JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 102, NO. C12, PAGES 26,841–26,850, NOVEMBER 30, 1997

Modeling the signal transfer of seawater $\delta^{18}O$ to the $\delta^{18}O$ of atmospheric oxygen using a diagnostic box model for the terrestrial and marine biosphere

Markus C. Leuenberger

Climate and Environmental Physics, University of Bern, Bern, Switzerland

Abstract. We make use of a simple diagnostic box model to determine the sensitivities of the influencing parameters for the isotopic signal transfer of seawater oxygen to atmospheric oxygen. We calculate the $\delta^{18}O$ of atmospheric oxygen from prescribed oxygen fluxes of the living and dead biomes on land and in the ocean, respectively. The model is driven by an assumed (experiment 1) or measured (experiments 2 and 3) temporal seawater $\delta^{18}O$ signal and a land biomass estimation. In experiment 1, we calculated the required changes of several model parameters in order to study fast variations of $\delta^{18}O$ of atmospheric oxygen as seen in the Greenland Ice Core Project (GRIP) ice at depths assigned to the Eemian time period. Our calculations support evidence of stratigraphic problems at these depths in the GRIP ice core. In experiment 2, we adjusted the model output, which was driven by the benthic seawater $\delta^{18}O$ record from V19-30, to the measured Greenland Ice Sheet Project 2 $\delta^{18}O$ record of atmospheric oxygen for the last 110,000 years, by varying the model parameter. Single and multiparameter matchings were performed. The results for single-parameter runs exceed the uncertainty ranges for most of the parameters, while multiparameter variations are well within these ranges. The model calculations are most sensitive to the land respiration factor. Our results support the findings of *Van de Water et al.* [1994] that the fractionations associated with biomes activities were most probably lower during cold periods, which could point to a combination of fractionations with different temperature dependencies. The model results indicate periods of higher marine biological activity during the ice age than today. Temporal variations of the model parameters show a double peak around 10000 and 8000 years ago, which could be associated with meltwater pulses, as shown in experiment 3. However, they are hardly the well-known Fairbanks [*Fairbanks et al.*, 1992] pulses since these occur 3000 to 4000 years earlier.

Introduction

Dating is one of the most important tasks when reconstructing changes of climate relevant parameter. There are a limited number of dating methods covering different possible dating intervals and uncertainties. Since these uncertainties become larger the older the dating interval is, it is very helpful to make use of global parameters, such as $\delta^{18}O$ of atmospheric oxygen (δ_a) [*Sowers et al.*, 1993] or methane [*Chappellaz et al.*, 1993] in order to synchronize records from different locations and archives, which then allows us to compare these records for other parameters. In sea sediment cores, $\delta^{18}O$ measurements of benthic foraminifera document changes of the isotopic oxygen composition of seawater (δ_o), which are dependent on the land ice volume. The large land ice extent for the last glacial maximum corresponds to an enriched δ_0 value of about 1.2‰. *Bender et al.* [1985] and *Horibe et al.* [1985] found that δ_a, as conserved in ice, is enriched compared to present-day values, indicating an isotope signal transfer from seawater to the atmosphere through hydrological (transpiration, evapotranspiration) and biochemical (photosynthesis, respiration) processes. Since it was shown that there is hardly any oxygen isotope fractionation associated with photosynthesis, the Dole effect of about 23.5‰ (e.g., the difference between δ_a and δ_o) is mainly given by the fractionation of respiration processes [see *Bender and Sowers*, 1994]. Over the last few years, progress has been made with the discovery of effects such as gravitational enrichment of heavier gas components due to molecular diffusion within the porous firn layer [*Schwander*, 1989; *Schwander et al.*, 1993], and firn-densification-dependent variations of ice-gas age differences (J. Schwander, personnel communication 1996), as well as reconsideration of the Dole effect [*Bender et al.*, 1994]. Together with new measurements of fractionation factors for land and marine biota respiration by *Guy et al.* [1989, 1992, 1993] and *Kiddon et al.* [1993], this has led to a better understanding of the so-called Dole effect. Because any changes associated with the biosphere reservoirs could have an influence on the Dole effect, the estimates of the land biomass change between glacial and interglacial times are of importance for this study. In contrast to *Prentice and Fung* [1990] who saw hardly any effect of terrestrial carbon storage to climate change, *Adams et al.* [1990] *and Friedlingstein et al.* [1992] have estimated a decreased land biomass for glacial times. The estimated change of about 1000 Gt C by Adams et al. is more than 3 times larger than that quoted by Friedlingstein et al. and is not compatible with the results of *Van de Water et al.* [1994] for ^{13}C fractionation changes as shown by *Bird et al.* [1994].

Paper number 97JC00160.
0148-0227/97/97JC-00160$09.00

Up to now, there are hardly any model studies looking at the variability of the Dole effect [*Sowers et al.*, 1991], its influencing parameter, and their sensitivities [*Bender and Sowers*, 1994]. However, exactly this is needed in order not only to synchronize records from the same archives, such as ice, but also to allow a more detailed comparison with sea sediment cores. This study tries to quantify the influences of several parameters on the Dole effect, such as fractionation factors and the ocean-to-land photosynthesis flux ratio on the Dole effect, and to estimate their sensitivities.

Model Description

The model is based on a four-box biosphere model. It consists of a "living" and "dead" biomass box each for the terrestrial and the marine biosphere, respectively. The same structure was used for both the ocean and the land reservoir. In Figure 1, we give the carbon and oxygen reservoir sizes and the assumed oxygen fluxes per year. Changes in the isotopic composition of atmospheric oxygen are calculated according to (1), given here in the Delta-Notation. Equation (1) is an approximation; for a correct determination of the isotopic variation, we used the ratio notation (R_x) instead of the delta notation (δ_x), which are defined as follows:

$$\delta_x = (R_x/R_{\mathrm{ref}} - 1) \times 1000\ ‰$$

where R_x = $^{18}O/^{16}O$ of reservoirs x and R_{ref} = $^{18}O/^{16}O$ of the reference material.

The isotopic composition of water oxygen is referenced to standard mean ocean water (SMOW), whereas isotopic ratios of atmospheric oxygen are expressed as deviations from modern atmospheric air oxygen.

