A model of the Earth’s Dole effect

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Received 28 February 2003; revised 11 August 2003; accepted 21 October 2003; published 16 January 2004.

[1] The Earth’s Dole effect describes the isotopic $^{18}O/^{16}O$-enrichment of atmospheric oxygen with respect to ocean water, amounting under today’s conditions to 23.5%. We have developed a model of the Earth’s Dole effect by combining the results of three-dimensional models of the oceanic and terrestrial carbon and oxygen cycles with results of atmospheric general circulation models (AGCMs) with built-in water isotope diagnostics. We obtain a range from 22.4% to 23.3% for the isotopic enrichment of atmospheric oxygen. We estimate a stronger contribution to the global Dole effect by the terrestrial relative to the marine biosphere in contrast to previous studies. This is primarily caused by a modeled high leaf water enrichment of 5–6%. Leaf water enrichment rises by ~1% to 6–7% when we use it to fit the observed 23.5% of the global Dole effect. The present model is designed to be utilized in forthcoming paleo studies allowing a quantitative analysis of long-term observations from polar ice cores. INDEX TERMS: 0330 Atmospheric Composition and Structure: Geochemical cycles; 1040 Geochemistry: Isotopic composition/chemistry; 1610 Global Change: Atmosphere (0315, 0325); 1854 Hydrology: Precipitation (3354); KEYWORDS: carbon cycle, Dole effect, water isotopes


1. Introduction

[2] The Dole effect (DE in the following), i.e., the isotopic $^{18}O/^{16}O$-enrichment of atmospheric oxygen with respect to ocean water, is affected by a number of different processes in the global cycle of oceanic and of water: strength and type of terrestrial and marine oxygen fluxes, evapotranspiration, and humidity over the continents [Bender et al., 1994b]. Modeling of the DE is therefore a valuable test case of Earth system models which integrate biological and climatic components. Furthermore, variations of the DE in the Quaternary have large implications for the interpretation and dating of polar ice cores [Bender et al., 1994a, 1994b; Jouzel et al., 2002; Shackleton, 2000]. A prognostic model of the DE therefore will help to identify the relevant forcing factors affecting the DE in the past.

[3] Measurements of the isotopic composition of a number of bioactive atmospheric gases were used to better separate and quantify the natural and anthropogenic perturbation of the global cycles of carbon and oxygen [Keeling, 1960, 1995]. Because of the integrating tendency of the atmosphere, this approach avoids the problem of deducing general information from spatially and temporally highly variable local measurements. For example, the carbon isotopic composition of CO$_2$ has been used to separate marine and terrestrial sources [Ciais et al., 1995] and the oxygen isotopic relation of CO$_2$, C$^{18}O$C$^{16}O$, C$^{16}O$C$^{18}O$, to separate the gross exchange fluxes of terrestrial ecosystems [Ciais et al., 1997a, 1997b; Farquhar et al., 1993; Peylin et al., 1999]. The $^{18}O/^{16}O$ oxygen, $\delta^{18}O_{Atm}$, has up to now primarily been used in paleoclimatic studies [Bender et al., 1994a, 1994b; Sowers et al., 1991]. The long atmospheric residence time of oxygen of approximately 1200 years [Bender et al., 1994b], and the fact that within today’s measuring precision no interhemispheric gradient has been detected, make the $\delta^{18}O_{Atm}$ signal an interesting tool to synchronize Northern and Southern Hemispheric ice core records. Similar to the oxygen isotopic tracer of CO$_2$, $\delta^{18}O_{Atm}$ is strongly affected by photosynthesis and respiration in the carbon/oxygen cycle and by the hydrological cycle. The enrichment of today’s atmospheric oxygen of 23.5% Vienna-Standard Mean Ocean Water (V-SMOW) [see Craig, 1961] relative to its largest source, the global oceans, was called the Dole effect [Dole, 1935; Mortara and Titani, 1936]. Similar to the isotopic tracers of carbon dioxide (CO$_2$, C$^{18}O$C$^{16}O$, C$^{16}O$C$^{18}O$), spatial and temporal variations of $\delta^{18}O_{Atm}$ must exist, however, because of the large atmospheric abundance of oxygen, these are expected to be very small and have not been observed in modern air samples until now. It will need at least 1 order of magnitude higher precision of modern mass spectrometric techniques

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for measuring such variations. However, air bubbles enclosed in ice samples from polar ice cores exhibit deviations from the modern value of up to $0.7\%$ [Bender et al., 1994b; Malaize et al., 1999; Sowers et al., 1991], demonstrating drastic changes in the carbon and the hydrological cycle in the past.

[4] We present here a diagnostic model of the DE based on the output of spatially and temporally resolved biochemical models of the $O_2$ cycle. These models include built-in diagnostic modules for calculating the various isotope fractionations as a function of local climate conditions. Formerly, highly parameterized modeling efforts to understand the DE and its variations in the past focused on the sensitivity of the calculation to the various assumptions applied [Leuenberger, 1997]. In contrast, the model presented here provides a process-based approach for inferring the DE. It estimates today’s and past DE from first principles solely as a consequence of the corresponding climate conditions.

[5] Section 2 reviews the present understanding of the processes controlling the DE. In section 3 we present the model components and discuss in detail the methods utilized to combine model results and to estimate the DE in this study. We next focus in section 4 on the spatial signature of the result and the uncertainties in the model. Finally, we conclude with a discussion of possible applications of the model to learn about long-term changes of the DE during the Pleistocene and what follows in the future.

