Contribution of soil respiration in tropical, temperate, and boreal forests to the ^{18}O enrichment of atmospheric O_2

Alon Angert,[1,2] Eugeni Barkan,[1] Bruce Barnett,[3] Enrico Brugnoli,[4] Eric A. Davidson,[5] Julianna Fessenden,[6] Somsak Maneepong,[7] Nipa Panapitukkul,[8] James T. Randerson,[6] Kathleen Savage,[5] Dan Yakir,[9] and Boaz Luz[1]

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[1] The ^{18}O content of atmospheric O_2 is an important tracer for past changes in the biosphere. Its quantitative use depends on knowledge of the discrimination against ^{18}O associated with the various O_2 consumption processes. Here we evaluated, for the first time, the in situ ^{18}O discrimination associated with soil respiration in natural ecosystems. The discrimination was estimated from the measured $[O_2]$ and $\delta^{18}O$ of O_2 in the soil-air. The discriminations that were found are 10.1 ± 1.5‰, 17.8 ± 1.0‰, and 22.5 ± 3.6‰, for tropical, temperate, and boreal forests, respectively, 17.9 ± 2.5‰ for Mediterranean woodland, and 15.4 ± 1.6‰ for tropical shrub land. Current understanding of the isotopic composition of atmospheric O_2 is based on the assumption that the magnitude of the fractionation in soil respiration is identical to that of dark respiration through the cytochrome pathway alone (~18‰). The discrimination we found in the tropical sites is significantly lower, and is explained by slow diffusion in soil aggregates and root tissues that limits the O_2 concentration in the consumption sites. The high discrimination in the boreal sites may be the result of high engagement of the alternative oxidase pathway (AOX), which has high discrimination associated with it (~27‰). The intermediate discrimination (~18‰) in the temperate and Mediterranean sites can be explained by the opposing effects of AOX and diffusion limitation that cancel out. Since soil respiration is a major component of the global oxygen uptake, the contribution of large variations in the discrimination, observed here, to the global Dole Effect should be considered in global scale studies. *INDEX TERMS:* 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1040 Geochemistry: Isotopic composition/chemistry; 1615 Global Change: Biogeochemical processes (4805); *KEYWORDS:* Dole Effect, oxygen isotopes, soil respiration

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1. Introduction

[2] The ^{18}O enrichment of atmospheric O_2 with respect to ocean water is known as the "Dole Effect." Changes in the Dole Effect have been used to infer past variations in the ratio of marine to terrestrial biospheric production, related to past climatic changes [*Bender et al.*, 1994]. In addition, the present-day Dole Effect (23.5‰ with respect to SMOW [*Kroopnick and Craig*, 1972]) is an important constraint to our interpretations of the present oxygen cycle and of the carbon cycle coupled to it [*Bender et al.*, 1994].

[3] The major cause of the Dole Effect is the preferential removal of ^{16}O by biological uptake mechanisms [*Lane and Dole*, 1956]. Additional smaller fractionations occur in gas exchange at the ocean surface and leaves, and in photochemical reactions in the stratosphere [*Bender et al.*, 1994]. A second important contribution to the Dole Effect comes from terrestrial photosynthesis. In photosynthesis, O_2 is produced without isotopic fractionation from the substrate water [*Guy et al.*, 1993]. Thus O_2 produced by marine

[1]Institute of Earth Sciences, Hebrew University of Jerusalem, Givat-Ram, Jerusalem, Israel.
[2]Now at Atmospheric Science Center, University of California Berkeley, Berkeley, California, USA.
[3]Department of Geosciences, Princeton University, Princeton, New Jersey, USA.
[4]CNR Istituto per l'Agroselvicoltura, Porano, Italy.
[5]Woods Hole Research Center, Woods Hole, Massachusetts, USA.
[6]Divisions of Engineering and Applied Science and Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, USA.
[7]Institute of Agricultural Technology, Wailailak University, Nakhon Si Thammarat, Thailand.
[8]Department of Earth Sciences, Faculty of Natural Resources, Prince of Songkla University, Songkla, Thailand.
[9]Department of Environmental Sciences and Energy Research, Weizmann Institute of Science, Rehovot, Israel.

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photosynthesis has the same isotopic composition as seawater. In contrast, terrestrial photosynthesis produces O_2 that is enriched in ^{18}O in comparison to seawater, because the substrate water in leaves is enriched by evapotranspiration [*Dongmann*, 1974]. Owing to this difference, an increased Dole Effect has been interpreted to indicate an increased rate of terrestrial production relative to marine production.

[4] In recent studies of variations in the Dole Effect [*Beerling*, 1999; *Bender et al.*, 1994; *Malaize et al.*, 1999] it was assumed that global terrestrial respiration preferentially discriminates against ^{18}O by 18‰, with respect to ^{16}O. This value is based on measurements of the discrimination associated with "regular" dark respiration that involves the cytochrome oxidase (COX) in isolated mitochondria and plant tissues [*Guy et al.*, 1989; *Robinson et al.*, 1992]. However, *Guy et al.* [1989] also noted that when O_2 diffusion to the consumption site is restricted, the discrimination of a system would depend not only on the intrinsic discrimination in the consumption, D_{con}, but also on the discrimination in diffusion, D_{diff}, and the relative rates of consumption and diffusion. This was shown in detail for CO_2 consumption by leaves [*Farquhar et al.*, 1982],

$$D = D_{diff} + (D_{con} - D_{diff})C_i/C_a, \quad (1)$$

where D is the overall discrimination, and C_a, C_i are the substrate concentrations in the ambient air and in the reaction site respectively. Since the discrimination in diffusion is lower than that of biological uptake, the combined effect of these two processes is lower than that of the biochemical uptake alone.

[5] About 77 Pg C/yr (6.4 Pmol C/yr) of CO_2 are released from soils [*Raich and Potter*, 1995], and thus an equivalent amount of O_2 is consumed. Compared with an estimate of terrestrial carbon gross primary between 100 and 150 Pg C/yr (or 8 and 13 Pmol C/yr), approximately two thirds of terrestrial dark respiration is accounted for by soil respiration (both root and microbial).

[6] In soils, rates of O_2 diffusion to the consumption sites, inside soil aggregates and roots can be slow relative to consumption. As a result, the overall discrimination against ^{18}O in soil respiration can be expected to be weaker than that of dark respiration alone. This effect can be countered, however, by engagement of respiration via the alternative-oxidase pathway (AOX [*Guy et al.*, 1989; *Robinson et al.*, 1992]). The ^{18}O discrimination in this pathway is about 27‰ (for non-green tissues [*Ribas-Carbo et al.*, 2000]), and an increase in the overall soil discrimination is expected if this mechanism is engaged.

[7] *Angert and Luz* [2001] estimated ^{18}O discrimination in root respiration and found evidence for both the effect of diffusion limitations, that decreases the discrimination, and the effect of the AOX, that increase the discrimination. In another study, *Angert et al.* [2001] found that in the field, overall ^{18}O discrimination of soils was as low as ~12‰, at two orchard sites in Israel with either clayey or sandy soils. Clearly, reduced discrimination due to diffusion limitation was the dominant effect in these sites. Such large variations in ^{18}O discrimination (e.g., between the generally assumed value of 18‰ to observed values of 12‰) can significantly influence interpretations of the global Dole effect. Global-scale evaluation of their significance is therefore needed, with emphasis on regions with high rates of soil respiration.

[8] In the present study we estimated the discrimination against ^{18}O in soil respiration in a range of representative ecosystems. These included one tropical forest site, two temperate forest sites, and two boreal forest sites, as well as two Mediterranean woodland sites and one tropical shrub land site. Combined, tropical temperate and boreal forests contribute about 70% of global soil respiration. The results reported here provide a first assessment of the global significance of the newly observed, large, variations in ^{18}O discrimination of soils.

2. Methods

2.1. Sites Description

[9] The tropical forest site is located in the Thone Nga Chang Wild Life Reserve near Hat Yai, Thailand (7°00′N, 100°15′E). This is a secondary forest that is dominated by species such as *Dipterocarpus alatus*, *Dipterocarpus grandiflorus*, *Anisotera glaba*, *rtocarpus lanceafolius* and *Hopea odarata*. The soil series in the area is defined as slope complex, Typic Paleudult. The parent material is old alluvium and transported material from clastic rocks. The soil is well drained and water table level is below 1 m throughout the year. The site is subject to tropical monsoon climate with an annual rainfall of 2000 mm.

[10] The first temperate forest site is located at the woods of the Institute for Advanced Study in Princeton, New Jersey (40°19′53"N, 74°40′32"W). The forest in the sampling site is at least 270 years old and is dominated by maple (*Acer saccharum*) and beech (*Fagus grandifolia*). The soil texture is sandy loam and the soil is well drained.

[11] The second temperate forest site is located on the Prospect Hill tract of Harvard Forest, near Petersham, Massachusetts (42°32′N, 72°11′W) at 340 m elevation. This mixed hardwood forest is about 60 years old and is dominated by red oak (*Quercus rubra*) and red maple (*Acer rubrum*), with some stands of hemlock, white pine, and red pine. The sampling site was at the base of the tower for eddy covariance flux measurements. The soil is classified as Typic Dystrocrept, the texture is sandy loam, and the soil is well drained.