Equation (1) reads

$$\begin{aligned} M\,(\delta_a\, dc_a/dt + c_a\, d\delta_a/dt) = \; & +F_p\,(\delta_o + \varepsilon_h) \\ & - (F_v + \mathrm{F}_s)\,(\delta_a + \varepsilon_r) \\ & + F_{op}\,\delta_o \\ & - F_{or}\,(\delta_a + \varepsilon^* + \varepsilon_{or}) \\ & - F_d\,(\delta_a + \varepsilon^* + \varepsilon_d) \end{aligned} \qquad (1)$$

where M is the number of moles of air in the atmosphere; c_a is the mole fraction of O_2 in the atmosphere; F_p and F_{op} are the

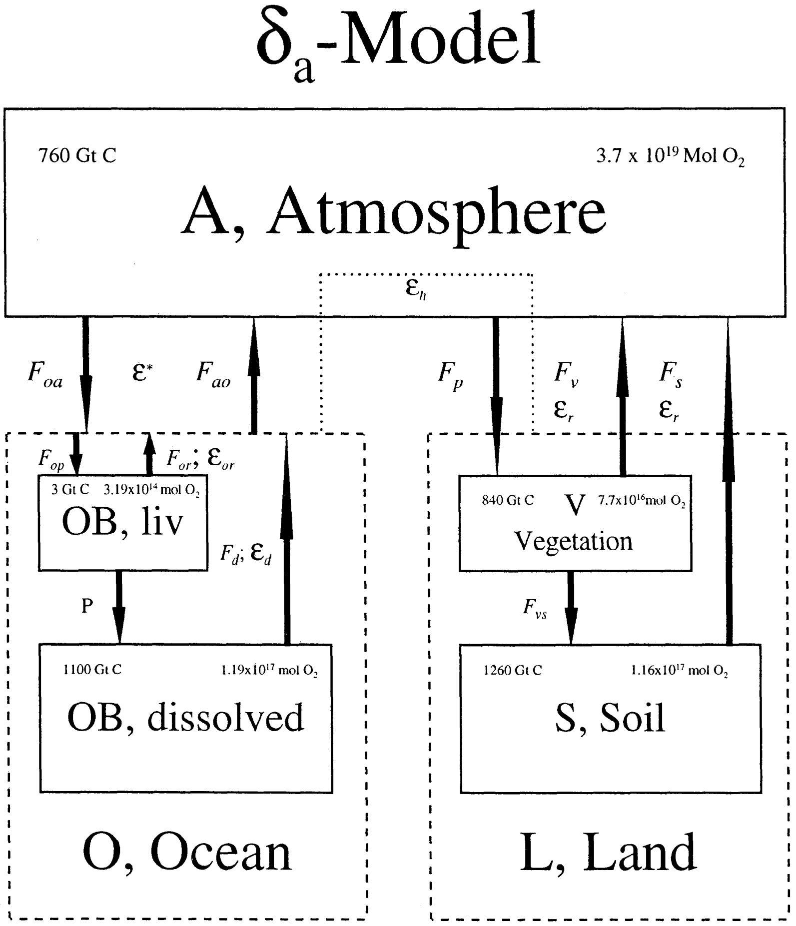

Figure 1. Scheme of the model. On the right- and left-hand side of each box you will find the oxygen and carbon storage amounts given in moles of O_2 and gigatons of carbon, respectively. With F_x and ε_x, we denote oxygen fluxes and their corresponding isotopic fractionations. The oxygen exchange between the atmosphere and the ocean is much faster than the time intervals we are interested in; therefore we assume an isotopic equilibrium between these two reservoirs. Hence the fluxes F_{oa} and F_{ao} are not used for our calculations. We further assume that F_d equals the particle flux, P, with a time delay of 250 years for water mixing [*Siegenthaler*, 1983].

annual fluxes of O_2 associated with terrestrial and marine photosynthesis; F_v, F_s ,and F_{or} are the annual gross fluxes for consumed O_2 by plant and soil respiration on land and marine respirative processes in the surface ocean, respectively; F_d is the annual respiration flux in the deep ocean; ε_h is the fractionation associated with the hydrological processes involved; ε_r , ε_{or} , and ε_d are the fractionations during the respiration on land and in the ocean; ε^* is the equilibrium fractionation between dissolved O_2 in water and atmospheric oxygen; δ_a is the isotopic composition of atmospheric oxygen; and δ_o is the isotopic composition of seawater.

With this equation, we implicitly assume that the fractionation associated with oxidizing the nutrients is similar to the respiration fractionation of organic material and that the oxygen released by the nutrients during photosynthesis is similar to the water oxygen used. We use a time step of 100 years; hence oxygen turnover times for the terrestrial reservoirs, which are of the order of a few years to few decades for vegetation and soil, respectively, can be neglected. However, we adopted a delay of 250 years, based on vertical water velocities for oxygen produced by decomposition of organic material in the deep ocean.

To solve (1) for $d\delta_a/dt$ we use an estimated change in $\delta^{18}O$ of seawater (δ_o) derived from benthic foraminifera, V19-30 [*Pisias et al.*, 1984; *Shackleton and Pisias*, 1985], corrected for a temperature influence as discussed by *Sowers et al.* [1993], and prescribed oxygen fluxes. These fluxes are based on estimated CO_2 fluxes and were converted to oxygen fluxes using the O_2/C factors ($(O_2/C)_\ell$ =1.1 for the terrestrial biosphere and $(O_2/C)_o$ =1.3 for the marine biosphere) as given by *Keeling and Shertz* [1992] and *Keeling et al.* [1996]). Generally, the temporal variations of the carbon fluxes and therefore the oxygen fluxes are calculated from changes in the photosynthesis and respiration relevant temperature and precipitation (see, for instance, *Friedlingsstein et al.* [1992]). Here we used a simpler approach: The fluxes were assumed to vary linearly with the biomass size. On the basis of the major methane concentration changes we adopt a variation for the land biomass according to Figure 2 in the range 1680-2100 Gt C. This corresponds to a maximum decrease of 420 Gt C during the full glaciation, taking 2100 Gt C as the preindustrial value. This is of course very simplistic, but for a first approximation the fluxes (photosynthesis and respiration) have to be dependent on the amount of biomass. Variations of these fluxes due to climate conditions such as temperature, precipitation, humidity, and so forth, as well as changes in plant communities, are not explicitly taken into account. However, a lower reservoir size for glacial times will implicitly represent some of these dependencies.