2. Dole Effect

[6] Bender et al. [1994b] reviewed the progress that has been made in the last 15 years to better estimate the various fractionation processes of the oxygen isotopes and calculated a global balance of the different sources and sinks of $^{18}O$ of atmospheric oxygen. Figure 1 shows in a schematic way the results of Bender et al. [1994b] based on their estimated $O_2$ fluxes and fractionation coefficients (see also Table 1). Respiration represents a variety of processes, which oxidize organic carbon and release CO$_2$ while consuming molecular $O_2$. During respirative consumption of oxygen, most of the $O_2$ sink components are accompanied by a fractionation of approximately $20\%$. In the terrestrial domain a more or less direct exchange of the consumed oxygen with the atmospheric reservoir takes place. Dissolved oxygen, $O_{2\text{DISS}}$, in the deep ocean, however, represents an oxygen pool that exchanges with the atmosphere solely on the long timescale of oceanic deep water circulation (100 to 1000 years). Respirative fractionation therefore enriches $O_{2\text{DISS}}$ considerably, particularly in oceanic regions with high remineralization rates and comparably low exchange rates with the surface ocean and the overlying atmosphere. $\delta^{18}O_{\text{DISS}}$ denotes the $^{18}O/^{16}O$-relation in the dissolved oxygen, $O_{2\text{DISS}}$. The $\delta^{18}O_{\text{DISS}}$ is enriched by as much as $15\%$ relative to the atmospheric signal, that means $38\%$ relative to V-SMOW [Kroopnick, 1987]. As a consequence, the contribution of mineralization in the deep ocean to the atmospheric DE decreases its value, with an asymptotic value of $12\%$ [Bender et al., 1994b]. The larger part (about $95\%$) of oceanic respiration, however, takes place in the euphotic layer where dissolved $O_2$ has a residence time of a few weeks and therefore is in close isotopic equilibrium with the atmosphere. Here the respirative fractionation was estimated, similar to the terrestrial environment, to be $20\%$. Summarizing the role of respiration in controlling the DE, Bender et al. concluded that land or ocean respiration alone cannot explain the observed high value of $23.5\%$ (respiration effects sum up to $18.8\%$) and that in the terrestrial and the marine biosphere, respirative fractionation is about equally strong.

[7] In vitro experiments of Guy et al. [1993] demonstrated that during the photosynthetic production of $O_2$, there is no additional fractionation relative to the water from which the oxygen isotopes originate. For the marine domain, therefore, photosynthesis is a source of $O_2$ being in equilibrium with the isotopic composition of water in the euphotic zone. From early water isotope measurements, it has long been known that ocean surface water varies typically between $-1.5\%$ in polar regions to $+0.5\%$ in the tropics [Craig and Gordon, 1965; Schmidt, 1999]. The area-weighted global average is close to $0\%$, which is thus a good estimate for the isotopic composition of the oxygen released during photosynthetic activity of plankton. In the terrestrial environment, the water surrounding the biochemical diagenesis of oxygen is strongly enriched by evapotranspiration from leaves. Plant transpiration correlates with photosynthetic $O_2$ emissions to the atmosphere. Water taken up by the roots is transpired through the leaves. During evaporation and diffusion through the stomata and through the leaf boundary layer, an enrichment of the remaining leaf water takes place. According to different studies, this enrichment amounts to a global production-weighted average of between $+4–+8\%$ [Dongmann, 1974; Farquhar et al., 1993]. This enrichment of leaf water depends on a number of factors, some of them are “external” to the plants. For example, the rainout of air masses affects the isotopic composition of the soil water taken up by the plants, or relative humidity close to the stomata controls the balance between evaporation and diffusion out of the stomata. It also depends on “internal” processes, such as the mixing between depleted sapwater and enriched evaporative water within the leaves. The terrestrial $^{18}O$/$^{16}O$ flux therefore is strongly influenced both by the external boundary condition imposed by water isotope physics and by internal processes affecting the turnover of water in leaves. Anthropogenic combustion processes, accompanied by fractionation as well, were not considered assuming that today’s DE has not yet been altered by them to measurable extent. The budget presented here therefore primarily reflects pre-industrial conditions.

[8] To calculate the DE, Bender et al. [1994b] sum up the different fractionation factors discussed above weighted with the respective oxygen fluxes. Owing to the considerable (more than $4\%$) difference between the oceanic and the terrestrial contribution to the global DE, the relation between the respective production rates (annual turnover of moles of $O_2$), $P_D$ for the ocean and $P_T$ for the terrestrial environment, is crucial in the calculation. It was estimated to $P_D/P_T \sim 1/2$. With these numbers the best guess of the global DE amounts to $20.4\%$, considerably underestimating the observed value.
This gave rise to speculations that some important terms in the calculation might have been neglected, such as fractionation effects during the diffusion of oxygen in soils. However, the estimation is also accompanied by considerable uncertainties, the largest being the global isotopic composition of leaf water and the relative oxygen turnover rates in the terrestrial and the marine domain.

3. Model Construction

The overall DE results (in the context of the following formulas we use the symbol $\Delta$ for the magnitude of the DE) from the combination of ocean processes of isotopic $O_2$ enrichment termed DO or “ocean Dole effect” and of the terrestrial equivalent DT, termed the “terrestrial Dole effect,”

$$\Delta = \delta^{18}O_{\text{ATM}} - \delta^{18}O_{\text{OW}} = F\Delta_0 + (1 - F)\Delta_T - \varepsilon_{\text{ST}},$$  

with $P_O$ and $P_T$ being the $O_2$ fluxes of gross oceanic and terrestrial productivity, respectively, and the factor $F = P_O / P_T$.

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### Table 1. Budget of the DE According to This Study and Bender et al. [1994b]a

<table>
<thead>
<tr>
<th>Component</th>
<th>This Study</th>
<th>Bender et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ocean production $P_O$, Pmol $O_2$/year</td>
<td>7.61</td>
<td>12.</td>
</tr>
<tr>
<td>Terr. production $P_T$, Pmol $O_2$/year</td>
<td>16.7</td>
<td>18.90</td>
</tr>
<tr>
<td>Terrestrial Dole effect $\Delta_T$, %</td>
<td>26.9 (25.9)</td>
<td>22.4</td>
</tr>
<tr>
<td>Terrestrial Dole effect, %</td>
<td>0.3 (0.4)</td>
<td>0.59</td>
</tr>
<tr>
<td>Total Dole effect $\Delta$, %</td>
<td>23.5 (22.9)</td>
<td>20.8</td>
</tr>
<tr>
<td>Total Dole effect, %</td>
<td>0. (0.4)</td>
<td></td>
</tr>
</tbody>
</table>

aAll isotope values are given in $\%$ deviation relative to VSMOW. For terrestrial effect values, the median and the corresponding standard variation of the three model simulations (ECHAM/SILVAN; ECHAM/SLAVE; GISS/SLAVE) are shown here. The values in brackets specify the values without correction for the diurnal effect (see text for details).
The term $\varepsilon_{ST}$ is a small fractionation of 0.4% [Bender et al., 1994b] due to an isotopic exchange between O$_2$ and CO$_2$ in the stratosphere. Respiratory uptake of O$_2$ preferentially consumes the light oxygen atoms $^{16}$O, thus leaving the source oxygen reservoir isotopically enriched by approximately 20% depending on the type of respiration (see below). Photosynthetic production of O$_2$ releases oxygen isotopically labeled with the water surrounding the chloroplasts. In the ocean biosphere, this corresponds to the mean isotopic composition of water in the euphotic layer, $\delta^{18}$O$_{EUPH}$. In the terrestrial domain, it corresponds to the isotope value of leaf water, $\delta^{18}$O$_{LEAF}$. It is mainly this evaporative enrichment, subsequently transferred onto atmospheric oxygen, that makes $\Delta_{T}$ larger than $\Delta_{O}$. Because of this difference, a change in the relationship between the oceanic, $P_{O}$, and the terrestrial production rates, $P_{T}$, directly influences the DE.