[12] The two boreal forest sites are part of a post-fire chronosequence in interior Alaska (63°49.2′N 144°58.6′W, 450 m elevation). In a mature black spruce forest site with an age of over 100 years (hereinafter referred to as the "boreal undisturbed site") dominant species included black spruce (*Picea mariana*) and feather moss (*Hylecomium*), and the soil is a clay loam [*O'Neill*, 2000]. A second nearby site experienced a severe fire in 1994 that removed almost all of the surface organic layer (hereinafter referred to as the boreal burned site) [*O'Neill*, 2000]. Currently, the dominant vegetation at the boreal burned site is Aspen (*Populus tremuloides*). Mean annual temperature is −2.2°C and mean annual rainfall is 29.8 cm.

[13] The tropical shrub site was also located in Thailand (8°36′N, 99°55′E). The site was formerly used for a former rice field, which abandoned about 8 years before the sampling. The soil is classified as Aeric Paleaquult, fine-loamy mixed soil. Soil textures of 0- to 35-cm horizons are silty clay loam, and 35- to 100-cm horizons are sandy clay loam. Parent material of the soil is old alluvium.

[14] The first Mediterranean woodland site was located on the bank of Refaim Stream (~31°5′N, ~34°6′E) near Jerusalem, Israel. The vegetation at the site is dominated by common oak (*Quercus calliprinos*). The soil is sandy clay loam. The parent material is carbonate rock and the soil is well-drained. The climate is Mediterranean with average annual rainfall of 550 mm, and a distinct dry season in summer (June–September). Winter minimum temperature is usually above the freezing point.

[15] The second Mediterranean woodland site is located in Porano, Province of Terni, Italy (42°41′N, 12°06′E), at an elevation of 460 m. The sampling site is a park dominated by *Cedrus* spp. (*Cedrus deodara*) with several neighboring *Quercus pubescens* and some *Prunus* species (*Prunus lusitanica*). The soil is a loamy-sand Dystic Xerocrept, with considerable amount of organic matter (4% or more). The rock substrate is a mixture of volcanic material (Quaternary) deposited on a matrix of Pliocene sandy clay. The climate is sub-humid Mediterranean typical of the inland of the Italian Peninsula with average annual rainfall of 810 mm, with the most abundant precipitation during fall (October–November) and a distinct dry season in summer (July–August). The average annual mean temperature is 13°C. During winter, there is very limited frost, and the monthly average minimum temperature is normally above 0°C.

2.2. Soil-Air Sampling and Mass Spectrometry

[16] We decided on a sampling strategy that will allow us to cover as many sites as possible, and will also allow taking relatively large number of replicates of each sample. The later is important because of the small signal expected in $\delta^{18}O$ in well-drained soils. Since we also expected the variations with depth to be close to the detection limit, and since measuring $\delta^{18}O$ and $[O_2]$ in the precision we needed is time consuming, we took samples only from one to three depths at each site. In this way we could also use existing soil tubes where they were available.

[17] The sampling technique was based on established procedure [*Angert et al.*, 2001]. Briefly, soil air was drawn from tubes that were inserted in the soil, and was collected in 4 cm^3 pre-evacuated glass flasks. Before sampling, the dead space in the tubing and flasks were purged with soil air. Up to nine replicates were taken at each sampling depth.

[18] Three types of soil tubes were used. In the tropical forest site and in the tropical shrub, we used Nalgene™ tube that was placed in a vertically drilled hole. The hole was filled with a layer of sand around the opening of the tube, and the rest of the hole was filed back with the soil that was removed while drilling. In the first temperate forest and in the Mediterranean woodland sites, we used a stainless steel tube (10 mm ID, 12.5 mm OD) that was pushed into a smaller diameter pilot hole made by hammering a pointed steel rod into the soil. The tube end was pointed to ensure easy insertion into the pilot hole, and 2-mm-diameter holes were drilled above the pointed end for soil air collection. An 8-mm-diameter rod inserted inside the tube reduced its dead volume. In the second temperate forest site and in the boreal sites, we used existing stainless steel tubes that were previously installed into the soil. The diameter of the tubes was 1/8" in the second temperate forest, and 8 mm [*O'Neill*, 2000] in the boreal forest. The soil tubes were also horizontally distributed; that is, different depths at the same site do not correspond to same exact location.

[19] Oxygen concentrations were calculated from the ratio of O_2 to Ar, assuming that since argon is inert, its concentration is constant [*Angert et al.*, 2001]. The ratio of O_2 to Ar was determined by mass spectrometric analysis of the same sample used for isotopic analysis. Sample preparation and mass spectrometry followed procedures described by *Luz et al.* [1999, 2002]. The preparation of the sample included cryogenic removal of water vapor and CO_2, followed by chromatographic separation of N_2. When pure O_2-Ar mixture is analyzed, it is not necessary to correct the measured $\delta^{18}O$ for the effect of N_2 interference in the ion source of the mass spectrometer [*Emerson et al.*, 1999; *Sowers and Bender*, 1989]. This enables very accurate measurements over a broad range of O_2/N_2 ratios. The results are presented with respect to an air standard (HLA) that represents all atmospheric oxygen, where

$$\delta^{18}O(‰) = \left[\left(^{18}O/^{16}O\right)_{sample}/\left(^{18}O/^{16}O\right)_{HLA} - 1\right].$$

The analytical error was ±0.02‰ and ±0.02% for $\delta^{18}O$ and $[O_2]$, respectively.

[20] The isotopic discrimination effect (D) is related to the instantaneous fractionation factor ($D = (1-\alpha_{p-s})\cdot 10^3$). The instantaneous fractionation factor is defined as $\alpha_{p-s} = R_p/R_s$, where R_s and R_p are the isotopic ratio ($^{18}O/^{16}O$) of the oxygen substrate and the respired O_2, respectively. (Following *Guy et al.* [1989], we report the isotopic discrimination as D. In various other papers the discrimination is reported as ε, where $\varepsilon = -D$).

2.3. Temperature Data

[21] At the second temperature forest site (Harvard forest), the daily average surface temperature and the temperature at the sampling depth was calculated from temperature data collected continuously (at 4 cm, and 85 cm depth) as a part of an ongoing ecosystem and eddy covariance studies [*Savage and Davidson*, 2001; *Wofsy et al.*, 1993].

[22] At the boreal forest sites, daily average temperature at the surface was estimated from a set of continuous measurements at nearby sites (another undisturbed boreal forest and a recently disturbed site that burned in June of 1999) where flux towers were located. At these two remote sites, surface temperature was estimated from a buried thermocouple at 2 cm. In addition, temperature measurements were conducted in the sampling site, at the depth of the buried tubes and at the surface, at the time of O_2 sampling. These measurements were in fair agreement with the continuous measurements. In the rest of the sites, the

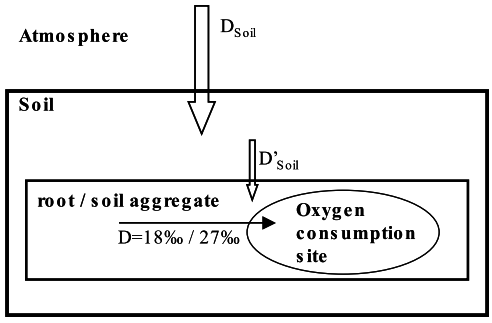

Figure 1. Schematic representation of diffusion and fractionation of oxygen in soils. Oxygen first diffuses from the atmosphere to the soil column, and then diffuses into roots or soil aggregates where it can be consumed by respiration. The overall discrimination of the soil system (in respect to the atmosphere) is given by D_{soil}, while the discrimination by the root/soil aggregate (with respect to the soil air) is given by D'_{soil}. The biochemical discrimination in respiration is 18‰ for the COX and 27‰ for the AOX.

average surface temperature was obtained from concurrent diurnal sampling, and temperatures at the sampling depth where taken at the time of sampling.

3. Results and Discussion

3.1. Estimating the Isotopic Discrimination From In Situ Measurements

[23] The diffusion of O_2 from the atmosphere to the sites where it is consumed (by bacteria, fungi, and roots mitochondria), can be divided into two steps (Figure 1). In the first step, O_2 diffuse from the atmosphere to the soil column, through the (air-filled) soil macro-pores. In the second step, some of the O_2 diffuse in liquid phase, from the macro-pores to the consumption sites that located inside roots or soil aggregates. We will note the overall discrimination of the soil system (that includes the two diffusion steps and the biological consumption) as D_{soil}. The discrimination associated with uptake by the roots and soil aggregates against soil air (including only the second diffusion step and the biological consumption) will be note as D'_{soil}. Both steps of diffusion can have an effect on the overall discrimination of the soil system. However, since the diffusion in the first step is in gas phase and the discrimination associated with it (14‰) is close to that of dark respiration (18‰), it is expected to cause only a small change in the overall discrimination. Moreover, since most of the respiration takes place in the top of the soil where O_2 concentrations are close to the atmospheric ones, the effect of the diffusion in the soil profile is expected to be even weaker. In contrast to that, the discrimination by diffusion in liquid phase is close to zero, and because of the slow diffusion rates in liquid, strong gradients are expected. As a result, the second step is expected to significantly decrease the overall discrimination.