The hydrological part of the model, indicated as dotted lines in Figure 1, is parameterizied only by one parameter, ε_h. This fractionation, ε_h, stands for many isotope shifts associated with different processes. The temperature-dependent transpiration/condensation processes associated with the water cycle are countered by the leaf water enrichment. This leaf water enrichment is, among other parameters, dependent on the isotopic composition of water vapor in the air and relative humidity as summarized by *Farquhar et al.* [1993] and *Saurer et al.* [1997].

Furthermore, we took advantage of the fact that the ocean-atmosphere gas exchange is much faster than the variation of δ_a and δ_o we are interested in, hence assuming isotopic equilibrium between $\delta^{18}O$ of dissolved oxygen and δ_a, denoted here as ε^*. This equilibrium fractionation between dissolved O_2 and atmospheric O_2, ε^*, is well known to be 0.7±0.1‰ [*Benson and Krause*, 1984].

A summary of the few data available for the fractionation factors ε_{or} and ε_r associated with marine and terrestrial respiration is given by *Bender et al.* [1994]. They vary in a wide range from -17 to -25‰ , but the mean values seem to be very close for these two different organic communities with -18.8‰ for ε_r and - 20‰ for ε_{or}. The uncertainty of both fractionation factors is 2-3‰ [*Kiddon et al.*, 1993].

The atmospheric oxygen pool is estimated to be 3.7 x 10^{19}

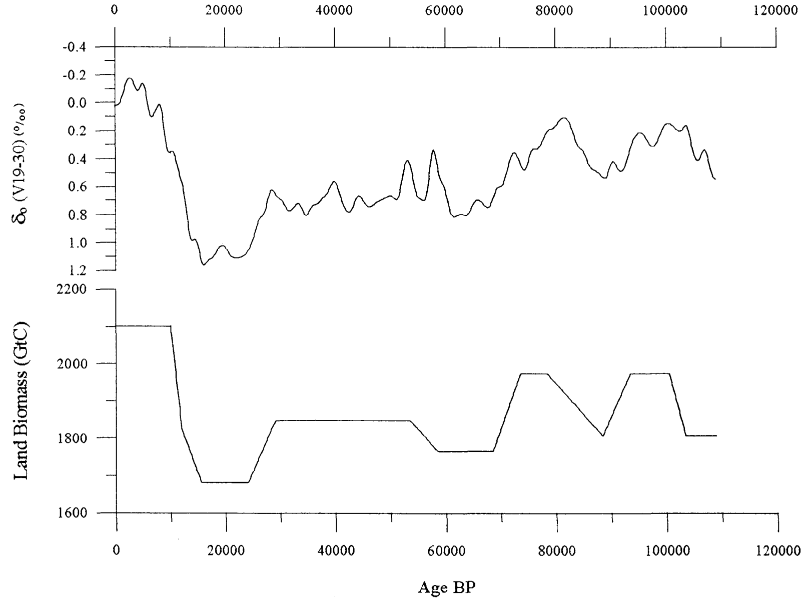

Figure 2. Driving records of the model for experiments 2 and 3. (top) Temporal development of δ_o as reconstructed from foraminifera [*Pisias et al.*, 1984; *Shackleton and Pisias*, 1985] for the V19-30 sea-sediment core and corrected for a temperature influence as discussed by *Sowers et al.* [1993]. (bottom) An assumed land biomass change based on major methane changes.

mol. Using mean oxygen fluxes due to photosynthesis of 1.16 x 10^{16} mol/yr (corresponding to 125 Gt C/yr) for the land biosphere and 0.48 x 10^{16} mol/yr (45 Gt C/yr) for the ocean biosphere leads to residence times for atmospheric oxygen of about 3200 years with the land biomass ($\tau_\ell = [O_2]/F_p$) and 7750 years with the marine biomass ($\tau_o = [O_2]/F_{op}$), respectively. This leads to a mean residence time of about 2250 years for atmospheric oxygen due to biospheric activities. Therefore a value of 6.15‰ for ε_h is required in order to solve (1) for today's condition (using the values as given in Table 1). This value for the fractionation during the vaporization, precipitation, and evapotranspiration processes lies within the range estimated by *Dongman et al* [1974] and *Schleser* [1978, 1979] of 4-8‰ but is considerably higher than the value given by *Farquhar et al.* [1993] of 4.4‰.

Results and Discussion

General Remarks

Equation (1) shows us that while the terrestrial biosphere terms tend to increase the Dole effect, since (ε_h - ε_r) is mostly larger than today's Dole effect of 23.5‰, the marine biosphere terms decrease it because $-(\varepsilon^* + \varepsilon_{or})$ is always lower than today's Dole effect. A decrease in terrestrial biosphere activity, as indicated by the different estimates of land biomass, would lower the Dole effect, whereas a decrease in marine biospheric activity would increase it. Hence changes in the ocean-to-land photosynthesis ratio $\zeta = F_{op} / F_p$ will be important for the Dole effect. As mentioned above, the land biomass is assumed to change in the interval 1680-2100 Gt C between glacial and interglacial times. This corresponds to a range of the terrestrial biomass oxygen flux of 0.92-1.16 x 10^{16} mol O_2/yr and hence to a residence time interval τ_ℓ of 3200-4000 years using 3.7 x 10^{19} mol O_2 for the atmospheric oxygen content. When we calculate from (1) the range of photosynthesis flux F_{op} or the residence time, τ_o, for different combinations of (ε_r ,ε_{or}) and ε_h within their uncertainties, it seems very unlikely that ε_{or} is more negative than ε_r. The obtained fluxes F_{op} and residence times τ_o are either too high or too low (even negative) to be realistic, because they are a measure for ocean carbon pools which hardly can change more than a few times today's values. Therefore these calculations rather point to a difference of 3-6‰ between ε_r and ε_{or}, with ε_{or} close to the higher end (-17‰) stated by *Kiddon et al.* [1993] or even more positive or conversely a lower value for ε_r. This contradicts the fact that the measured mean values of ε_r and ε_{or} are similar (-20‰). Uncertainties of ε_d are not relevant for this finding since the particle flux is much lower than the surface respiratory flux. However, due to lack of data, especially for the evapotranspiration and the oceanic biomass, we cannot minimize the range of ε_r and ε_{or} with confidence. We therefore used the values given by *Bender and Sowers* [1994] as best estimates.