[10] We estimate the terrestrial and the oceanic DE, $\Delta_{T}$ and $\Delta_{O}$, and the corresponding O$_2$ production rates, $P_{O}$ and $P_{T}$, using a hierarchy of different models (Figure 2). The
Typically, the relative humidity is a prognostic variable temporally representative for the humidity within the canopy. The largest activity is typically observed close to sunlight maximum. However, physiological adaptations of plants avoiding large moisture losses at noon or climate conditions such as cloud coverage make the diurnal productivity cycle more complex than a linear function of net incoming radiation. A mechanistically correct computation of the isotopic composition of leaf water would therefore need to synchronize and detail simulation of all these processes, which was not possible here. It was these uncertainties that lead Bender et al. [1994b] to conclude “that the biggest current uncertainty lies in the $\delta^{18}O$ of leaf water.” Nevertheless, it seems reasonable to argue that the effective relative humidity relevant for the $\delta^{18}O$ signal in the emitted $O_2$ must be considerably biased toward midday values which are typically lower than the monthly mean average.

Here $h$ denotes the relative humidity near the plant stomata, $\delta^{18}O_{Vap}$ and $\delta^{18}O_{Gwat}$ denote the $^{18}O$ content of vapor in the first model layer and of groundwater, respectively. $\varepsilon_{EQUIL}$ describes the isotopic fractionation under equilibrium conditions ($\approx 10\%$, Table 2), and $\varepsilon_{KIN}$ describes the strong kinetic fractionation during diffusive exchange of water molecules out of the stomata ($\approx 26\%$, Table 2). Typically, $\delta^{18}O_{Gwat}$ is about 10% more enriched than $\delta^{18}O_{Vap}$. With the values given above, the difference between the first and the second term in the Craig and Gordon equation amounts to approximately 16%. Consequently, a large $h$ diminishes $\delta^{18}O_{LEAF}$; a lower $h$ gives more weight to the kinetic fractionation and thus enhances $\delta^{18}O_{LEAF}$. Therefore, in this calculation, the specified relative humidity close to the plant stomata during daytime photosynthesis is crucial.

Unfortunately, the employed monthly fields of relative humidity of both AGCMs are neither spatially nor temporally representative for the humidity within the canopy. First, the relative humidity is a prognostic variable calculated in the lowermost AGCM layer. This is at a height of about 30 m in the ECHAM model and at about 150 m in the GISS model. However, the relevant humidity in the Craig and Gordon [1965] formula (equation (2)) is the humidity at the leaf surface, which is normally higher than the humidity within the canopy or in the overlying free atmosphere. Second, and probably most important, over a daily cycle the relative humidity in the canopy undergoes large variations as does the isotopic composition of leaf water [Bariac et al., 1994; Förstel, 1978]. In different forest types, daily amplitudes of $\delta^{18}O_{LEAF}$ of up to 10–15‰ have been measured demonstrating the importance of computing $\delta^{18}O_{LEAF}$ synchronously with the daily cycle of $O_2$ fluxes. Moreover, the isotopic composition of sap water shows a large daily amplitude of about 2‰. This is most probably due to an increasing pumping depth of the plant’s root system during daytime when the demand of water for transpiration becomes larger [Bariac et al., 1994]. Therefore $\delta^{18}O_{LEAF}$ (and thus the relative humidity) relevant for the $O_2$ fluxes has to be estimated during the photosynthetic activity of plants. The largest activity is typically observed close to sunlight maximum. However, physiological adaptations of plants avoiding large moisture losses at noon or climate conditions such as cloud coverage make the diurnal productivity cycle more complex than a linear function of net incoming radiation [Kim and Verma, 1991]. A mechanistically correct computation of the isotopic composition of leaf water would therefore need to synchronize and detail simulation of all these processes, which was not possible here. It was these uncertainties that lead Bender et al. [1994b] to conclude “that the biggest current uncertainty lies in the $\delta^{18}O$ of leaf water.” Nevertheless, it seems reasonable to argue that the effective relative humidity relevant for the $\delta^{18}O$ signal in the emitted $O_2$ must be considerably biased toward midday values which are typically lower than the monthly mean average.
Table 2. List of Symbols Employed in the Text