[24] In agreement with the above expectations, *Angert et al.* [2001] found for their sites only a small difference between D_{soil} and D'_{soil} (less than ~0.5‰,). This small difference leads us to focus the current study on estimating D'_{soil} and to assume that $D_{soil} \approx D'_{soil}$ (i.e., we did not measure detailed concentration profiles necessary to estimate the effect of the first diffusion step). However, it should be noted that although the fractionation by diffusion in the soil column changes only slightly the effect of soils on the isotopic composition of the atmosphere, it still has large effect on the isotopic composition of soil air, and hence must be taken into account when interpreting measurements of soil-air δ^{18}O.

3.1.1. Simple One-Box Model

[25] In order to evaluate soil discrimination, we used the measured $[O_2]$ and δ^{18}O in soil air as inputs to a simple one-box model [*Angert et al.*, 2001] (will be derived again below). The model considers only respiration and diffusion (*Angert et al.* [2001] discuss why other processes are negligible), and assumes homogeneity with respect to $[O_2]$ and ^{18}O and steady state with respect to fluxes, concentrations, and isotopic composition. The steady state assumption was validated by comparing samples taken from the same sites at 10- to 40-hour intervals (no rain event disrupted the soil-air during these intervals). The model also assumes identical O_2 concentration and isotopic composition near the surface of the soil and in the free atmosphere. This assumption was previously validated by *Angert et al.* [2001]. An implicit assumption of the one-box model is that the discrimination is constant with depth. The insignificant variability of the discrimination with depth found at one site [*Angert et al.*, 2001] gives some support for this assumption.

[26] The model was shown [*Angert et al.*, 2001] to give almost identical results to a more sophisticated numerical model under steady state conditions. More sophisticated analytical or numerical models require data on the respiration and diffusivity profiles in the soil. Since such data were not available in most of our sites, and since our sampling strategy (see section 2.2.) limited our ability to estimate it independently, we preferred not to assume arbitrary respiration and diffusion profiles, and applied the simple model.

[27] The derivation of the model is as follows: Temporal change in O_2 concentrations in the soil ($[O_2]_s$) is given by

$$\frac{d[O_2]_s}{dt} = I - O - R, \tag{2}$$

where i is the incoming diffusion flux, O is the outgoing diffusion flux, and R is the consumption flux in the soil. Temporal changes in the δ^{18}O value of soil O_2 ($\delta^{18}O_s$) are given by

$$\frac{d\left([O_2]_s \cdot \delta^{18}O_s\right)}{dt} = I \cdot \left(\delta^{18}O_{atm} - D_{diff}\right) - O \cdot \left(\delta^{18}O_s - D_{diff}\right) - R \cdot \left(\delta^{18}O_s - D'_{soil}\right), \tag{3}$$

where D_{diff} is the ^{18}O discrimination in diffusion in air (14‰, derived from the theory of binary diffusion of gases [*Mason and Marrero*, 1970]), D'_{soil} is the overall ^{18}O discrimination relative to soil air (as discussed earlier, it integrates both the biochemical uptake and the micro-scale

Table 1. Summary of the Data Including Temperature (Both at the Sampling Depth and at the Surface) O_2 Concentration, $\delta^{18}O$, and the Calculated Discrimination in the Different Sampling Times and Different Sites[a]

Site	Date and Time	Depth	[O2]%	[O2]% STD	$\delta^{18}O$	$\delta^{18}O$ STD	T (Soil)	T (Surface)	ΔT	D'_{soil}	D'_{soil} STD	n
Tropical forest	15-Feb-01 12:00	60	17.66	0.03	−0.15	0.02				13.0	0.1	2
Tropical forest	12-May-01 8:30	40	18.65	0.26	−0.61	0.03	25.6	27.5	1.9	8.4	0.6	3
Tropical forest	12-May-01 17:30	40	18.50		−0.44		25.6	27.5	1.9	10.2		1
Tropical forest	12-Jun-01 8:30	60	19.72	0.09	−0.31	0.02	26.9	27.5	0.6	8.6	0.7	4
Tropical forest	12-Jun-01 17:30	60	19.58		−0.19		26.9	27.5	0.6	11.0		1
Tropical forest	2-Aug-01 8:40	40	18.97	0.06	−0.41	0.04	25.7	26.5	0.8	9.5	0.4	4
Tropical forest	2-Aug-01 17:10	40	19.08	0.09	−0.34	0.03	25.7	26.5	0.8	9.9	0.4	3
Tropical forest	2-Aug-01 8:40	60	18.28	0.03	−0.5	0.1	25.7	26.5	0.8	10.0	0.8	3
Tropical forest	2-Aug-01 17:10	60	18.21	0.29	−0.44	0.08	25.7	26.5	0.8	10.5	0.6	6
Tropical forest average										**10.1**	**1.5**	
Temperate forest 1	24-May-01 14:50	60	19.36	0.04	0.42	0.03	14.5	18.5	4	18.2	0.3	9
Temperate forest 1	25-May-01 15:30	60	19.42	0.02	0.35	0.02	14.5	18.5	4	17.4	0.2	9
Temperate forest 1 average										**17.8**	**0.6**	
Temperate forest 2	30-May-01 11:50	85	20.44	0.02	0.14	0.02	9	9.6	0.6	19.1	0.8	7
Temperate forest 2	31-Jul-01 9:45	85	20.22	0.03	0.15	0.03	12.9	15.3	2.4	16.4	1.0	8
Temperate forest 2	1-Aug-01 10:00	85	20.22	0.04	0.20	0.04	12.9	15.3	2.4	18.0	0.9	5
Temperate forest 2 average										**17.9**	**1.4**	
Boreal undisturbed	27-Aug-01 17:30	155	20.59	0.13	0.16	0.06	6.2	8.4	2.2	19.6	1.8	5
Boreal undisturbed	28-Aug-01 9:10	155	20.62	0.12	0.19	0.03	6.2	8.4	2.2	23.1	1.7	4
Boreal undisturbed	27-Aug-01 15:40	145	19.94	0.55	0.62	0.39	6.3	8.4	2.1	24.9	2.1	4
Boreal undisturbed	28-Aug-01 9:00	145	19.44	0.07	0.77	0.07	6.3	8.4	2.1	24.0	0.7	3
Boreal undisturbed average										**22.9**	**2.3**	
Boreal burned	19-Jul-01 15:40	85	20.43	0.05	0.50	0.04	11.1	19.4	8.3	25.4	1.2	5
Boreal burned	19-Jul-01 16:00	105	19.96	0.08	0.50	0.07	6.2	19.4	13.2	17.1	1.2	5
Boreal burned	20-Jul-01 8:50	105	20.06	0.19	0.50	0.14	6.2	19.4	13.2	17.3	2.6	9
Boreal burned	27-Aug-01 17:15	85	20.42	0.11	0.42	0.11	9.1	13.6	4.5	25.7	1.9	5
Boreal burned	28-Aug-01 8:50	85	20.50	0.17	0.21	0.08	9.1	13.6	4.5	18.0	2.0	3
Boreal burned	27-Aug-01 17:00	105	20.57	0.04	0.38	0.03	7	13.6	6.6	25.4	1.0	5
Boreal burned	28-Aug-01 8:45	105	20.47	0.21	0.44	0.12	7	13.6	6.6	25.9	1.6	4
Boreal burned average										**22.1**	**4.4**	
Med. woodland 1	10-Jan-00 13:00	90	19.45	0.42	0.37	0.02	13.1	12.1	1	18.9	0.1	4
Med. woodland 1	12-Jan-00 8:20	90	19.46	0.02	0.37	0.03	13.1	12.1	1	18.8	0.3	8
Med. woodland 1 average										**18.8**	**0.1**	
Med. woodland 2	17-Aug-01 9:05	50	20.19	0.10	0.12	0.06	22	25	3	15.0	1.6	9
Med. woodland 2	17-Aug-01 19:10	50	20.03	0.09	0.30	0.05	22	25	3	19.0	0.7	7
Med. woodland 2 average										**17.0**	**2.8**	
Tropical shrub	22-Jul-01 6:40	60	15.21	0.36	0.20	0.19		31		14.7	0.7	4
Tropical shrub	22-Jul-01 17:40	60	15.15	0.21	0.17	0.11		31		14.6	0.4	4
Tropical shrub	25-Jul-01 15:30	60	16.07	0.14	0.66	0.14		31		16.8	0.5	4
Tropical shrub average										**15.4**	**1.6**	

[a]The number of replicates is given by n, and STD is standard deviation.

diffusion effects), and $\delta^{18}O_s$ and $\delta^{18}O_{atm}$ are the $\delta^{18}O$ values of the soil and atmospheric O_2, respectively.

[28] Since we are interested in the change in $\delta^{18}O$ relative to atmospheric oxygen, $\delta^{18}O_{atm}$ is zero and can be omitted.