The best estimate for ε_h is obtained by adjusting the modeled δ_a to the present-day Dole effect of 23.5‰. Hence changes in ε_r and/or ε_{or}, ε_d will be compensated by ε_h in order to match today's Dole effect. This has the following implications: 1. Since ε_h and ε_r are additive (see (1)), a change in the best estimate for ε_r corresponds exactly to the same shift in ε_h. 2. Therefore a different best estimate for ε_r do not affect the characteristics of the atmospheric oxygen signal in our runs. 3. Changes in ε_{or} do require an altering of the oxygen fluxes (hence τ_o, τ_ℓ) and/or δ_o changes in order to maintain the output signal (δ_a'). 4. Equation (1) also shows that any changes in oxygen fluxes (τ_o, τ_ℓ) will be transferred to the signal of atmospheric oxygen. Therefore it is possible that the atmospheric signal seems to react before any changes in δ_o are present; hence we have to be very careful in interpreting changes of $\delta^{18}O$ of atmospheric oxygen. 5. If the terrestrial oxygen respiration fluxes (F_v and F_s) are increased by a factor of 1.5 as *Bender et al.* [1994] used, the transfer is then faster and the corresponding output signal is damped by a factor of nearly 2 but conserving the main features as shown in experiment 2.

Table 1. Model Variables and Their Assumed or Calculated Values Used in the Text

Variable	Description	Today's Value	Unit
c_a	mole fraction of O_2 in air	0.2095	1
δ_a	isotopic composition of atmospheric oxygen	GISP2	‰
δ_o	O isotope composition of water in the ocean (SMOW scale)	V19-30	‰
ε_d	mean fractionation during decomposition of dissolved organic matter (deep ocean)	-12.0	‰
ε_h	summarized fractionations of water cycle effects (transpiration, condensation, evapotranspiration, etc.)	-6.15	‰
ε_r	mean fractionation during respiration on land	-18.8	‰
ε_{or}	mean fractionation during respiration in the surface ocean	-20.0	‰
ε^*	isotope equilibrium fractionation between dissolved and atmospheric O_2	-0.7	‰
F_d	molar flux of O_2 due to decomposition of dissolved organic matter	0.48 x 10^{15}	mol O_2/yr
F_p	gross molar flux of O_2 due to photosynthesis on land	1.16 x 10^{16}	mol O_2/yr
F_v	molar flux of O_2 due to respiration of land vegetation	0.58 x 10^{16}	mol O_2/yr
F_s	molar flux of O_2 due to soil respiration on land	0.58 x 10^{16}	mol O_2/yr
F_{op}	molar flux of O_2 due to photosynthesis in the ocean	0.48 x 10^{16}	mol O_2/yr
F_{or}	molar flux of O_2 due to respiration in the surface ocean	0.43 x 10^{16}	mol O_2/yr
M	number of moles of air in the atmosphere	1.77 x 10^{20}	
$[O_2] = M\,c_a$	atmospheric oxygen content	3.70 x 10^{19}	mol O_2
$(O_2/C)_o$	O_2/C ratio in the ocean	1.30	1
$(O_2/C)_\ell$	O_2/C ratio on land	1.10	1
τ_ℓ	residence time of atmospheric O_2 due to photosynthesis on land	3200	yr
τ_o	residence time of atmospheric O_2 due to photosynthesis in the ocean	7750	yr
ζ	ratio of F_{op}/F_p	0.41	1

Experiment 1

This experiment was motivated by the results *of Fuchs and Leuenberger* [1996] for the isotopic composition of oxygen trapped in the Greenland Ice Core Project (GRIP) ice core. These δ_a measurements showed fast (< 1000 years) and large (2/3 of glacial-to-interglacial change) transitions for ice assigned to the last warm period, the Eemian. We believe that these transitions arise from stratigraphic disorder. The main arguments for this conclusion were (1) that there is no evidence of fast variations in the $\delta^{18}O$ records of seawater and therefore (2) the required change of the biomass would be very dramatic and unrealistic considering that the other parameters influencing the Dole effect stayed more or less constant [*Sowers et al.*, 1993; *Bender and Sowers*, 1994]. In Figure 3, the measured δ_a on GRIP ice [*Fuchs and Leuenberger*, 1996] is plotted along with the calculated changes for the oxygen flux ratio, ε_h, ε_{or}, and δ_o, required to explain these fast variations. The runs were performed with only one variable meaning that the whole δ_a variations were ascribed to this variable and all other parameters were held constant. Here δ_o was set to 0‰, first, since the V19-30 record [*Pisias et al.*, 1984] does not show any abrupt changes during this time interval which would significantly influence these results, and second, since we suspect that the assigned GRIP timescale is not reliable in this time period.

One can see that the oxygen flux variations of more than ±100% are not realistic in the sense of either buildup or destruction of a biomass, at least not for the land biosphere. Even negative values are required to match these dramatic atmospheric changes using a constant land biomass of 2100 Gt C. Not even a collapse of the ocean biomass is enough to explain these shifts. The lower variability over the last glacial-interglacial cycle (see other experiments) compared to the changes we discuss here points to other influences, which are discussed in detail by *Chappellaz et al.* [this issue]. The variations in ε_h 2.8-11.3‰ or ε_{or} -11 to -32‰ calculated in order to match the $\delta^{18}O$ of atmospheric oxygen as measured in GRIP ice are larger than the ranges 4-8‰ given by *Dongman et al.* [1974] and -15 to -25‰ by *Kiddon et al.* [1993]. An interesting result is obtained when we ascribe all δ_a variations to changes of the forcing signal of δ_o, holding all other parameters constant. This is another indication that the measured δ_a values point to stratigraphic problems, as the measured and modeled seawater $\delta^{18}O$ signals are not compatible, even not if a smoothing of model-derived $\delta^{18}O$ due to water mixing is considered. Especially, the fast transitions from negative to positive δ_o values are not realistic since building up a considerable ice sheet takes many thousands of years. We have not performed a multivariable run which would lower the amplitudes as for experiment 2, but the variation would certainly stay unrealistically high. Hence these results strengthen the hypothesis that these fast shifts seen in δ_a and in detailed methane measurements [see *Chappellaz et al.*, this issue] are a result of stratigraphic disorder.

