\delta^{13}C$ measurements are smoothed relative to the actual past atmospheric variations. This smoothing has been quantified with a firn model for the high time resolution DE08 site on Law Dome, and can be represented by age distributions that are readily available and easy to use. We found that the decadal-scale differences between fluxes from four different terrestrial biosphere models do survive ice core smoothing, implying that the Law Dome ice core record will be useful for refining these types of model calculations. We also found that errors in the net fluxes due to ignoring climate-induced variations in isotopic discrimination in an inversion calculation were less than 0.1 Gt C yr^{-1} on decadal timescales, compared to the 0.8 Gt C yr^{-1} estimated for the interannual timescale by *Scholze et al.* [2003].

Appendix A: Using Age Distributions to Smooth $\delta^{13}CO_2$

[22] Smoothing $\delta^{13}CO_2$ with the age distributions is more complicated than smoothing CO_2. In the firn model, we run CO_2 and $^{13}CO_2$ separately, then combine them to give the isotopic ratio, $\delta^{13}C$. This is because ^{12}C and ^{13}C diffuse at slightly different rates in the firn, and this causes a fractionation that alters $\delta^{13}C$ relative to the atmosphere [*Trudinger et al.*, 1997]. We can think of this in terms of the mean age of the air. A sample of air from a particular depth contains ^{12}C and ^{13}C with slightly different mean ages, so that the ice core $\delta^{13}C$ differs from the atmospheric $\delta^{13}C$ by an offset that is typically up to a few per mil in samples corresponding to high CO_2 growth rates [*Trudinger et al.*, 1997]. *Trudinger et al.* [1997] described a correction for this fractionation, which involves running the firn model with the ^{13}C atmospheric record using the diffusion coefficients for both CO_2 and $^{13}CO_2$, and the difference between the $\delta^{13}C$ for these two runs gives the 'isotopic diffusion correction'. (The diffusion correction is required in addition to the correction for gravitational fractionation, which is well understood and can be determined from measured $\delta^{15}N_2$ [*Sowers et al.*, 1989].)

[23] We have generated two different age distributions for $^{13}CO_2$, the first is centered on the mean age of $^{12}CO_2$, so that it avoids introducing the fractionation effect described

above, while the second is centered on the mean age of $^{13}CO_2$, so it will introduce the fractionation effect. The second case would be useful for direct comparison with ice core measurements that have not been corrected for the fractionation due to diffusion, or for determining the diffusion correction. The first case is useful for investigating the smoothing without worrying about the fractionation due to diffusion, and is what we used in section 4.

[24] The diffusion correction is proportional to the atmospheric growth rate of CO_2 [*Trudinger*, 2000]. Therefore the CO_2 record that is used to determine the correction can have a large impact on the diffusion correction. In particular, the effect of fractionation that is seen in the ice core $\delta^{13}CO_2$ measurements was caused by the true atmospheric history of CO_2 and $\delta^{13}CO_2$, and this will differ from the effect modeled with a smoothed version of the true atmospheric history. Since these variations are lost due to the firn diffusion and ice core smoothing, we cannot exactly reproduce the effect with smoothed concentrations. This must be kept in mind when deciding which of the $^{13}CO_2$ pulses are more appropriate for an application.

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