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^{18}$OATM</td>
<td>$^{18}$O/$^{16}$O isotopic composition of atmospheric oxygen</td>
</tr>
<tr>
<td>$\delta^{18}$OW</td>
<td>$^{18}$O/$^{16}$O isotopic composition of mean ocean water</td>
</tr>
<tr>
<td>$\Delta = \delta^{18}$OATM $- \delta^{18}$OW</td>
<td>magnitude of the overall Dole effect</td>
</tr>
<tr>
<td>$\Delta$O</td>
<td>oceanic Dole effect</td>
</tr>
<tr>
<td>$\Delta_T$</td>
<td>terrestrial Dole effect</td>
</tr>
<tr>
<td>$F$</td>
<td>$P\gamma$/$P\epsilon$+$P_T$ relation of oceanic $O_2$ production to the total $O_2$ production</td>
</tr>
<tr>
<td>$\delta^{18}$Oeuph</td>
<td>$^{18}$O of water in the euphotic layer of the ocean</td>
</tr>
<tr>
<td>$\delta^{18}$Oleaf</td>
<td>$^{18}$O of water in the terrestrial biosphere (Leaves)</td>
</tr>
<tr>
<td>$\delta^{18}$Oground</td>
<td>$^{18}$O of groundwater</td>
</tr>
<tr>
<td>$\delta^{18}$Ovap</td>
<td>$^{18}$O of vapor in the canopy</td>
</tr>
<tr>
<td>$h$</td>
<td>surface-near relative air humidity</td>
</tr>
<tr>
<td>$T_i$, $T_{MAX}$, $T_{MIN}$</td>
<td>surface-near air temperature; monthly maximal and minimal daily temperature</td>
</tr>
<tr>
<td>$T_{nEW}$, $T_{OLDC}$</td>
<td>air temperature after and before correction, $\gamma$ correction factor (see section 3.1.1)</td>
</tr>
<tr>
<td>$T_{LEAF}$</td>
<td>leaf temperature</td>
</tr>
<tr>
<td>$R_{ECO}$</td>
<td>ecosystem respiration = autotrophic + heterotrophic respiration</td>
</tr>
<tr>
<td>$A$</td>
<td>assimilation rate</td>
</tr>
<tr>
<td>$R_{LEAF}$</td>
<td>leaf respiration equals 15% of $A$</td>
</tr>
<tr>
<td>NPP</td>
<td>net primary productivity (CO$_2$)</td>
</tr>
<tr>
<td>GPP</td>
<td>gross primary productivity (CO$_2$)</td>
</tr>
<tr>
<td>GPP$_{O_2}$</td>
<td>$O_2$ flux corresponding to the gross primary productivity; GPP$<em>{O_2}$ is balanced by $R</em>{ECO}$</td>
</tr>
<tr>
<td>$R_{PHOTO}$, $PHO_2$</td>
<td>$O_2$ consuming flux during photosynthesis exactly balanced by a production rate of $O_2$, PHO$_2$</td>
</tr>
<tr>
<td>$R_{MEHLER}$, $P_{MEHLER}$</td>
<td>$O_2$ flux corresponding to other $O_2$ reactions during photosynthesis, estimated as 10% of $R_{ECO}$</td>
</tr>
<tr>
<td>$\gamma$, $\zeta = \gamma/\gamma$</td>
<td>oxygenation and carboxylation rate in moles of RuBP (ribulose bisphosphate) and their relation as defined by Farquhar et al. [1980]</td>
</tr>
<tr>
<td>$\Gamma^*$</td>
<td>CO$_2$ compensation point calculated as by Lloyd and Farquhar [1994]</td>
</tr>
<tr>
<td>$C_i$</td>
<td>inner cellular CO$_2$ concentration calculated as by Lloyd and Farquhar [1994]</td>
</tr>
<tr>
<td>$\alpha_{ECO}$</td>
<td>fractionation at ecosystem respiration; $= 95% \times 19.2%$ (cytochrome pathway) + $5% \times 30.8%$ (alternative pathway) = 20.35% (J. Berry, personal communication, 2002) [Robinson et al., 1992]</td>
</tr>
<tr>
<td>$\alpha_{PHOTO}$</td>
<td>fractionation at photosynthesis = 21.7% [Guy et al., 1993]</td>
</tr>
<tr>
<td>$\alpha_{MEHLER}$</td>
<td>fractionation during the Mehler reaction = 15.3% [Guy et al., 1993]</td>
</tr>
<tr>
<td>$\alpha_{EQUIL}$</td>
<td>$= 9.35%$ at 25°C, equilibrium fractionation during the phase transition between water vapor and liquid water [Farquhar et al., 1989]</td>
</tr>
<tr>
<td>$\delta_{AIN}$</td>
<td>$-26.35%$ kinetic fractionation during diffusion of water vapor from inside the leaf to the air [Farquhar et al., 1989]</td>
</tr>
<tr>
<td>$O_2$DSS</td>
<td>dissolved molecular oxygen in the ocean</td>
</tr>
<tr>
<td>$\delta^{18}$ODISS</td>
<td>$^{18}$O/$^{16}$O-relationship of $O_2$DSS in $\delta$-notation</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>ocean salinity</td>
</tr>
<tr>
<td>$\Omega_{GLOBAL}$</td>
<td>global mean ocean salinity</td>
</tr>
<tr>
<td>PP</td>
<td>marine primary productivity</td>
</tr>
<tr>
<td>Rem</td>
<td>organic remineralized within the euphotic layer</td>
</tr>
<tr>
<td>Rem</td>
<td>organic remineralized within the euphotic layer</td>
</tr>
<tr>
<td>f-ratio, $f$ = (PP-Rem)/PP</td>
<td>f-ratio of exported organic material to primary productivity as defined by Eppley and Peterson [1979]</td>
</tr>
</tbody>
</table>

0.05 and 0.14. This corresponds to a reduction of the effective relative humidity near the leaves of up to 15% compared to the monthly mean average computed by the AGCMs.

3.1.2. Oxygen Fluxes of the Terrestrial Biosphere

We infer the biome distribution and the terrestrial $O_2$ fluxes of photosynthesis and total respiration from two global TBM, SLAVE [Friedlingstein et al., 1992, 1995a, 1995b] and SILVAN [Kaduk, 1996; Kaduk and Heimann, 1996]. The biome distribution is predicted by a classification scheme being part of the SLAVE model and by the BIOME1 model for SILVAN. The respiratory uptake of $O_2$ discriminates against the heavier isotope $^{18}O$ in a different manner for (1) ecosystem respiration, $R_{ECO}$, i.e., the sum of autotrophic and heterotrophic respiration, (cytochrome and alternative pathway), (2) photosrespiration, $R_{PHOTO}$, and (3) several other $O_2$ consuming reactions such as the Mehler reaction or chlororespiration, which we subsume under the Mehler reaction in a generic manner, $R_{MEHLER}$. All three quantities are estimated separately. The terrestrial Dole effect $\Delta_T$ is then calculated on the grid of the corresponding TBM on a monthly basis. This yields

$$\Delta_T = \left( \sum_{i=1}^{i=M} \frac{P_t^{i} \cdot R_{ECO}^{i} + \delta^{18}O_{ATM} - \delta^{18}O_{OW}}{P_T} \right) / \Delta_T.$$

The derivation of this formula is very similar to the computation of the steady state budget of other isotopic tracers (for example, for the $^{18}O$ in CO$_2$ of Ciais et al. [1997a]).

Assuming that the biosphere model is in a steady state, these respiratory fluxes are exactly balanced over a year by corresponding $O_2$ fluxes released during photosynthesis. Each of the oxygen consumption fluxes is affected by a specific, spatially and temporally constant fractionation, $\delta^{18}O_{ECO}$, $\delta^{18}O_{PHOTO}$, and $\delta^{18}O_{MEHLER}$. Here $\delta^{18}O_{ECO}$ is estimated as a weighted mean of fractionation during the cytochrome and
the alternative pathway, and \( \varepsilon_{\text{MEHLER}} \) is chosen as the measured fractionation of the Mehler reaction (see Table 2). On top of that, \( \mathcal{O}_2 \) in water is enriched by about 0.7% with respect to air [Benson and Krause, 1984] so that the overall respiratory fractionation is reduced by this amount.