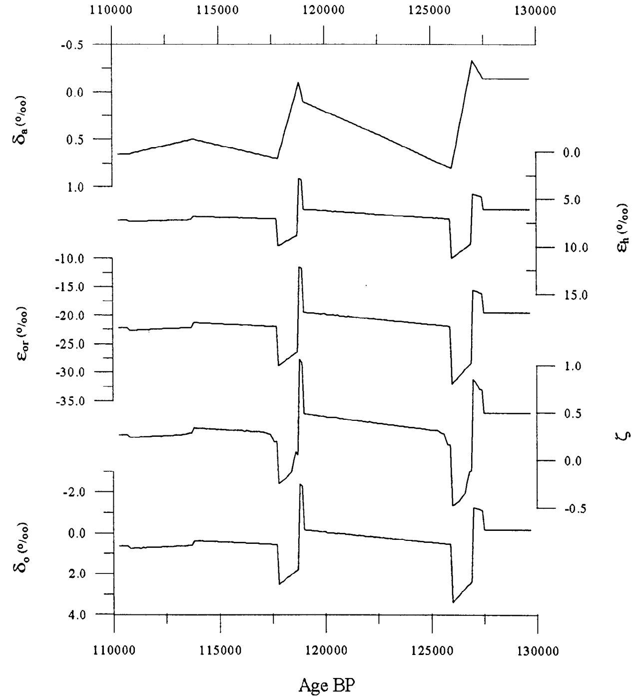

Figure 3. GRIP Eemian experiment. The top panel shows the measured δ_a record as taken from *Fuchs and Leuenberger* [1996]. The other curves show the model parameter variations, which are required to match the measured δ_a. Note that only one parameter per run was adjusted and δ_o was set to 0‰ (except when calculating δ_o itself), since (1) the δ_o from V19-30 shows no major deviations during the time interval of interest and (2) the dating of the GRIP core at these depths is questionable.

Experiment 2

In this experiment, we made use of the δ_a measurements on the Greenland Ice Sheet Project 2 (GISP2) ice core by *Sowers et al.* [1994] in order to compare the required variation of any model parameter to match δ_a with its uncertainty range. The forcing functions were the δ_o values of benthic foraminifera from the V19-30 core and the assumed variation of land biomass according to Figure 2, prescribing the oxygen fluxes. The δ_a record was interpolated to yield an equidistant record (100 years) and then smoothed with a 1100-year running mean. It is essential for this kind of calculation that the assigned age scales are accurate. As the age scale for GISP2 has been constructed from the corresponding Vostok age scale for ages older than 37,000 years [*Bender et al.*, 1994; *Mayewski and Bender*, 1995] and the Vostok scale was correlated with the higher-resolution short SPECMAP (e.g., timescale based on stacked $\delta^{18}O$ of foraminifera records [Pisias et al., 1984]; Martinson et al., [1987]) scale [*Sowers et al.*, 1993], we have at least the best possible matching for these records available today.

Figure 4 shows us the variations of the model parameter required to get the measured δ_a of GISP2 from the original ocean signal of V19-30. There is a good correlation between these variations, which is not too surprising since (1) is linear in these parameters; hence more or less linear correlations are expected. As in experiment 1, the variations of the model parameters required to match the measured δ_a are larger than the given range of uncertainty associated with every parameter for today's condition, except for the hydrological fractionation ε_h.

Single-variable runs. First, we will discuss the main trends, before looking at temporal changes. For the fractionation factor (ε_r, ε_{or}, ε_d), we would expect more negative values during glacial times, because most of the fractionations increase with decreasing temperatures. The fact that the

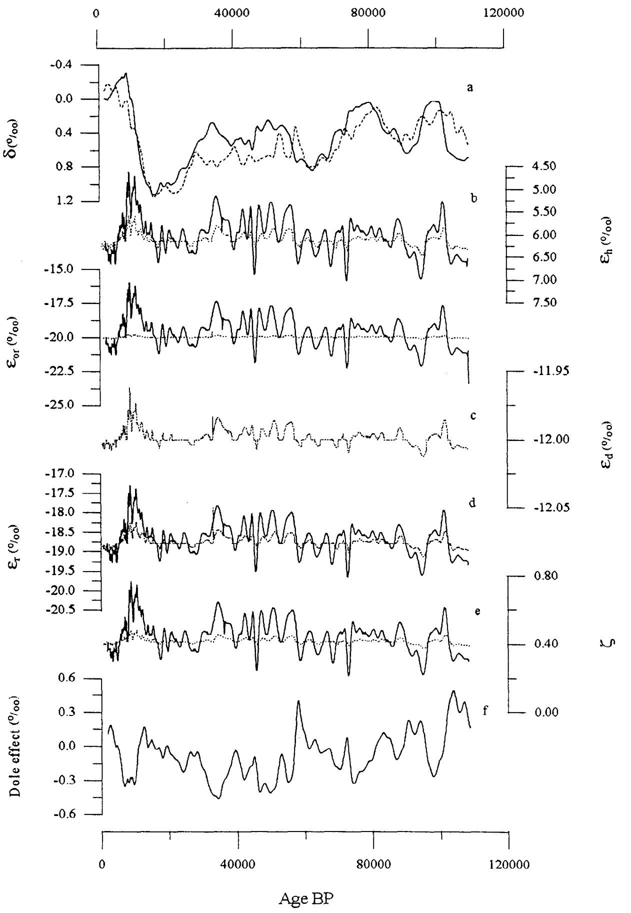

Figure 4. GISP2 δ_a record matching for the last 110,000 years. (a), Solid line, δ_a for GISP2 adopted *from Bender et al.*, [1994]; dashed line, δ_o as reconstructed from foraminifera of the V19-30 sea sediment core [*Pisias et al.*, 1984; *Shackleton and Pisias*, 1985]. (b-e), Model parameter variations required to match the δ_a. Solid lines, single-variable runs; dashed lines, multivariable runs (see text). (f), Dole effect, e.g., difference of (δ_a - δ_o) (see Figure 4a).