[29] Rewriting the left side of equation (3) as

$$\frac{d[O_2]_s}{dt}\cdot\delta^{18}O_s+\frac{d\delta^{18}O_s}{dt}\cdot[O_2]_s$$

and substituting equation (2) into equation (3) yields

$$\frac{d\delta^{18}O_s}{dt}=\frac{R\cdot D'_{soil}-(I-O)\cdot D_{diff}-I\cdot\delta^{18}O_s}{[O_2]_s}. \quad (4)$$

[30] By designating the ambient O_2 concentration as $[O_2]_a$, and the diffusivity of the soil divided by the depth as k, we can write the relationships: $I = k\cdot[O_2]_a$, and $O = k\cdot[O_2]_s$. Using these relationships and assuming steady state gives

$$D'_{soil}=\frac{\delta^{18}O_s}{1-[O_2]_s/[O_2]_a}+D_{diff}. \quad (5)$$

[31] When the variations in the isotopic composition of soil air are small, as in the current study, the effect of thermal diffusion must be taken into account. This effect causes the heavier isotopic species to concentrate at the cold end of a temperature gradient. The magnitude of this effect on the isotopic composition is given by [*Severinghaus et al.*, 2001]

$$\delta^{18}O_{td}=\Delta T\Omega. \quad (6)$$

[32] The term $\delta^{18}O_{td}$ stands for the $\delta^{18}O$ of soil air that would be expected due only to thermal diffusion, and Ω is the thermal diffusion coefficient for $\delta^{18}O$. This coefficient was calculated from the Ω value for $\delta^{15}N$ (0.0158 for an average temperature of 15°C after *Boersma-Klein and Vries* [1966] and *Severinghaus et al.* [2001]) and the relative thermal diffusion sensitivity of $\delta^{18}O$ and $\delta^{15}N$ [*Severinghaus et al.*, 2001] as 0.0262. Since the effect of diurnal temperature variations of surface temperature on the isotopic composition of soil air is negligible (except in the top 20 cm) [*Angert et al.*, 2001], ΔT can be assumed to be the difference between the average temperature at the soil surface, and the temperature at the sampling depth.

[33] The fractionation of soil air by thermal diffusion is independent of the fractionation by respiration. Hence, in

order to isolate the effect of respiration on soil air, the effect of thermal diffusion can be simply subtracted for the $\delta^{18}O$ of soil air. As a result, equation (5) becomes

$$D'_{soil} = \frac{\delta^{18}O_s - \delta^{18}O_{td}}{1 - [O_2]_s/[O_2]_a} + D_{diff}. \quad (7)$$

[34] This approach for including the thermal diffusion effect in the one-box model has been verified by an improved version of the numerical model described by *Angert et al.* [2001]. In this model the soil profile is divided into five 30-cm-thick layers. In each layer the balance of $^{16}O^{16}O$ and $^{16}O^{18}O$ concentrations is calculated, separately for each isotope species, from the diffusion and respiration fluxes by a finite difference approximation. In the improved version the effect of thermal diffusion was included by introducing changes in the diffusion fluxes of $^{16}O^{18}O$ in accordance to the temperature gradient.

[35] The average discrimination for each site was evaluated by first averaging the $\delta^{18}O$ and $[O_2]$ of all the replicates of a given sample, and second by averaging the D'_{soil} values for the different samples (Table 1). By binning our results this way, both the standard deviations within and between samples are presented for D'_{soil}. The within-sample standard deviation represents sampling and analytical uncertainty, while the between-sample standard deviation may indicate real temporal and spatial (different depths in the same site do not refer to exact same location) variation in D'_{soil}.

3.1.2. Additional Complexities

[36] There are some additional questions that must be discussed before the one-box model described above could be used to estimate the O_2 discrimination from the field data.

[37] One of these questions is the applicability of the treatment of thermal diffusion in the model to non-monotonous soil temperature profiles (i.e., temperature profiles that show some meanders and do not simply increase or decrease with depth). Such temperature profiles were not uncommon in our sites (data not shown). To calculate the combined effect of thermal diffusion and respiration in such profiles, we used the numerical model described in the previous section. Using this model, we found that the effect of monotonous temperature change (simple increase or decrease in temperature with depth) is identical to that of a non-monotonous one, as long as the temperature differences between the sampling depth and the surface in both cases are equal. Hence, applying equation (6) for non-monotonous temperature profiles is justified.

[38] Another problem that must be dealt with is the possible mixing of atmospheric air with soil air, or mixing between soil-air from an adjacent depth, at the time of sampling. Such mixing could occur through a leak in the sampling device (unlikely), or through the flow of air in the soil alongside the sampling tube. Such mixing could be identified by differences among replicates that are larger than the laboratory analytical uncertainty, and a scatter in O_2 concentration that correlates with $\delta^{18}O$ variations. Luckily, such mixing will change the denominator of equation (7) in the same ratio as the change in $\delta^{18}O_s$ (versus the atmosphere). This is so, because the denominator represents the fraction of oxygen in the soil relative to the atmosphere. As a result, the change in the calculated D'_{soil} will be small if $\delta^{18}O_{td}$ is relatively small (there will be no change if $\delta^{18}O_{td}$ is zero).

[39] For example, if 20% of a soil air sample with $\delta O_2/Ar$ of −30‰ and $\delta^{18}O$ of 0.4‰ would be replaced with atmospheric air, the calculated D'_{soil} will be reduced by about 1‰ if ΔT is 5°C. Mixing with air from another depth will cause even smaller error in the calculated D (if the discrimination is constant with depth). The magnitude of the error introduced by mixing rises with the temperature gradient and the oxygen concentrations in the soil. Since such mixing will always cause the calculated discrimination to be lower than the real one, the discrimination estimated from samples in which such error is evident should be taken as a minimum estimate.

[40] Additional complexity is introduced by the fact that in wetland plant species (and possibly in some grasses [*De Willigen and Van Noordwijk*, 1989]), oxygen is supplied to the roots through an internal pathway that transfers oxygen from the aboveground plant parts (leaves or stem) to the roots. This internal transport is induced by diffusion in some plants [*Armstrong et al.*, 1994; *Grosse and Frick*, 1999], and by pressurized mechanisms in others [*Buchel and Grosse*, 1990; *Grosse et al.*, 1996]. The oxygen transferred to the roots may be of either photosynthetic oxygen produced in the leaves, or atmospheric oxygen that is taken up through the bark of trees. These combinations of different transport mechanisms and O_2 sources can result in discriminations different from those during consumption in the soil profile. However, the discrimination in the internal pathway cannot be evaluated by studying $[O_2]$ and $\delta^{18}O$ profiles in soils, and therefore the discriminations in wetlands and grasslands were not evaluated in this study.

[41] In boreal forests, oxygen produced in photosynthesis by mosses may diffuse into the soil before it is mixed with the atmosphere. Oxygen produced by photosynthesis has identical isotopic composition as the substrate water used for its production [*Guy et al.*, 1993], and hence it is considerably depleted in ^{18}O relative to atmospheric oxygen. Diffusion of such unmixed photosynthetic oxygen to the soil will reduce the $\delta^{18}O$ of the soil air, and will cause an erroneously low estimate of D'_{soil}. However, the very high D'_{soil} values measured in our boreal sites seems to indicate that such diffusion of unmixed photosynthetic oxygen did not occur.

3.2. Data Quality

[42] A summary of the results is presented in Table 1, and the full data set is presented in Table 2. In most of the sites the within-sample error in the estimated discrimination was relatively small (<1‰), and there were no large differences between the discrimination found for different sampling dates. In addition, the steady state assumption was validated at each site, for at least part of the soil experiments.

[43] In the second Mediterranean site, in the undisturbed boreal site, and especially in the burned boreal site the standard error in the estimated discrimination within samples was relatively large (>1‰). As discussed in section 3.1.2., the source of this error is probably field-sampling problems that caused mixing of atmospheric air or soil-air from an

adjacent depth into the sample, but the effect of such sampling problems on the calculated discrimination is small. An extreme example of such mixing can be seen in the sample taken in the boreal, undisturbed site on August 19 from 105 cm depth (Table 2), where the discrimination calculated for different replicates of the same sample ranged for 14–20‰. Since such sampling problems will lower the calculated discrimination, the actual discrimination in these sites is probably closer to the high end of the range given. The sampling errors also caused relatively large differences between samples in these sites.

[44] Samples in which the standard deviation of D'_{soil} was greater than 3‰, and samples in which the $[O_2]$ data was very noisy (standard deviation > 0.6%) due to sampling problems, were excluded from the summary of discriminations in the sites presented in Table 1 (all values are given in Table 2).

[45] For the tropical shrub and for one sampling date in the tropical forest, there were no temperature data. However, because of the relatively stable climate in the tropics, the difference between the soil temperature and the average air temperature is small and the thermal diffusion effect can be neglected.

[46] Some uncertainty in the estimated discrimination results from uncertainty in the thermal diffusion coefficients, and the average temperature of the surface. However, a sensitivity analysis shows that this uncertainty is relatively small, and even in the boreal forest were it magnitude is maximum (because of the strong thermal gradient) it is less than 1‰.