[16] The terrestrial \( \mathcal{O}_2 \) production, \( P_T \), is isotopically tagged by the leaf water as it is produced during water splitting reactions during photosynthesis. For the sake of clarity, we distinguish the oxygen fluxes relevant in this study from the corresponding carbon fluxes by an index, \( \mathcal{O}_2 \), attached to the usual terms, that is \( \text{GPP}_\mathcal{O}_2 \) (\( \text{PHOO}_2 \)) for the oxygen released during photosynthesis (photorespiration) and corresponding to the carbon Gross Primary Production, \( \text{GPP} \). With this notation, we thus have \( P_T = \text{GPP}_\mathcal{O}_2 + \text{PHOO}_2 + \text{P}_{\text{Mehler}} \). Both TBMs are using quite different methods for estimating \( P_T \), which are explained in detail as follows.

[17] 1. The SLAVE model uses the biome classification scheme following Olson et al. [1985] and aggregates the original 52 biomes of the Olson scheme to 9 biomes. The biomes grassland and savannah are recombined into C3 and C4 type grasses according to a \( \mathcal{O}_2 \) dependent threshold temperature criteria [Haxeltine and Prentice, 1996]. This separation is of particular importance because C4 grasses avoid the energetic disadvantages of photorespiration by a mechanism that concentrates \( \mathcal{O}_2 \) in specialized plant tissue. The SLAVE model first infers the net primary production (NPP) following a light use efficiency formulation [Field et al., 1995]. The assimilation rate, \( A \), is calculated by means of a simple linear relationship from NPP using a biome dependent factor, \( \varphi \), which describes the proportion of \( A \) lost as plant respiration [Lloyd and Farquhar, 1994]: \( A = \text{NPP} / (1 - \varphi) \). Subsequently, GPP is calculated assuming a fixed percentage of 15% of leaf respiration, \( R_{\text{LEAF}} \): \( \text{GPP} = A + R_{\text{LEAF}} = 1.15 \times A \). The percentage of \( R_{\text{LEAF}} \), which denotes mitochondrial \( \mathcal{O}_2 \) release through the stomata is a very stable estimate obtained from mechanistic biosphere models [Farquhar et al., 1980]. In the next step, photorespiration is estimated as a fraction of the calculated GPP. According to Farquhar et al. [1980] the parameter \( \xi \) describes the molar relation of oxygenation, \( \mathcal{O}_o \), to carboxylation, \( \mathcal{O}_c \), of the primary carbon acceptor molecule ribulose bisphosphate, RuBP, i.e., \( \xi = \mathcal{O}_o / \mathcal{O}_c \). From the stoichiometry of the photorespirative reaction [von Caemmerer, 2000], one knows that for each oxygenation the plant loses half a mole of \( \mathcal{O}_2 \). Therefore, in terms of \( \mathcal{O}_2 \) fluxes, the gross primary production reads as

\[
\text{GPP} = \text{Carboxylation} - 1/2 \times \text{Oxygenation} = (1 - 0.5 \times \xi) \times \mathcal{O}_c.
\]

In terms of \( \mathcal{O}_2 \) we have

\[
\text{GPP}_\mathcal{O}_2 = \text{Carboxylation} + \text{Oxygenation} = (1 + \xi) \times \mathcal{O}_c.
\]

This means that for each mole of photospired \( \mathcal{O}_2 \) (0.5\( \xi \)), three moles of \( \mathcal{O}_2 \) (1.5\( \xi \)) are involved: 2 moles for the oxidation of RuBP and 1 mole for the oxidation of Phosphoglycolate. The \( \mathcal{O}_2 \) compensation point, \( \mathcal{G}_* \), is defined as the \( \mathcal{O}_2 \) concentration with as much carboxylation as oxygenation: \( \xi = 2 \mathcal{G}_*/\mathcal{C}_i \). In summary, the relation of GPP to \( \text{GPP}_\mathcal{O}_2 \) then reads as

\[
\frac{\text{GPP}_\mathcal{O}_2}{\text{GPP}} = (1 + \xi)/(1 - 0.5 \times \xi) = (\mathcal{C}_i + 2\mathcal{G}_*)/(\mathcal{C}_i - \mathcal{G}_*) \frac{1}{2}
\]

Following Lloyd and Farquhar [1994], we estimate \( \mathcal{G}_* \) simply as \( \mathcal{G}_* = 2 \times \mathcal{T}_{\text{new}} \) where \( \mathcal{T}_{\text{new}} \) denotes the modified air temperature (see Table 2). \( \mathcal{C}_i \) is calculated as a function of biome dependent parameters [Lloyd and Farquhar, 1994]. However, it is possible that an additional half a mole of \( \mathcal{O}_2 \) is used within photorespiration for the regeneration of products of the glycine cycle (J. Berry, personal communication, 2002). Additional \( \mathcal{O}_2 \) consumptions like the Mehler reaction are estimated for both TBMs as 10% of GPP (D. Yakir, personal communication, 2001).

[18] 2. The SILVAN model, the second biosphere model used in this study, is a mechanistic model based on our knowledge of the biochemistry of plants. It calculates photosynthetic fluxes (\( \mathcal{O}_2 \), \( \mathcal{O}_2 \)) depending on monthly precipitation, temperature, and cloud coverage as external climate forcing (see Figure 2). Photosynthesis is deduced from the calculated GPP in the same manner as for the SLAVE model. Most of the physiological parameters of the model depend on the corresponding biome type determined by the BIOME1 classification scheme [Prentice et al., 1992]. Again, the original 18 biomes of SILVAN have been aggregated here to the same 9 biome types mentioned above. The biosphere ecosystem respiration in both models is assumed to be in equilibrium with climate and therefore balances annual photosynthesis both in terms of \( \mathcal{O}_2 \) and \( \mathcal{O}_2 \) fluxes for every grid cell. The TBMs are run with different observed climatologies from Shea [1986] and Cramer and Leemans [1991], respectively. Basic construction and principles employed in both TBMs are fundamentally different. SLAVE is a heuristic model calculating the \( \mathcal{O}_2 \) fluxes based on empirical relationships. Conversely, SILVAN uses mechanistic formulations for inferring photosynthesis. We therefore believe that the two TBMs allow us to bracket the range of possible solutions for the DE through different patterns and strengths of the modeled \( \mathcal{O}_2 \) fluxes.

3.2. Ocean

[19] In the early days of oceanic isotopic tracer studies the isotopic composition of dissolved oxygen has been discussed as a particularly interesting tracer of both marine productivity and oceanic circulation. It is the only tracer directly linked to the ocean carbon cycle that reacts nonlinearly on production and remineralization, i.e., not according to the fixed proportions of the Redfield ratio. Therefore it was suggested to use this isotope signal to separate biological and transport processes in the deep ocean [Bender, 1990; Kroopnick, 1987].