matching procedure leads to less negative fractionation factors for all respiration processes on land (ε_r) and in the surface and deep ocean (ε_{or}, ε_d) can point to the following three reasons: (1) The fractionation factors should be assumed more positive, (2) they are rather constant and the variability in the Dole effect comes from the other parameters, or (3) the fractionation parameters are indeed smaller for colder climates. One argument in favor of 1 is the calculations discussed in the "General Remarks" section that ε_{or} should be smaller than ε_r and toward the higher end of the given range by *Kiddon et al.* [1993]. However, this would lead to higher ε_h, further away from the value calculated by *Farquhar et al.* [1993]. The second possible explanation is rather unlikely since then the Dole variability has to be explained by major changes of ε_h and/or oxygen flux ratio changes. Most probably, 3 is correct, as it has already been shown that ^{13}C fractionation during photosynthesis was lower during glacial times on land [*Van de Water et al.*, 1994] and in the ocean [*Jasper and Hayes*, 1990; *Rau et al.*, 1991]. Therefore it is likely that oxygen fractionation during respiration is lower during colder periods. This does not necessarily contradict the general rule of increasing fractionation with lower temperature, as the fractionation could be a combination of several fractionations with different temperature dependencies. This would allow an opposite behavior of the overall fractionation with temperature without violating the general rule.

The parameter for the hydrological cycle (ε_h) becomes less positive in glacial times, indicating either a more depleted soil water or a lower evapotranspiration fractionation due to a higher humidity. These two influences work in opposite directions and should balance fairly well as the following calculation shows. First, the transpiration/condensation processes and the isotopic composition of the corresponding water and vapor depend on temperature. As this fractionation gets larger with decreasing temperature (-0.2‰/°C), we would expect a lower ε_h due to a lower δ^{18}O of soil water. Indeed, this is mainly what we observe in our calculations; see Figure 4. However, the leaf water enrichment, which is dependent on the relative humidity as summarized by *Farquhar et al.* [1993] and *Saurer et al.* [1997], is working against this decrease. Because lower temperature leads to lower humidity, the leaf water enrichment becomes larger (0.37‰/%), partly or fully compensating the temperature effect on the soil water. *Saurer et al.* [1997] found that the humidity dependence could be as low as 30% of the theoretical calculation. This could indicate that the temperature effect is stronger than the humidity effect, leading to less positive ε_h values.

The oxygen flux ratio is higher during cold periods; this would point to a larger marine biosphere as there is general agreement that the land biosphere was lower during these times. If all the changes of the Dole effect were due to changes in marine biomass, variations of more than 100% of today's value would be required.

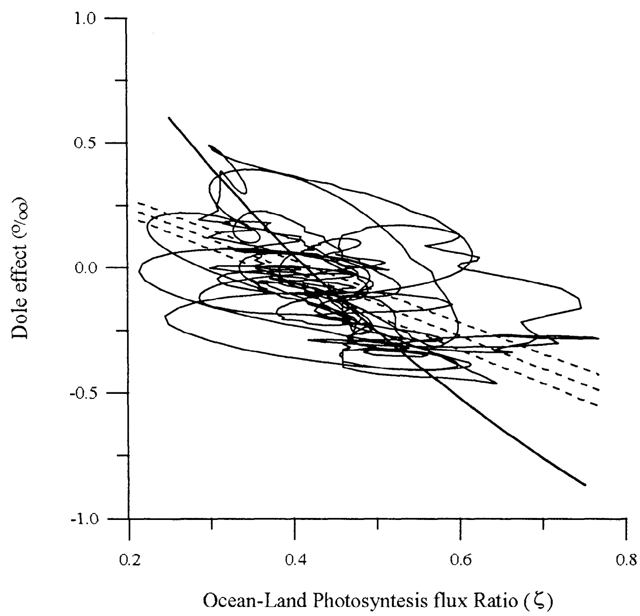

Figure 5. Sensitivity of the ocean-to-land photosynthesis flux ratio (ζ) to Dole effect changes. Thin solid line, Dole effect versus ocean-to-land photosynthesis flux ratio values from Figure 4 for one glacial-interglacial cycle 110,000 to 0 years B.P. Dashed lines, corresponding linear correlation ± 1 σ deviation lines. Thick solid line, equilibrium dependence of the Dole effect on the ocean-to-land photosynthesis flux ratio. The different slopes for the thick and dashed lines reflect the time dependence (O_2 exchange times) of these sensitivities; for example, dashed lines represent nonequilibrium sensitivities.

Sensitivities. The required variation of the model parameters to match the measured isotopic composition of atmospheric oxygen δ_a can be used to determine their sensitivities for Dole effect changes. As an example, we plotted the Dole effect versus the oxygen flux ratio in Figure 5. In Table 2 we summarize the sensitivities and their uncertainties for the main model parameters. The oxygen flux ratio, ζ, is the least sensitive parameter. For a change in the Dole effect of 1‰, nearly a 200 % change of today's oxygen flux ratio is needed, whereas only a 20 % change in the land respiration fractionation (ε_r) is required. The Dole effect is fairly sensitive to changes in the fractionation associated with the hydrological cycle (ε_h) and the ocean respiration fractionation (ε_{or}). Interestingly, changes in δ_o will be seen damped by a factor of 3 in the Dole effect since ocean variations are transferred to δ_a with a dampening of two thirds of its size. From Tables 2 and 3 it is obvious that variation of a single parameter cannot explain a 1‰ Dole effect change as the uncertainty ranges of the model parameter are smaller than the required changes. Therefore this supports the expectation that more than one parameter has an impact on the measured Dole effect change. That is why we would like to discuss in the following a multiparameter adjustment to obtain a more realistic estimation of real parameter changes.

Multivariable runs. The adjustments were made such that the square sum of the weighted differences of the variables from their best estimates was minimal. The weighting w_i was based on the uncertainty of every parameter in the form:

$$w_i\,(\Delta x_i)^2 = \text{constant}$$

where w_i is weight and Δx_i: is uncertainty of parameter i.

In Table 3, a summary of the parameters and their uncertainty as well as their weighting is given. The amplitude of the parameters decreased according to their weight, and their sensitivity compared to the single-variable runs is now within the uncertainty of today's values. The main structure, however, is maintained as can be seen from Figure 4.