3.3. Geographic and Ecosystem Variations in ^{18}O Discriminations

[47] Soil discriminations (D'_{soil}) varied significantly among ecosystems and were both lower and higher than the conventional value of 18‰ (Table 1). In the tropical forest site the mean D'_{soil} was 10 ± 1.5‰, much lower than expected, while it was higher than expected in the boreal forest sites (23 ± 2.3‰ undisturbed, and 22 ± 4.4‰ burned). In the temperate forest sites, D'_{soil} was intermediate (18 ± 0.6‰ and 18 ± 1.4‰) and was close to the conventional figure. The Mediterranean woodland sites also showed intermediate discrimination (19 ± 0.1‰, 17 ± 2.8‰), and the tropical shrub showed low discrimination (15 ± 1.6‰).

[48] The small discrimination at the tropical forest site is similar to the one measured in orchards in Israel (∼12‰, [*Angert et al.*, 2001]) and is significantly lower than the commonly accepted value for respiration (∼18‰ for the COX). This low discrimination is probably the result of diffusion limitation of O_2 transfer to the consumption sites in root tissues and in soil aggregates. This finding illustrates the importance of taking diffusion limitation into account when estimating the discrimination of natural soil systems.

[49] Large discrimination was observed in the boreal sites. Since artifacts induced by leaks could only reduce the estimated discrimination, the values found could be only explained by high fraction of respiration through the alternative oxidase pathway (AOX), for which the discrimination is strong (D = 27‰ for non green tissues [*Ribas-Carbo et al.*, 2000]). Quantitatively, the observed overall strong discrimination requires that about half of soil respiration in the boreal sites be through the AOX. This result contradicts current understanding of respiration, that attributes minor role to the AOX [*Cannell and Thornley*, 2000]. Because of the global importance of boreal forests, further investigation is clearly required to evaluate the contribution of AOX in boreal soils and on a global scale. The high rates of AOX in the boreal soils might be controlled by the low temperatures of the soil, since low temperature has been shown to induce higher rates of AOX in roots [*Reyes and Jennings*, 1997].

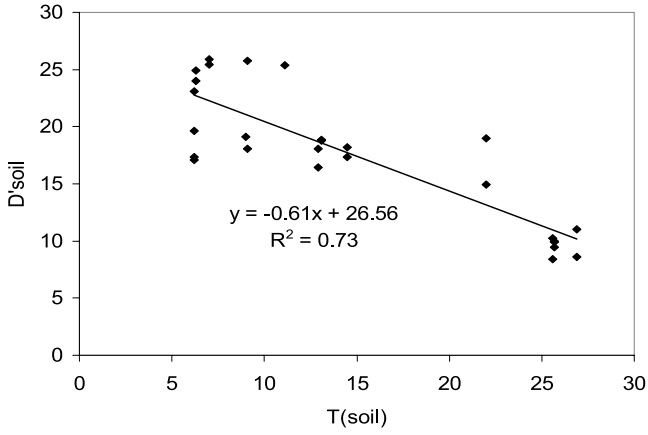

Figure 2. Measured discrimination against soil air O_2 in soil respiration (D'_{soil}) versus temperature at the sampling depth (T(soil)), for all the sites.

[50] The intermediate discrimination (∼18‰) in the temperate forest sites and in the Mediterranean woodland sites can be explained in two ways. It could result from dark respiration through the COX (D∼18‰) without any AOX engagement and with no diffusion limitation. Alternatively, the opposing effects of AOX and diffusion limitation on D'_{soil} may cancel out. Since there is no reason to believe that the diffusivity of root tissues in temperate forests is different from that in tropical ones, the latter explanation appears more likely.

[51] The variations in D'_{soil} among ecosystems was also reflected in a latitudinal trend, that may be controlled by a temperature trend. Smaller discrimination was usually found in sites with higher soil temperature, and the correlation between this two variables is relatively high (r^2 = 0.73, Figure 2). Temperature can influence the observed trend in two ways. First, the rate of soil respiration strongly depends on temperature [*Raich and Potter*, 1995; *Savage and Davidson*, 2001]. For a given diffusivity, higher respiration rate will lower internal $[O_2]$ levels and, consequently, will decrease the discrimination. Second, the activation of the AOX in roots and soils is negatively correlated with temperature [*Reyes and Jennings*, 1997]. Lower temperature would therefore result in greater proportion of AOX engagement and higher overall discrimination.

[52] As indicated by the correlation coefficient (r^2 = 0.73), almost a third of the observed variations in D'_{soil} are not explained by temperature. Several factors can influence D'_{soil}. These factors include temperature independent varia-

Table 2. Complete Data Set Including the Temperature (Both at the Sampling Depth and at the Surface) O_2 Concentration, $\delta^{18}O$, and the Calculated Discrimination in the Different Sampling Times and Different Sites[a]

Site	Date and Time	Depth	[O2]%	[O2]%STD	$\delta^{18}O$	$\delta^{18}O$ STD	T (Soil)	T (Surface)	ΔT	D'_{soil}	D'_{soil} STD	n
Tropical forest	15-Feb-01	60	17.67		−0.16					**13**		
Tropical forest	15-Feb-01	60	17.64		−0.14					**13**		
Average		**60**	**17.66**	**0.03**	**−0.15**	**0.02**				**13**	**0.1**	**2**
Tropical forest	12-May-01 8:30	**40**	18.37		−0.60		25.6	27.5	1.9	**9**		
Tropical forest	12-May-01 8:30	**40**	18.72		−0.64		25.6	27.5	1.9	**8**		
Tropical forest	12-May-01 8:30	**40**	18.87		−0.59		25.6	27.5	1.9	**8**		
Average		**40**	18.65	**0.26**	**−0.61**	**0.03**	**25.6**	**27.5**	**1.9**	**8**	**0.7**	**3**
Tropical forest	**12-May-01 17:30**	**40**	**18.50**		**−0.44**		**25.6**	**27.5**	**1.9**	**10**		**1**
Tropical forest	12-Jun-01 8:30	60	19.64		−0.32		26.9	27.5	0.6	**9**		
Tropical forest	12-Jun-01 8:30	60	19.83		−0.33		26.9	27.5	0.6	**8**		
Tropical forest	12-Jun-01 8:30	60	19.64		−0.28		26.9	27.5	0.6	**9**		
Tropical forest	12-Jun-01 8:30	60	19.75		−0.33		26.9	27.5	0.6	**8**		
Average		**60**	**19.72**	**0.09**	**−0.31**	**0.02**				**8**	**0.7**	**4**
Tropical forest	**12-Jun-01 17:30**	**60**	**19.58**		**−0.19**		**26.9**	**27.5**	**0.6**	**11**		**1**
Tropical forest	2-Aug-01 8:40	60	18.25		−0.40		25.7	26.5	0.8	**11**		
Tropical forest	2-Aug-01 8:40	60	18.26		−0.50		25.7	26.5	0.8	**10**		
Tropical forest	2-Aug-01 8:40	60	18.31		−0.59		25.7	26.5	0.8	**9**		
Average		**60**	**18.28**	**0.03**	**−0.5**	**0.1**	**25.7**	**26.5**	**0.8**	**10**	**0.8**	**3**
Tropical forest	2-Aug-01 17:10	60	17.94		−0.44		25.7	26.5	0.8	**11**		
Tropical forest	2-Aug-01 17:10	60	18.08		−0.48		25.7	26.5	0.8	**10**		
Tropical forest	2-Aug-01 17:10	60	18.17		−0.32		25.7	26.5	0.8	**11**		
Tropical forest	2-Aug-01 17:10	60	18.22		−0.56		25.7	26.5	0.8	**10**		
Tropical forest	2-Aug-01 17:10	60	18.77		−0.39		25.7	26.5	0.8	**10**		
Tropical forest	2-Aug-01 17:10	60	18.10		−0.45		25.7	26.5	0.8	**11**		**6**
Average		**60**	**18.21**	**0.29**	**−0.4**	**0.1**	**25.7**	**26.5**	**0.8**	**10**	**0.6**	
Tropical forest	2-Aug-01 8:40	40	18.90		−0.44		25.7	26.5	0.8	**9**		
Tropical forest	2-Aug-01 8:40	40	18.96		−0.44		25.7	26.5	0.8	**9**		
Tropical forest	2-Aug-01 8:40	40	18.98		−0.35		25.7	26.5	0.8	**10**		
Tropical forest	2-Aug-01 8:40	40	19.03		−0.40		25.7	26.5	0.8	**9**		
Average		**40**	**18.97**	0.06	−0.41	0.04	25.7	**26.5**	0.8	9	0.4	4
Tropical forest	2-Aug-01 17:10	40	19.13		−0.31		25.7	26.5	0.8	**10**		
Tropical forest	2-Aug-01 17:10	40	19.14		−0.37		25.7	26.5	0.8	**9**		
Tropical forest	2-Aug-01 17:10	40	18.97		−0.35		25.7	26.5	0.8	**10**		
Average		**40**	**19.08**	**0.09**	**−0.34**	**0.03**	**25.7**	**26.5**	**0.8**	**10**	**0.4**	**3**
Temperate forest 1	24-May-01 14:50	60	19.35		0.44		14.5	18.5	4.0	**18**		
Temperate forest 1	24-May-01 14:50	60	19.36		0.47		14.5	18.5	4.0	**19**		
Temperate forest 1	24-May-01 14:50	60	19.37		0.39		14.5	18.5	4.0	**18**		
Temperate forest 1	24-May-01 14:50	60	19.30		0.45		14.5	18.5	4.0	**18**		
Temperate forest 1	24-May-01 14:50	60	19.38		0.41		14.5	18.5	4.0	**18**		
Temperate forest 1	24-May-01 14:50	60	19.34		0.45		14.5	18.5	4.0	**18**		
Temperate forest 1	24-May-01 14:50	60	19.42		0.37		14.5	18.5	4.0	**18**		
Temperate forest 1	24-May-01 14:50	60	19.40		0.40		14.5	18.5	4.0	**18**		
Average		**60**	**19.36**	**0.04**	**0.42**	**0.03**	**14.5**	**18.5**	**4.0**	**18**	**0.3**	**9**
Temperate forest 1	25-May-01 15:30	60	19.39		0.37		14.5	18.5	4.0	**18**		
Temperate forest 1	25-May-01 15:30	60	19.44		0.32		14.5	18.5	4.0	**17**		
Temperate forest 1	25-May-01 15:30	60	19.44		0.34		14.5	18.5	4.0	**17**		
Temperate forest 1	25-May-01 15:30	60	19.41		0.37		14.5	18.5	4.0	**18**		
Temperate forest 1	25-May-01 15:30	60	19.42		0.34		14.5	18.5	4.0	**17**		
Temperate forest 1	25-May-01 15:30	60	19.42		0.34		14.5	18.5	4.0	**17**		
Temperate forest 1	25-May-01 15:30	60	19.39		0.36		14.5	18.5	4.0	**17**		
Temperate forest 1	25-May-01 15:30	60	19.42		0.35		14.5	18.5	4.0	**17**		
Average		**60**	**19.42**	**0.02**	**0.35**	**0.02**	**14.5**	**18.5**	**4.0**	**17**	**0.2**	**9**
Temperate forest 2	30-May-01 11:50	85	20.42		0.17		9.0	9.6	0.6	**20**		
Temperate forest 2	30-May-01 11:50	85	20.44		0.11		9.0	9.6	0.6	**18**		
Temperate forest 2	30-May-01 11:50	85	20.48		0.12		9.0	9.6	0.6	**19**		
Temperate forest 2	30-May-01 11:50	85	20.45		0.13		9.0	9.6	0.6	**19**		
Temperate forest 2	30-May-01 11:50	85	20.39		0.18		9.0	9.6	0.6	**20**		
Temperate forest 2	30-May-01 11:50	85	20.47		0.14		9.0	9.6	0.6	**20**		
Temperate forest 2	30-May-01 11:50	85	20.45		0.13		9.0	9.6	0.6	**19**		
Average		**85**	**20.44**	**0.03**	**0.14**	**0.02**	**9.0**	**9.6**	**0.6**	**19**	**0.8**	**7**
Temperate forest 2	31-Jul-01 9:45	85	20.22		0.12		12.9	15.3	2.4	**16**		
Temperate forest 2	31-Jul-01 9:45	85	20.21		0.18		12.9	15.3	2.4	**17**		
Temperate forest 2	31-Jul-01 9:45	85	20.11		0.18		12.9	15.3	2.4	**17**		
Temperate forest 2	31-Jul-01 9:45	85	20.20		0.16		12.9	15.3	2.4	**17**		
Temperate forest 2	31-Jul-01 9:45	85	20.32		0.17		12.9	15.3	2.4	**18**		
Temperate forest 2	31-Jul-01 9:45	85	20.36		0.08		12.9	15.3	2.4	**15**		
Temperate forest 2	31-Jul-01 9:45	85	20.23		0.14		12.9	15.3	2.4	**16**		
Temperate forest 2	31-Jul-01 9:45	85	20.09		0.15		12.9	15.3	2.4	**16**		
Average		**85**	**20.22**	**0.09**	**0.15**	**0.03**	**12.9**	**15.3**	**2.4**	**16**	**1.0**	**8**
Temperate forest 2	1-Aug-01 10:00	85	20.25		0.21		12.9	15.3	2.4	**19**		