[20] In our approach to model the marine DE, we use the global ocean carbon cycle model HAMOCC3.1 [Maier-Reimer, 1993; Six and Maier-Reimer, 1996]. It transports various biochemical tracers in an offline mode using monthly transport fluxes of a 3D-ocean general circulation model [Maier-Reimer et al., 1993]. HAMOCC3.1 includes a plankton sub-model to estimate the net marine primary productiv-
ity and oxygen consumption by heterotrophic respiration during remineralization. This plankton sub-model achieves a good representation of the fast biological overturning in the euphotic zone. It consists of five components: phytoplankton, zooplankton, detritus, dissolved organic carbon, and nutrients (PO$_4$). Inclusion of the plankton sub-model clearly improved the capacity of the model to simulate seasonal variations of pCO$_2$ and the corresponding O$_2$ fluxes. Radiative forcing at the ocean surface influencing the biological activity in the euphotic zone is taken from the ECHAM3 control simulation. We run HAMOCC3.1 in a reduced two and a half dimensional geometry, which allows us long-term integrations. The zonal resolution was changed to one Atlantic and one Pacific grid box by keeping a meridional resolution of 5 degrees and 11 layers in the vertical. An additional meridional mixing is parameterized to account for the zonal inhomogeneity of the 3D fluxes.

[21] Although the geometrical simplification of a two and a half dimensional ocean circulation does decrease the sensitivity of the model to non-zonal forcing mechanisms such as wind driven regional upwelling, the zonal version of the model simulates reasonably well the distribution of several oceanic tracers such as bomb C$_{14}$ and PO$_4$$^2$-$[$Benson and Krause, 1984$]$. The photosynthetic ocean source of O$_2$ matches isotopically the composition of leaf water deduced from the salinity field $\delta^{18}$O$_{ATM}$ which the ocean model attains in its biogeochemical steady state after some 10,000 years integration time. Both dissolved $^{16}$O$_2$ and $^{18}$O$^{16}$O are treated as independent geochemical tracers. A small temperature dependent fractionation of 0.7‰ takes place when atmospheric oxygen is dissolved into the sea $[Benson$ and $Krause$, 1984$]$. The respiratory sink of dissolved O$_2$ is represented in the model with a constant fractionation of 20‰. This value used in the study here is mainly due to the similarity of their respective background-conditions. A validation of these model results can only be achieved by future high precision measurements that possibly will allow estimating the latitudinal structure of the temperate effect'' of stable isotopes in precipitation $[Dansgaard$, 1964$]$. Over vegetated areas, lowest values are simulated over north-eastern Siberia $\delta^{18}$O$_{LEAF}$ $\sim$ $-16$‰ which results from very depleted surface waters on one hand and a relative humidity close to saturation on the other hand (see equation (2)). Very high values are reached in the subtropical dry belts of both hemispheres where productivity is low, however. The impact of these high values on the global DE remains therefore rather small. Over the tropical rain forests and seasonal forests of South America and Central Africa the models estimate a water isotopic depletion being more negative (between 5 and 10‰) compared to the adjacent savannah and semi-desert dominated regions. The only larger difference between both models appears in southeast Asia where the GISS model simulates nearly all year long humid conditions with a more depleted composition of leaf water than ECHAM, which is characterized by a marked seasonality of both humidity and the water isotopes caused by a too strong monsoon circulation.

[25] The striking overall correspondence of both models is also demonstrated in Figure 4a showing the zonal means of $\delta^{18}$O$_{LEAF}$ of the three analyzed model combinations. The maximal deviation between the zonal means amounts to 5−10‰ and is strongest in the subtropics where it is less relevant for the global DE. The differences between both TBMs (SLA VE/SILVAN) are apparently more significant. The global productivity of both models is quite similar (17.9 Pmol O$_2$ for SLAVE and 15.5 Pmol O$_2$ for SILVAN). However, the zonal distribution of the O$_2$ fluxes estimated by the SLAVE model (Figure 4b) shows a tropical production about twice as high as in northern midlatitudes. In contrast, the fluxes inferred by the SILVAN model are only about 40% stronger in the tropics than in midlatitudes. This has some consequences for the final latitudinal contribution to the DE (Figure 4c). The ECHAM/SILVAN DE gives more weight to middle northern and southern latitudes relative to the tropics than the two SLAVE model combinations. A validation of these model results can only be achieved by future high precision measurements that possibly will allow estimating the latitudinal structure of the $^{18}$O sources and sinks (for first results, see Seibt [2003]).

[26] As explained previously, we have recomputed the terrestrial oxygen fluxes (PMol) and the contribution to the DE (‰) into nine different biome types (Figures 5a and 5b, respectively). The strongest difference between the heuristic model (SLAVE) and the mechanistic model (SILVAN) is the different contribution of evergreen forest relative to C4 grasses and tropical seasonal forest. The SILVAN model computes for all three biomes a nearly equal contribution to the global balance of O$_2$ and the DE. The SLAVE model, however, estimates that the tropical evergreen forests contribute about 40% stronger to both budgets than C4 grasses or seasonal forest. This difference is principally due to the differences in both TBM’s biome classification scheme. It reflects largely the considerably higher fraction of grasslands in the biome distribution used in SILVAN which was predicted by the BIOME model compared to the SLAVE model. In both models, the biome type “grasslands” is then
separated into C3 and C4 grasses according to a temperature criterion.

4.2. Marine Environment

[27] The model calculates an isotopic composition of the atmosphere in the ocean-only simulation and thus a marine Dole effect $\Delta O$ of 16.97%. The simulated oceanic meridional distribution of $\delta^{18}O_{\text{DISS}}$ is shown in Figure 6a for both basins, Atlantic and Indo-Pacific, together with the corresponding $O_2$ distribution Figure 6b. The shown $\delta^{18}O_{\text{DISS}}$ values must be interpreted relative to the atmospheric equilibrium value $\Delta O$. As expected both tracers, $\delta^{18}O_{\text{DISS}}$ and $O_2$, are closely linked to each other. Zones of strong oxygen consumption are characterized by a correspondingly enriched $\delta^{18}O_{\text{DISS}}$ signal due to the fractionation during remineralization. A particularly strong signal can be seen in the tropical ocean just below the thermocline between 100 and 1000 m depth. Here the dissolved oxygen is enriched by about 14–16% in the Atlantic and by 45% in the Pacific. In the same regions the corresponding $O_2$ concentrations are lower by about 120 μmol/L in the Atlantic and 2 μmol/L in the Pacific. Whereas in the Atlantic basin the model results are quite realistic, both oxygen utilization and $\delta^{18}O_{\text{DISS}}$ values are not in agreement (both too large) with the observations in the Indo-Pacific [Kroopnick, 1987]. This disagreement is caused by the phenomenon of nutrient trapping which exists to some extent in nature too but is often largely overestimated in ocean carbon cycle models [Maier-Reimer, 1993; Najjar, 1990; Six and Maier-Reimer, 1996]. It reflects a positive feedback mechanism between intense production induced by upwelling nutrient-rich abyssal waters and remineralization of organic matter in the tropical divergence zone. It is not clear if this chronic problem of ocean models is a result of an oversimplification of the ocean’s biogeochemistry by neglecting longer-living carbon pools [Six and Maier-Reimer, 1996] or caused by problems in the circulation field [Aumont et al., 1999]. As in a previous study with