Temporal variations. There are several deviations of the ε_h toward less positive values, corresponding with the deviations of the oxygen flux ratio, ζ, toward more positive values, both indications of a smaller Dole effect. These deviations could be associated with meltwater pulses altering the isotope composition of sea surface waters. Hence a much more structured surface water $\delta^{18}O$ record is expected than suggested by the smooth deep sea record from V19-30. The most dominant excursions is a double peak at 8500 and 10,400 years ago, on the Greenland Ice Sheet Project 2 (GISP2) gas-age scale. Whether these two peaks have something to do with the well-known Fairbanks meltwater pulses [*Fairbanks et al.*, 1992] is the subject of experiment 3. One could argue that these temporal patterns will, first, be dependent on the differences in the age scales associated with the ocean and atmosphere record and, second, be dependent on different kinds of land biomass changes. We studied these possible implications and found that the results for the temporal pattern obtained here were robust against such variations. The low sensitivity for the oxygen flux ratio, ζ (see Table 2), indicates a low sensitivity for biomes changes since the oxygen fluxes are in first order driven by the biome size. Conformity in age scales for the records used is the best available so far, but futher improvement will help us to minimize uncertainties associated with dating and age scale comparisons. Furthermore, as will be seen in experiment 3, two different sets of gas-ice age differences do not principally change the temporal pattern. Additionally, when we use the stacked benthic record of *Duplessy and Labeyrie* [1988] instead of V19-30, the temporal pattern does not significantly change. Applying a multitaper spectral analysis for these parameter variations in Figure 4 yields the same frequencies as for the δ_a and δ_o, namely 23 and 12.8 kyr with a signification level of 0.95.

Table 2. Sensitivities for Model Parameters

Parameter	Sensitivity ‰/‰	1 σ Error ‰/‰	r^2	Relative Change per ‰ Dole Effect
δ_o	-0.39	± 0.01	0.39	
ε_d	-0.01	± 0.01	0.33	830 %
ε_h	0.29	± 0.01	0.33	56 %
ε_{or}	-0.11	± 0.01	0.33	45 %
ε_r	-0.29	± 0.01	0.33	20 %
ζ	-1.29	± 0.05	0.37	190 %

Table 3. Multivariable Run Parameter

Parameter	Best Estimates x_i	$(\Delta x_i)^2$	Weights	Relative Errors
ε_d	-12.0 ‰	4	1	17 %
ε_h	6.15 ‰	4	1	31 %
ε_{or}	-20.0 ‰	4	1	10 %
ε_r	-18.8 ‰	4	1	11 %
ζ	0.41	0.33	12	80 %

Experiment 3

From the studies of *Bender et al.* [1994] and *Sowers et al.* [1993] we know that the Dole effect did change less than 1‰ over time. However, in experiment 2, we showed that the variations of the parameters used for adjusting the model output to the measured δ_a were larger than the corresponding uncertainty ranges. We therefore cannot exclude the possibility that the benthic record used for δ_o (V19-30) does miss significant variations of surface waters which would be transferred to the atmospheric oxygen. The indications of melting events from temporal variations of ε_h discussed above led us to perform an experiment varying the input signal holding all the other parameters constant at the values required for today's Dole effect. Results for δ_o are given in Figures 6a and b. A much more structured ocean record δ_o than the smooth V19-30 benthic record is obtained. This is expected as ice melting events, with its highly depleted $\delta^{18}O$ water, will leave a negative excursion in the surface water. As we have ascribed all δ_a variations to the input signal, we must be careful in solely interpreting it as the surface water $\delta^{18}O$ signal, but at least it could show us the possible degree of variation due to melting events. Caution is further strengthened by the fact that the mean of the isotopic composition of surface waters does not equal the benthic deep ocean value, which must be a problem of a single-variable run overestimating the absolute changes. But, it would be coincidental that exactly the light peaks would all disappear running a multiparameter calculation.

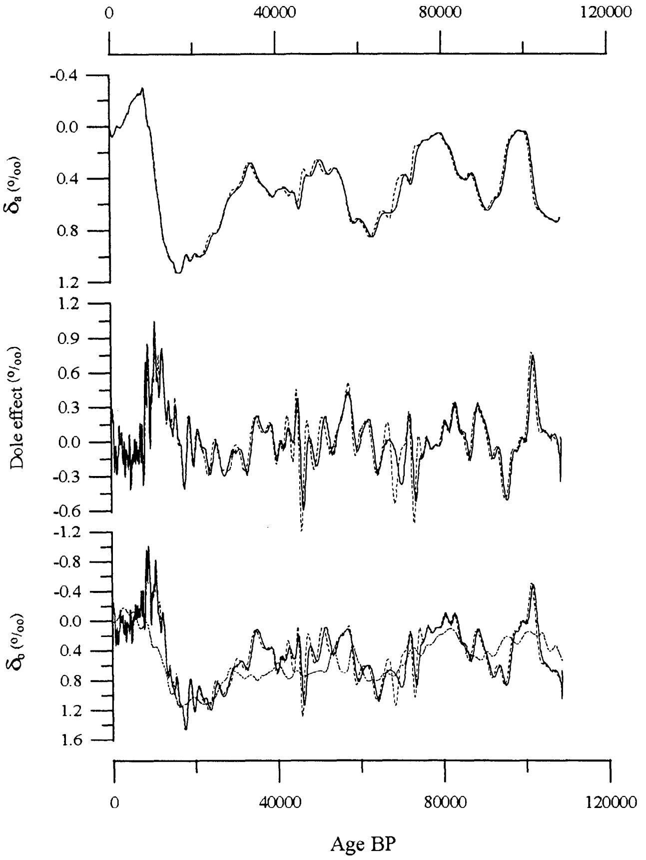

Figure 6a. Sea surface $\delta^{18}O$ reconstruction for the last 110,000 years. (top) Solid line, δ_a from GISP2 as published by *Bender et al.* [1994]; dashed line, δ_a from GISP2 but shifted by a new estimate of gas-ice age differences (see text). (middle) Dole effect, e.g., (δ_a - δ_o). (bottom) The δ_o needed to match δ_a of the top panel. All other model parameters were held constant. Dotted line, δ_o from V19-30 [*Pisias et al.*, 1984; *Shackleton and Pisias*, 1985].

This means that at least one other parameter must have changed. A good candidate is ε_r since our trend to lower fractionation during cold periods is in agreement with measurements as discussed above.