Table 2. (continued)

Site	Date and Time	Depth	[O2]%	[O2]%STD	$\delta^{18}O$	$\delta^{18}O$ STD	T (Soil)	T (Surface)	ΔT	D'_{soil}	D'_{soil} STD	n
Temperate forest 2	1-Aug-01 10:00	85	20.18		0.21		12.9	15.3	2.4	**18**		
Temperate forest 2	1-Aug-01 10:00	85	20.17		0.27		12.9	5.3	2.4	**20**		
Temperate forest 2	1-Aug-01 10:00	85	20.17		0.22		12.9	15.3	2.4	**18**		
Temperate forest 2	1-Aug-01 10:00	85	20.21		0.19		12.9	15.3	2.4	**18**		
Temperate forest 2	1-Aug-01 10:00	85	20.28		0.17		12.9	15.3	2.4	**17**		
Temperate forest 2	1-Aug-01 10:00	85	20.18		0.16		12.9	15.3	2.4	**17**		
Temperate forest 2	1-Aug-01 10:00	85	20.34		0.17		12.9	15.3	2.4	**18**		
Temperate forest 2	1-Aug-01 10:00	85	20.19		0.23		12.9	15.3	2.4	**19**		
Average		**85**	**20.22**	**0.06**	**0.20**	**0.04**	**12.9**	**15.3**	**2.4**	**18**	**0.9**	**5**
Boreal undisturbed	19-Jul-01 16:00	105	9.20		3.53		0.8	13.2	12.4	**20**		
Boreal undisturbed	19-Jul-01 16:00	105	14.65		0.97		0.8	13.2	12.4	**16**		
Boreal undisturbed	19-Jul-01 16:00	105	16.57		0.93		0.8	13.2	12.4	**17**		
Boreal undisturbed	19-Jul-01 16:00	105	13.42		1.58		0.8	13.2	12.4	**18**		
Boreal undisturbed	19-Jul-01 16:00	105	14.33		1.31		0.8	13.2	12.4	**17**		
Boreal undisturbed	19-Jul-01 16:00	105	19.86		0.33		0.8	13.2	12.4	**14**		
Average		**105**	**14.67**	**3.53**	**1**	**1**	**0.8**	**13.2**	**12.4**	**17**	**1.8**	**6**
Boreal undisturbed	19-Jul-01 17:00	125	20.45		0.70		3.8	13.2	9.4	**33**		
Boreal undisturbed	19-Jul-01 17:00	125	20.43		0.76		3.8	13.2	9.4	**35**		
Average		**125**	**20.44**	**0.01**	**0.73**	**0.02**	**3.8**	**13.2**	**9.4**	**34**	**0.6**	**2**
Boreal undisturbed	20-Jul-01	105	20.35		0.32		0.8	13.2	12.4	**14**		
Boreal undisturbed	20-Jul-01	105	20.54		0.15		0.8	13.2	12.4	**5**		
Boreal undisturbed	20-Jul-01	105	20.59		0.14		0.8	13.2	12.4	**4**		
Average		**105**	**20.50**	**0.13**	**0.2**	**0.1**	**0.8**	**13.2**	**12.4**	**8**	**5.6**	**3**
Boreal undisturbed	27-Aug-01 17:30	155	20.38		0.24		6.2	8.4	2.2	**21**		
Boreal undisturbed	27-Aug-01 17:30	155	20.55		0.18		6.2	8.4	2.2	**20**		
Boreal undisturbed	27-Aug-01 17:30	155	20.66		0.09		6.2	8.4	2.2	**17**		
Boreal undisturbed	27-Aug-01 17:30	155	20.67		0.13		6.2	8.4	2.2	**19**		
Boreal undisturbed	27-Aug-01 17:30	155	20.70		0.1		6.2	8.4	2.2	**21**		
Average		**155**	**20.59**	**0.13**	**0.2**	**0.1**	**6.2**	**8.4**	**2.2**	**20**	**1.8**	**5**
Boreal undisturbed	28-Aug-01 9:10	155	20.73		0.16		6.2	8.4	2.2	**24**		
Boreal undisturbed	28-Aug-01 9:10	155	20.67		0.18		6.2	8.4	2.2	**23**		
Boreal undisturbed	28-Aug-01 9:10	155	20.45		0.22		6.2	8.4	2.2	**21**		
Boreal undisturbed	28-Aug-01 9:10	155	20.65		0.21		6.2	8.4	2.2	**24**		
Average		**155**	**20.62**	**0.12**	**0.2**	**0.0**	**6.2**	**8.4**	**2.2**	**23**	**1.7**	**4**
Boreal undisturbed	27-Aug-01 15:40	145	19.97		0.57		6.3	8.4	2.1	**25**		
Boreal undisturbed	27-Aug-01 15:40	145	19.33		1.13		6.3	8.4	2.1	**28**		
Boreal undisturbed	27-Aug-01 15:40	145	19.80		0.61		6.3	8.4	2.1	**24**		
Boreal undisturbed	27-Aug-01 15:40	145	20.65		0.18		6.3	8.4	2.1	**23**		
Average		**145**	**19.94**	**0.55**	**0.6**	**0.4**	**6.3**	**8.4**	**2.1**	**25**	**2.1**	**4**
Boreal undisturbed	28-Aug-01 9:00	145	19.50		0.72		6.3	8.4	2.1	**24**		
Boreal undisturbed	28-Aug-01 9:00	145	19.45		0.75		6.3	8.4	2.1	**24**		
Boreal undisturbed	28-Aug-01 9:00	145	19.36		0.86		6.3	8.4	2.1	**25**		
Average		**145**	**19.44**	**0.07**	**0.8**	**0.1**	**6.3**	**8.4**	**2.1**	**24**	**0.7**	**3**
Boreal burned	19-Jul-01 15:40	85	20.38		0.53		11.1	19.4	8.3	**26**		
Boreal burned	19-Jul-01 15:40	85	20.42		0.45		11.1	19.4	8.3	**23**		
Boreal burned	19-Jul-01 15:40	85	20.51		0.47		11.1	19.4	8.3	**26**		
Boreal burned	19-Jul-01 15:40	85	20.46		0.48		11.1	19.4	8.3	**25**		
Boreal burned	19-Jul-01 15:40	85	20.38		0.55		11.1	19.4	8.3	**26**		
Average		**85**	**20.43**	**0.05**	**0.50**	**0.04**	**11.1**	**19.4**	**8.3**	**25**	**1.2**	**5**
Boreal burned	19-Jul-01 16:00	105	20.19		0.34		6.2	19.4	13.2	**14**		
Boreal burned	19-Jul-01 16:00	105	19.95		0.45		6.2	19.4	13.2	**16**		
Boreal burned	19-Jul-01 16:00	105	19.97		0.50		6.2	19.4	13.2	**17**		
Boreal burned	19-Jul-01 16:00	105	19.78		0.63		6.2	19.4	13.2	**19**		
Boreal burned	19-Jul-01 16:00	105	19.91		0.57		6.2	19.4	13.2	**19**		
Average		**105**	**19.96**	**0.08**	**0.50**	**0.07**	**6.2**	**19.4**	**13.2**	**17**	**1.2**	**5**
Boreal burned	20-Jul-01 8:50	105	20.15		0.51		6.2	19.4	13.2	**18**		
Boreal burned	20-Jul-01 8:50	105	20.28		0.32		6.2	19.4	13.2	**13**		
Boreal burned	20-Jul-01 8:50	105	19.82		0.81		6.2	19.4	13.2	**23**		
Boreal burned	20-Jul-01 8:50	105	20.27		0.45		6.2	19.4	13.2	**17**		
Boreal burned	20-Jul-01 8:50	105	19.92		0.50		6.2	19.4	13.2	**17**		
Boreal burned	20-Jul-01 8:50	105	19.93		0.48		6.2	19.4	13.2	**17**		
Boreal burned	20-Jul-01 8:50	105	19.83		0.57		6.2	19.4	13.2	**18**		
Boreal burned	20-Jul-01 8:50	105	20.23		0.37		6.2	19.4	13.2	**15**		
Boreal burned	20-Jul-01 8:50	105	20.12		0.47		6.2	19.4	13.2	**17**		
Average		**105**	**20.06**	**0.19**	**0.5**	**0.1**	**6.2**	**19.4**	**13.2**	**17**	**2.6**	**9**
Boreal burned	27-Aug-01 17:15	85	20.52		0.32		9.1	13.6	4.5	**24**		
Boreal burned	27-Aug-01 17:15	85	20.38		0.42		9.1	13.6	4.5	**25**		
Boreal burned	27-Aug-01 17:15	85	20.48		0.39		9.1	13.6	4.5	**26**		
Boreal burned	27-Aug-01 17:15	85	20.48		0.36		9.1	13.6	4.5	**25**		
Boreal burned	27-Aug-01 17:15	85	20.25		0.61		9.1	13.6	4.5	**29**		
Average		**85**	**20.42**	**0.11**	**0.4**	**0.1**	**9.1**	**13.6**	**4.5**	**26**	**1.9**	**5**