Figure 3. The $\delta^{18}O$ value of leaf water deduced from the Craig and Gordon [1965] formula (see text for details) using water isotope fields which were simulated by the (top) ECHAM and (bottom) GISS model. The global integral is $\delta^{18}O_{\text{Leaf}} = 6.8\%o$ for the ECHAM model and $\delta^{18}O_{\text{Leaf}} = 6.3\%o$ for the GISS model.
the three-dimensional HAMOCC3, the model results generally agree well with the comparably sparse observations from the GEOSECS program [Kroopnick, 1987]. The model, however, systematically tends to overestimate the isotopic oxygen enrichment as already noted by Maier-Reimer [1993]. Simulated $\delta^{18}$O$_{Diss}$ values of dissolved oxygen were larger than 35‰ corresponding approximately to an oxygen concentration lower than 30% relative to the saturation value. A detailed comparison between modeled and observed $\delta^{18}$O$_{Diss}$ concentration will become an interesting model application of the oxygen isotopes in the future but will not be further discussed here.

[28] In order to evaluate the simulated $\Delta_O$, we have to determine the main controls on $\Delta_O$. In particular we have to find out how strongly $\Delta_O$ is affected by the potentially overestimated nutrient trapping in the Pacific. The latter is certainly not a serious problem since the volume of the ocean concerned is quite small. Moreover, the low oxygen concentrations in the equatorial divergence zone guarantee that the overall $^{18}$O budget of the ocean is hardly affected by the locally overestimated $\delta^{18}$O$_{Diss}$ values. In contrast, the simulated $\delta^{18}$O$_{Diss}$ values in the deep ocean are nicely corroborated by observations. In the Atlantic below 2000 m, the observed $\delta^{18}$O$_{Diss}$ enrichment [Kroopnick, 1987] relative to the atmospheric value of 23.5‰ is in the range between 1 and 6‰ (the model simulates 2–4‰). In the Pacific, which is characterized by considerably older water masses, $\delta^{18}$O$_{Diss}$ vary between 4 and 8‰ (model: 4–12‰).

Figure 4. Zonal means of (a) $\delta^{18}$O$_{Leaf}$ derived from the three model combinations, (b) of terrestrial O$_2$ fluxes calculated by the two TBMs, and (c) of the terrestrial Dole effect $\Delta_T$ (see equation (3) in the text; units are ‰ per degree latitude; the latitudinal integral of the curves in Figure 4c gives the corresponding global terrestrial DE) again from the three model combinations.
Conversely, the more oxygen is produced in excess to respiration in the upper 100 m, the closer δ\textsuperscript{18}ODISS is to δ\textsuperscript{18}OEUPH (i.e., nearly 0% for today’s conditions).

The relation between net primary production and remineralization within the euphotic layer is usually expressed by the f-ratio, \( f = (PP - \text{Rem})/PP \) with PP as primary productivity and Rem as the part of PP which is already remineralized in the euphotic zone. HAMOCC3.1 simulates a global f-ratio of 0.2. This is in agreement with Eppley and Peterson [1979], who estimated a global value of \( f = 0.1 - 0.2 \). However, we calculate a net primary productivity of 62.9 GtC/yr which is well above all estimates based on observations such as the one by Eppley and Peterson [1979], who scaled up local observations (PP of about 19.1–23.7 GtC/yr) or by Antoine et al. [1996], who obtained a range of 36.5–45.6 GtC/yr on the basis of satellite observations. Still, these estimates are affected by large uncertainties, and therefore we consider our simulated value in accordance with our present knowledge of marine productivity. The simulated F ratio varies slightly both regionally (\( f = 0.19 - 0.21 \)) and seasonally (\( f = 0.17 - 0.23 \)).

Our hypothesis that the relation between PP and Rem, thus the f-ratio, controls the oceanic Dole effect was confirmed by a sensitivity experiment. We reduced artificially the export of organic material out of the euphotic layer and thus made more organic material available for respiration. This changing in the parameterization diminished the f-ratio to 0.1 and therefore gave more weight to the respiration fractionation of 20%. The oceanic DE rises as expected in this experiment to 18.27%.

In order to better assess the uncertainties in our ocean model, we now focus on two potentially important model assumptions. First, we assume that there is no planktonic autorespiration, a process that delivers energy for maintaining the biochemical reactions in terrestrial plants. Though it is sensible to assume that planktonic autorespiration is generally smaller than its analogue on land, no quantitative estimates of this process exist. In a sensitivity experiment,
we doubled the oceanic O2 flux by a part which is directly resired in the euphotic zone (hence the autorespiration would correspond to a fraction of 50% of the total respiration). This changed the global F value from 0.20 to 0.10 and enhanced the Dole effect by about 2%.

Second, our model assumes that \( \delta^{18}O_{EUPH} \) follows salinity in the entire ocean by a linear relationship of 0.5%/psu. There are, indeed, considerable regional deviations from this global relationship. In the tropics, for example, the \( ^{18}O \)-salinity relation is typically more flat, i.e., on the order of 0.3%/psu, whereas, in polar regions, it is steeper mainly due to isotopic effects induced during sea ice formation. However, a sensitivity study in which we prescribed the isotopic composition of the entire ocean to 0% demonstrated only a weak response of the DE (<0.1%) to the detailed geographical distribution of the surface isotope signal \( \delta^{18}O_{EUPH} \). This holds principally since the production weighted mean isotopic composition of the ocean’s surface waters is in both cases approximately 0%. Strong marine productivity in high latitudes with isotopically more depleted surface waters are nearly balanced by an equally strong production in the upwelling zones of low latitudes with more enriched surface waters.

5. Discussion and Perspectives

[34] In our model construction, we match the observed DE by tuning the least known quantity, i.e., the isotopic composition of leaf water, \( \delta^{18}O_{LEAF} \). Even without any tuning, our process-based results (between 22.4% and 23.3%) are already close to the observations. Nevertheless, this cannot be taken as an argument against possible additional fractionation effects such as by diffusion of oxygen molecules in soils [Angert et al., 2001], which have not been taken into account in this study.