Main light peaks are present at 8,2, 8,7, 10,4, 12,1, 13,7, 15,3, 18,4, 20,6, 24,5, 34,4, 42,2, 44,5, 47,0, 50,6, 56,0, 61,0, 66,5, 72,0, 88,0, 101,3 kyr. The two major peaks at 8.5 and 10.4 kyr cannot be the well-known Fairbanks meltwater pulses, as they have been dated with the U/Th method to have occurred at 11 and 14.1 kyr ago [*Bard et al.*, 1990a, b]. Even considering an uncertainty of the U/Th ages of about 1000 years, comparing the two major melting events measured on the Papua New Guinea drill core and the Barbados core [*Edwards et al.*, 1993] does resolve this age discrepency. An error of 3000-4000 years in the GISP2 age scale at around 10,000 years can be excluded as this was measured by seasonal signal counting [*Meese et al.*, 1994]. The gas-ice age difference was calculated to be 240 to 630 years for GISP2 [*Sowers and Bender*, 1995]. Recently, new temperature records were reconstructed from the bore hole temperature measurements at GISP2 [*Cuffey et al.*, 1995] and the Greenland Ice Core Project (GRIP) [*Johnsen et al.*, 1995], indicating that the temperature difference between glacial and interglacial times was underestimated by as much as 10°C. If this were true, then the gas-ice age differences would be nearly twice as large for glacial times. Hence the δ_a transitions from glacial-to-interglacial time would become steeper, which in turn would enlarge the deviations in Figures 6a and 6b around 12,000-16,000 years ago. We ran the model with a new estimate of gas-ice differences by J. Schwander (personnel communication, 1996). This amplifies the small light peaks at 12.1 and 13.7 kyr a little, and they could be an indication of the Barbados meltwater pulses as can be seen from Figure 6b. A consequence of these arguments is that there should be many meltwater pulses yet to be discovered in sea sediments cores. A detailed discussion of these "light" peaks would be to speculative at this time, since there is still too much uncertainty in the many parameters involved, as well as in the dating of the records used.

Summary and Outlook

Our results with a simple model indicate that the transfer of the ocean $\delta^{18}O$ signal to the atmosphere is dependent on many parameters and that the Dole effect variations cannot be explained by a single parameter. The most sensitive variable is the land respiration fractionation (ε_r), whereas the deep ocean fractionation (ε_d) and the oxygen flux ratio (ζ) show much lower sensitivities; other parameters are moderately sensitive. Hence explaining the fast and large changes in δ_a for the GRIP Eemian ice solely by changing oxygen fluxes and therefore biomes, we would have to change the marine biomass by

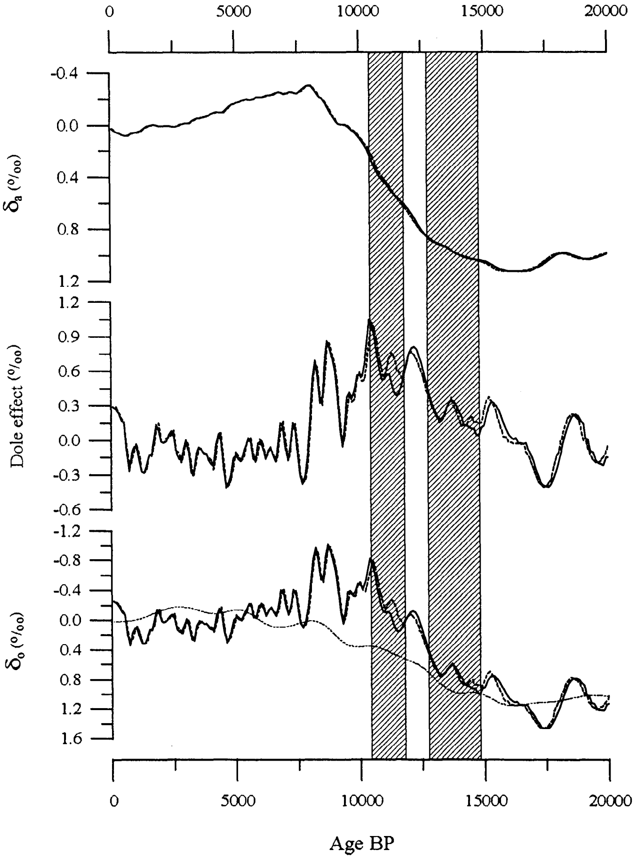

Figure 6b. Enlargement of Figure 6a for the last 20,000 years. The hatched areas represent the time intervals with uncertainties for the main two meltwater pulses, [*Edwards et al.*, 1993].

much more than ±100%, which is unrealistically high. Therefore, as discussed by *Fuchs and Leuenberger* [1996], stratigraphic disorder is the most plausible explanation. The results obtained by matching the model output to the measured GISP2 δ_a lead to smaller fractionations during cold periods, in agreement with results for the photosynthetic ^{13}C discrimination on land and in the ocean. This finding does not necessarily contradict the general rule of higher fractionation for lower temperature when allowing the fractionation discussed here to be a combination of at least two fractionation factors with different temperature dependencies.

In contrast to the single parameter matching, the multiparameter adjustment yields required changes to match the output signal to the measured δ_a values which are within their uncertainty range of today's values. The temporal pattern of these changes could point to several meltwater events. A reconstruction of the input signal, assuming constant model parameters, yields a record which could represent the main features of the surface seawater $\delta^{18}O$. In this signal, several light isotope peaks are seen which would indicate many more meltwater events than the large two Barbados pulses. Comparisons with existing surface ocean $\delta^{18}O$ records will help us to do the next step. Furthermore, it would be very helpful to have more studies looking at fractionation factors and O_2/C ratios associated with respiration processes, especially for soil. We have preliminary results for a grassland-type soil which point to a smaller fractionation and a higher O_2/C ratio for soil respiration than assumed in this study, even taking diffusion effects into account. This further increases the difficulty to explain today's Dole effect as mentioned by *Bender and Sowers* [1994]. Hence soil studies would allow us to understand better today's Dole effect, as well as the temporal variability of the bio-physico-chemical processes associated with it.

Acknowledgments. I like to thank T. Sowers and M. Bender for supplying me with the GISP2 $\delta^{18}O$ record and S. Borella and D. Peel for many helpful discussions. This work was supported by the Swiss National Science Foundation.

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Markus Leuenberger, Climate and Environmental Physics, University of Bern, Sidlerstrasse 5, 3012 Bern, Switzerland. (e-mail: leuenberger@climate.unibe.ch).

(Received January 15, 1996; revised December 2, 1996; accepted January 16, 1997.)