Table 2. (continued)

Site	Date and Time	Depth	[O2]%	[O2]%STD	$\delta^{18}O$	$\delta^{18}O$ STD	T (Soil)	T (Surface)	ΔT	D'_{soil}	D'_{soil} STD	n
Boreal burned	28-Aug-01 8:50	85	20.31		0.31		9.1	13.6	4.5	**20**		
Boreal burned	28-Aug-01 8:50	85	20.56		0.17		9.1	13.6	4.5	**17**		
Boreal burned	28-Aug-01 8:50	85	20.63		0.16		9.1	13.6	4.5	**17**		
Average		**85**	**20.50**	**0.17**	**0.2**	**0.1**	**9.1**	**13.6**	**4.5**	**18**	**2.0**	**3**
Boreal burned	27-Aug-01 17:00	105	20.57		0.41		7.0	13.6	6.6	**27**		
Boreal burned	27-Aug-01 17:00	105	20.57		0.39		7.0	13.6	6.6	**26**		
Boreal burned	27-Aug-01 17:00	105	20.61		0.35		7.0	13.6	6.6	**25**		
Boreal burned	27-Aug-01 17:00	105	20.61		0.34		7.0	13.6	6.6	**24**		
Boreal burned	27-Aug-01 17:00	105	20.50		0.41		7.0	13.6	6.6	**25**		
Average		**105**	**20.57**	**0.04**	**0.4**	**0.03**	**7.0**	**13.6**	**6.6**	**25**	**1.0**	**5**
Boreal burned	28-Aug-01 8:45	105	20.63		0.37		7.0	13.6	6.6	**27**		
Boreal burned	28-Aug-01 8:45	105	20.58		0.35		7.0	13.6	6.6	**24**		
Boreal burned	28-Aug-01 8:45	105	20.54		0.44		7.0	13.6	6.6	**27**		
Boreal burned	28-Aug-01 8:45	105	20.16		0.61		7.0	13.6	6.6	**26**		
Average		**105**	**20.47**	**0.21**	**0.4**	**0.1**	**7.0**	**13.6**	**6.6**	**26**	**1.6**	**4**
Med. woodland 1	10-Jan-00 13:00	90	19.44		0.38		13.1	12.1	1	**19**		
Med. woodland 1	10-Jan-00 13:00	90	19.48		0.38		13.1	12.1	1	**19**		
Med. woodland 1	10-Jan-00 13:00	90	19.48		0.35		13.1	12.1	1	**19**		
Med. woodland 1	10-Jan-00 13:00	90	19.43		0.40		13.1	12.1	1	**19**		
Med. woodland 1	10-Jan-00 13:00	90	19.42		0.33		13.1	12.1	1	**18**		
Med. woodland 1	10-Jan-00 13:00	90	19.48		0.33		13.1	12.1	1	**18**		
Med. woodland 1	10-Jan-00 13:00	90	19.48		0.38		13.1	12.1	1	**19**		
Med. woodland 1	10-Jan-00 13:00	90	19.44		0.38		13.1	12.1	1	**19**		
Med. woodland 1	10-Jan-00 13:00	90	19.41		0.37		13.1	12.1	1	**19**		
Med. woodland 1	10-Jan-00 13:00	90	19.45		0.37		13.1	12.1	1	**19**		
Average		**90**	**19.45**	**0.42**	**0.37**	**0.02**	**13.1**	**12.1**	**1**	**19**	**0.1**	**4**
Med. woodland 1	12-Jan-00 8:20	90	19.48		0.32		13.1	12.1	1	**18**		
Med. woodland 1	12-Jan-00 8:20	90	19.47		0.36		13.1	12.1	1	**19**		
Med. woodland 1	12-Jan-00 8:20	90	19.46		0.37		13.1	12.1	1	**19**		
Med. woodland 1	12-Jan-00 8:20	90	19.46		0.36		13.1	12.1	1	**19**		
Med. woodland 1	12-Jan-00 8:20	90	19.43		0.39		13.1	12.1	1	**19**		
Med. woodland 1	12-Jan-00 8:20	90	19.48		0.36		13.1	12.1	1	**19**		
Med. woodland 1	12-Jan-00 8:20	90	19.46		0.40		13.1	12.1	1	**19**		
Med. woodland 1	12-Jan-00 8:20	90	19.46		0.37		13.1	12.1	1	**19**		
Average		90	**19.46**	**0.02**	**0.37**	**0.03**	**13.1**	**12.1**	**1**	**19**	**0.3**	**8**
Med. woodland 2	17-Aug-01 9:05	50	20.04		0.25		22.0	25.0	3.0	**18**		
Med. woodland 2	17-Aug-01 9:05	50	20.27		0.04		22.0	25.0	3.0	**13**		
Med. woodland 2	17-Aug-01 9:05	50	20.20		0.14		22.0	25.0	3.0	**16**		
Med. woodland 2	17-Aug-01 9:05	50	20.19		0.09		22.0	25.0	3.0	**14**		
Med. woodland 2	17-Aug-01 9:05	50	20.23		0.11		22.0	25.0	3.0	**15**		
Med. woodland 2	17-Aug-01 9:05	50	20.07		0.15		22.0	25.0	3.0	**16**		
Med. woodland 2	17-Aug-01 9:05	50	20.27		0.08		22.0	25.0	3.0	**14**		
Med. woodland 2	17-Aug-01 9:05	50	20.32		0.06		22.0	25.0	3.0	**13**		
Med. woodland 2	17-Aug-01 9:05	50	20.12		0.14		22.0	25.0	3.0	**16**		
Average		**50**	**20.19**	**0.10**	**0.1**	**0.1**	**22.0**	**25.0**	**3.0**	**15**	**1.6**	**9**
Med. woodland 2	17-Aug-01 19:10	50	20.02		0.28		22.0	25.0	3.0	**18**		
Med. woodland 2	17-Aug-01 19:10	50	20.13		0.24		22.0	25.0	3.0	**18**		
Med. woodland 2	17-Aug-01 19:10	50	20.03		0.30		22.0	25.0	3.0	**19**		
Med. woodland 2	17-Aug-01 19:10	50	19.99		0.32		22.0	25.0	3.0	**19**		
Med. woodland 2	17-Aug-01 19:10	50	19.91		0.40		22.0	25.0	3.0	**20**		
Med. woodland 2	17-Aug-01 19:10	50	20.16		0.25		22.0	25.0	3.0	**19**		
Med. woodland 2	17-Aug-01 19:10	50	19.97		0.31		22.0	25.0	3.0	**19**		
Average		**50**	**20.03**	**0.09**	**0.3**	**0.1**	**22.0**	**25.0**	**3.0**	**19**	**0.7**	**7**
Tropical shrub	22-Jul-01 6:40	60	15.05		0.34			31		**15**		
Tropical shrub	22-Jul-01 6:40	60	15.67		−0.06			31		**14**		
Tropical shrub	22-Jul-01 6:40	60	15.28		0.18			31		**15**		
Tropical shrub	22-Jul-01 6:40	60	14.82		0.35			31		**15**		
Average		**60**	**15.21**	**0.36**	**0.2**	**0.2**		**31**		**15**	**0.7**	**4**
Tropical shrub	22-Jul-01 17:40	60	14.95		0.18			31		**15**		
Tropical shrub	22-Jul-01 17:40	60	15.20		0.16			31		**15**		
Tropical shrub	22-Jul-01 17:40	60	15.02		0.29			31		**15**		
Tropical shrub	22-Jul-01 17:40	60	15.43		0.04			31		**14**		
Average		**60**	**15.15**	**0.21**	**0.2**	**0.1**		**31**		**15**	**0.4**	**4**
Tropical shrub	25-Jul-01 15:30	60	16.27		0.47			31		**16**		
Tropical shrub	25-Jul-01 15:30	60	15.93		0.79			31		**17**		
Tropical shrub	25-Jul-01 15:30	60	16.04		0.66			31		**17**		
Tropical shrub	25-Jul-01 15:30	60	16.03		0.72			31		**17**		
Average		**60**	**16.07**	**0.14**	**0.7**	**0.1**		**31**		**17**	**0.5**	**4**