[35] A regional comparison between our estimates of \( \delta^{18}O_{LEAF} \) and the rare observations is unfortunately not feasible. Differences between various plant species within
the same biome type are quite large [Wang and Yakir, 1995] and make it necessary to compute δ^{18}O_{LEAF} for each biome from each of the composing plant species.

[36] The relatively good process-based prediction of the DE is mainly due to a larger global δ^{18}O_{LEAF} estimated by both AGCMs employed here, ECHAM3 and GISS model, than assumed in previous studies. However, as already pointed out by Keeling [1995], such a large enrichment in leaf water is not in agreement with our current understanding of the global budget of δ^{18}O in CO₂. Basically the same processes but with an opposite sign affect the global isotopic cycle of C^{18}O^{18}O. When plants consume CO₂ during photosynthesis they produce O₂ and vice versa during respiration. With the best estimates for the various CO₂ fluxes Farquhar et al. [1993] could balance the C^{18}O^{18}O budget by assuming a global leaf water enrichment of 4.4% compared to the value of 6.1–6.8% as deduced here. However, there are some significant differences between the geochemical cycles of O₂ and CO₂. First, in the presence of the catalyzing enzyme carbonic anhydrase, ubiquitous in plant tissue, carbon dioxide equilibrates isotopically in a very short time with the surrounding water. Since about two thirds of the CO₂ entering the stomata is directly rediffused, a large part of the isotopically affected CO₂ does not proceed to the chloroplasts where the uptake of CO₂ takes place and finally the O₂ molecules are emitted by the photosynthetic reaction. The possible isotopic differences between leaf water at the surface of the stomata, containing the isotopic composition of CO₂ and inner cellular chloroplast water, relevant for the isotopic composition of O₂, does however enlarge even the problem of constructing a common budget of δ^{18}O of CO₂ and O₂. The water directly exposed to the evaporation into the stomata is isotopically more enriched than the chloroplast water. The spatial separation of CO₂ and O₂ equilibration and the isotopic difference of water at both locations in plant tissue might help to reconcile both budgets. A further possibility for a higher δ^{18}O_{LEAF} tagging the produced O₂ compared to the CO₂ was discussed by Gillon and Yakir [2001]. The effective activity of the carbonic anhydrase shows strong plant type dependent variability. In particular, in C₄ plants, the activity of the carbonic anhydrase enzyme is nearly 60% lower than in equivalent C₃ plants. On the basis of in situ measurements, the authors estimated an effective global equilibration for the CO₂ of only 80%. Second, CO₂ produced by heterotrophic respiration diffuses through the soil column and equilibrates all the time with the surrounding soil water. According to the estimates of Miller et al. [1999] and Riley et al. [2002], the emitted CO₂ is in equilibrium with soil water below 15 cm. A lower isotopic composition of soil water than calculated by Ciais et al. [1997a] and Farquhar et al. [1993], and an increased isotopic composition of leaf water could bring both isotope budgets into agreement (M. Bender, cited according to Keeling [1995]). A mechanistic description of such processes in soils, however, involves a detailed description of evaporation from soils affecting the δ^{18}O gradient of water in the soil and of water uptake in various depths by plant roots controlling the isotopic composition of leaf water. Such an isotope soil hydrology is neither built into the GISS nor into the ECHAM model, which both describe soil processes by a simple one-layer bucket model.

[37] Comparing our estimates of global terrestrial and marine O₂ fluxes and corresponding DEs with the estimates of Bender et al. [1994b] reveals some interesting features. Our model calculation estimates the annual production of O₂ in both environments smaller than in Bender et al.’s approach (P₀ is about 40% and P₇ about 15% smaller than in the budget of Bender et al. [1994b]) resulting in a relation between the marine and the terrestrial productivity of about one half relative to about two thirds in the work of Bender et al. [1994b]. Consequently, there is a slightly different contribution to the overall DE by both biospheres in the two approaches.

[38] The lower production rates of O₂ in our calculation results in an atmospheric O₂ turnover time of about 1500 years in contrast to the 1200 years inferred from Bender et al. [1994b]. Given that these O₂ fluxes are most probably even lower during glacial conditions, this has some consequences when interpreting the δ^{18}O_ATM signal of ice cores and its leads and lags relative to the other information deduced from the ice such as CO₂ or local temperature [Broecker and Henderson, 1998].

[39] Furthermore, our oceanic Dole effect is about 2% lower as in the work of Bender et al. [1994b]. This result certainly needs further investigation, for example with different oceanic biosphere models like our terrestrial approach with different TBMs. In situ measurements performed at all U.S. JGOFS stations indicate, for example, a considerably lower relation between productivity inferred from C³¹ incubated water samples and O₂ production than the one used in our model. The additional O₂ fluxes might be related to autorespirative processes such as photorespiration or the Mehler reaction in the ocean biosphere (M. Bender, personal communication, 2002). The sensitivity experiment (50% larger O₂ fluxes and hence lower f-ratio) discussed above captures such a scenario and resulted in a 2% larger oceanic DE.

[40] Furthermore, it is planned to address the problem of the diverging isotope budgets of CO₂ and O₂ by using a mechanistic TBM built into the ECHAM model. This will also allow us to calculate synchronously over the daily cycle the isotopic composition of leaf and soil water together with the biospheric fluxes of O₂ and CO₂ [Cuntz et al., 2003a, 2003b].

[41] The difference between Δ₁ and Δ₀ estimated from our standard experiment becomes as large as 10.7% instead of 4% in M. Bender’s best guess (see Table 1). The difference has to be weighted by the relation between terrestrial and marine productivity. Even slight changes in the relation of P₀ and P₇ the quaternary then have a strong impact on the DE. The astonishing stability of the DE observed over the last two glacial interglacial cycles (±0.5%) argues for strong natural compensation effects between the different processes affecting the DE, at least on timescales beyond a few thousand years. Such compensating effects, however, might not operate over the next few hundred years when substantial anthropogenically induced changes may affect the Earth’s climate and the terrestrial and marine biosphere. Process-based models of the Earth’s
Dole effect such as the one described here are needed to explore the factors responsible for the apparent stability of the Dole effect in the past, and to estimate possible shifts of the Dole effect in the future.

[42] Acknowledgments. This paper profited a lot by extremely helpful discussions with Joe Berry, Christopher Still, Suzanne von Caemmerer, and Graham Farquhar. We are also grateful for the detailed and constructive comments of three anonymous reviewers.

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