[a]The number of replicates is given by n, and STD is standard deviation.

tions in the rates of respiration and/or AOX engagement and heterogeneity in the diffusivities of soil columns, roots, and micro-aggregates. The soil column diffusivity is controlled by the soil texture and water content, where the diffusivity of roots and micro-aggregate is harder to predict. The similar discrimination found for two orchard sites with markedly different soil textures [*Angert et al.*, 2001] indicates that, at least for these sites, the limiting diffusion that controls the discrimination occurs inside roots and micro-aggregates, and hence is hard to estimate and model from first principles. The large variations in the discrimination measured in the present study should motivate further investigations of the factors that control them. These investigations should be carried out at more detailed spatial and temporal scales.

[53] Although there is clearly room for more research, the present study provides first estimates of variations in D'_{soil} across ecosystem and geographical locations, and extends earlier findings [*Angert and Luz*, 2001; *Angert et al.*, 2001] of significant deviations of this parameter from the commonly used 18‰ value. The average discriminations binned by ecosystem were 10.1 ± 1.5‰ for the tropical forest, 17.8 ± 1.0‰ for the temperate forest, 22.4 ± 3.6‰ for the boreal forest, 17.9 ± 2.5‰ for the Mediterranean woodland, and 15.4 ± 1.6‰ for the tropical shrub land.

3.4. Implications for the Dole Effect

[54] Assuming, for a first approximation, that the D'_{soil} values estimated in the present study represent their respective ecosystems, we can assess their potential effect on the global Dole Effect. Although this is a crude estimate that will require further validation, it provides an assessment of the uncertainty involved in the application of the constant D_{soil} value (18‰) extrapolated from laboratory experiments.

[55] To obtain a global scale D_{soil}, we first assume that $D_{soil} = D'_{soil}$ (see section 3.1.), and then scale the D'_{soil} values of the three major ecosystems studied by their corresponding net primary production (NPP). The latter, in turn, should be tightly correlated with total (heterotrophic plus autotrophic) soil respiration. From the global NPP estimates of *Xiao et al.* [1997], we calculated that tropical, temperate, and boreal forests contribute 40%, 19%, and 8% of global soil respiration, respectively. Using the average discriminations we estimated (10.1‰, 17.8‰, and 22.4‰, respectively) and assuming that the discrimination in other ecosystems equals the weighted average discrimination in these three ecosystems, we obtain a value of 13.8‰ for global soil discrimination.

[56] This value is considerably smaller than that used for terrestrial ecosystems so far (18‰), and suggests that in global soil respiration the effect of diffusion limitation is significant and is likely to be dominant over that of alternative respiration. Since global soil respiration contributes about one quarter of global O_2 consumption (23%, [*Angert et al.*, 2001]), adopting our first estimate of D_{soil} = 13.8‰ would lower the calculated Dole Effect by about 1‰ (0.23 × [18−13.8]). This, in turn, would increase the discrepancy between current prediction of the Dole Effect (20.8‰ [*Bender et al.*, 1994]) and the observed value (23.5‰ [*Kroopnick and Craig*, 1972]).

[57] Notably, such a discrepancy may be resolved by recent studies that indicate that other contributions to the Dole Effect may be underestimated. For example, *Gillon and Yakir* [2001] show that evaporative enrichment of ^{18}O in leaf water is stronger than previously estimated. Likewise, *Luz et al.* [2002] and *Angert et al.* [2003] demonstrated the importance of AOX engagement, with strong ^{18}O enrichment, in illuminated plankton and higher plants, respectively.

[58] The observed dependence of D_{soil} on ecosystem type implies that changes in the Dole Effect may result from changes in the global proportions of soil respiration contributed by different ecosystems. Accepting our preliminary estimates leads to the conclusion that the Dole Effect is sensitive to the contribution of tropical forests to global soil respiration. Hence effects of diffusion (as well as that of the AOX) should be considered in interpretations of magnitude of the present Dole Effect, as well as its variations during glacial-interglacial cycles.

4. Conclusions

[59] The discrimination against O_2 that is associated with soil respiration was measured for the first time in sites that represent three globally important ecosystems. On the basis of these sites, we estimated a discrimination of 10.1 ± 1.5‰, 17.8 ± 1.0‰, and 22.4 ± 3.6‰, for tropical, temperate, and boreal forests, respectively. In addition, the discrimination for Mediterranean woodland was estimates as 17.8 ± 2.5‰, and that for tropical shrub as 15.4 ± 1.6‰. Using these figures, we estimate a global weighted average discrimination in soil respiration of 13.8‰. This global estimate lowers the calculated Dole Effect by about 1‰. These findings should be considered in future model studies of the Dole Effect.

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A. Angert, Atmospheric Science Center, University of California Berkeley, MC 4767, 307 McCone Hall, Berkeley, CA 94720-4767, USA. (angert@atmos.berkeley.edu)

E. Barkan and B. Luz, Institute of Earth Sciences, Hebrew University of Jerusalem, Givat-Ram, Jerusalem 91904, Israel. (eugenib@cc.huji.ac.il; boaz.luz@huji.ac.il)

B. Barnett, Department of Geosciences, M48 Guyot Hall, Princeton University, Princeton, NJ 08544, USA. (bbarnett@Princeton.edu)

E. Brugnoli, CNR Istituto per l'Agroselvicoltura, Via Marconi 2, I-05010 Porano (TR), Italy. (brugnoli@ias.tr.cnr.it)

E. A. Davidson and K. Savage, Woods Hole Research Center, P.O. Box 296, 13 Church Street, Woods Hole, MA 02543, USA. (edavidson@whrc.org; savage@whrc.org)

J. Fessenden and J. T. Randerson, Divisions of Engineering and Applied Science and Geological and Planetary Sciences, California Institute of Technology, Mail Stop 100-23, Pasadena, CA 91125, USA. (julianna@lanl.gov; jimr@gps.caltech.edu)

S. Maneepong, Institute of Agricultural Technology, Wailailak University, Thasala, Nakhon Si Thammarat 80160, Thailand. (msomsak@praduu2.wu.ac.th)

N. Panapitukkul, Department of Earth Sciences, Faculty of Natural Resources, Prince of Songkla University, Hat Yai, Songkla 90110, Thailand. (pnipa@ratree.psu.ac.th)

D. Yakir, Department of Environmental Sciences and Energy Research, Weizmann Institute of Science, Rehovot 76100, Israel. (dan.yakir@weizmann.ac.il)