Changes in the O_2/N_2 ratio of the atmosphere during recent decades reflected in the composition of air in the firn at Vostok Station, Antarctica

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Abstract. Samples of air at various depths in firn were collected at Vostok Station, Antarctica, and analyzed for $\delta^{15}N$ of N_2, O_2/N_2 ratio, and CO_2. The ultimate objective of this work is to constrain the recent rate of the atmospheric $[O_2]$ decrease, thereby providing a direct experimental constraint on net CO_2 fluxes into the ocean and the land biosphere. $\delta^{15}N$ increases with depth, because of gravitational enrichment, at approximately the rate predicted by the barometric equation. Gravitationally corrected CO_2 decreases with depth to 308 ppmV at 101.9 m depth, because deeper air is older and less contaminated with anthropogenic CO_2. The gravitationally corrected O_2/N_2 ratio increases with depth mainly because burning fossil fuel consumes O_2. Samples in the top 20 m of the firn have anomalously high CO_2 concentrations and anomalously low O_2/N_2 ratios. Samples below 96.2 m depth have anomalously high O_2/N_2 ratios. Between 30 and 96.2 m depth, the gravitationally corrected increase in the O_2/N_2 ratio is nearly equal to that computed from the rate of O_2 consumption by combustion of fossil fuels. Our results indicate that the rate of anthropogenic O_2 consumption can be accurately constrained by future firn air studies.

Introduction

In their landmark paper on the atmospheric O_2 cycle, *Keeling and Shertz* [1992] showed that the O_2/N_2 ratio of air is decreasing by about 0.018 ‰ / yr. They argued that accurate measurements of the rate of this increase, together with ancillary data, would allow one to constrain the rates of CO_2 uptake by the land biosphere and the ocean. The basis for this approach is that the ocean does not buffer the O_2 concentration of the atmosphere. The only anthropogenic O_2 fluxes are due to consumption associated with the burning of fossil fuels (which is well known) and net production associated with the growth of the land biosphere. Ongoing efforts to monitor changes in the O_2/N_2 ratio of air [*Keeling*, 1988; *Keeling and Shertz*, 1992; *Bender et al.*, 1992] will constrain the rate of

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oceanic uptake and net biosphere conversion by the end of the current decade, when the directly measured change will be large enough to allow accurate calculation of the secular trend.

By studying air in the firn of polar ice sheets, we can determine the rate of anthropogenic oxygen uptake during the last several decades, and thus constrain biospheric conversion and oceanic uptake during this recent period. The firn is the porous layer of incompletely compacted snow at the top of an ice sheet. Its impedance is such that the gas at its base is a mixture of air from the last several decades [*Schwander et al.*, 1993]. To investigate the possibility of measuring anthropogenic O_2 uptake from firn air studies, we sampled firn air at Vostok Station, East Antarctica (78°28' S, 106° 48' E, 3502 m elevation). At this site, the firn extends to 102 m depth. Between 90 - 102 m depth, open porosity diminishes as sintering of ice crystals traps gas in isolated bubbles [J. M. Barnola, unpublished results].

Three factors affect the composition of firn air. First, the top 10 - 20 m of the firn can be mixed convectively due to wind stress at the surface [*Colbeck*, 1989]. Such mixing would make the composition of gases in the upper part of the firn identical to that of the contemporary atmosphere. Second, below the zone of mixing, the concentration of each gas and each isotope is described by the barometric equation: $(P_z/P_0) =$ exp (mgz/RT) [*Craig et al.*, 1988; *Schwander*, 1989; *Sowers et al.*, 1989], where P is pressure, z is depth, m is mass, g is the gravitational acceleration, R is the ideal gas constant, and T is absolute temperature. According to this equation, gases are fractionated such that heavy gases and isotopes are progressively enriched with depth. The enrichment is directly proportional to the mass difference [*Craig et al.*, 1988]. Third, the composition of gases in the firn are continuously equilibrating, by molecular diffusion, with the changing composition of the atmosphere. The increasing atmospheric concentration of CO_2 creates a concentration gradient which drives CO_2 downwards towards the base of the firn. Analogously, the decreasing atmospheric concentration of O_2 causes diffusion of that gas out of the firn and into the atmosphere. Fluxes are given by the equation:

$$F = D(d[C-C_{eq}]/dz) \qquad (1)$$

C is concentration, C_{eq} is the equilibrium concentration (=

C_0exp[mgz/RT]), and D is diffusivity. We can use this equation to model the time-dependent distribution of O$_2$ and CO$_2$ in the firn [*Schwander et al.*, 1993]. Diffusivity depends on the molecular mass and diameter of each gas, temperature, pressure, and the porosity and tortuosity of the snow. Relevant equations and data are summarized by *Schwander* [1989] and *Schwander et al.* [1993].

A potential fourth effect on firn air composition is upward advection of air through the firn, at the rate of order 0.1 m/yr, associated with compaction. However diffusion, given a typical diffusivity of 100 m^2/yr, will overwhelm the effect of advection.

Experimental methods and results

We sampled air in firn at Vostok using a method similar to that of *Schwander et al.* [1993]. Briefly, one lowers a 3 m long rubber sleeve to the base of the drill hole in the firn, inflates the sleeve so that it expands against the walls and seals the bottom of the hole, and then pumps air through a tube with an intake below the sleeve. At least 500 L of firn air are pumped to waste from each depth before samples are collected. We stored samples in 2 L glass flasks with Leuwers-Hapert glass valves having viton O-rings. The O$_2$/N$_2$ ratios and CO$_2$ concentrations in these flasks are stable for at least 4 months at levels of ± 0.005 ‰ and 0.2 ppmV, respectively.

CO$_2$ was measured at Laboratoire de Glaciologie et Geophysique de l'Environnement using a Varian 3300 gas chromatograph equipped with a thermal conductivity detector. Gas in each flask was analyzed three to five times on 0.5 to 2 cm^3 (STP) aliquots of sample. The external reproducibility (2 σ) is ± 1.5 ppmV.

δ^{15}N and δO$_2$/N$_2$ were measured at U. R. I. using a Finnigan MAT 251 isotope ratio mass spectrometer with a glass inlet line and Leuwers - Hapert valves. About 25 cm^3 STP of dry sample is admitted to the inlet line and anlyzed against a similar aliquot of a dry air standard. The inlet line operates at 1 atm pressure and the sample and reference are admitted to the changeover valve through 1 m long, 10 μm i. d. glass capillary tubing. The O$_2$/N$_2$ ratio is measured from the ratio of the mass 32 (^{16}O$_2$) and 29 (^{15}N^{14}N) peaks with the mass spectrometer operating in the normal sample/reference switching mode. Precision, based on most replicates reported here, is ± 0.003 ‰ for δ^{15}N of N$_2$ and ± 0.005 ‰ for δO$_2$/N$_2$. The precision of the samples from 100 m depth is poorer, for reasons suggested below.

In Figure 1, we plot δ^{15}N, gravitationally corrected CO$_2$ concentration, and gravitationally corrected δO$_2$/N$_2$ vs. depth. The gravitational correction is made by subtracting (44-28.5)xδ^{15}Nx[CO$_2$]/1000 from the measured CO$_2$ concentration and (32-29)x δ^{15}N from the measured δO$_2$/N$_2$ value. δ^{15}N and δO$_2$/N$_2$ increase with depth while the CO$_2$ concentration generally decreases with depth. The δO$_2$/N$_2$ increase is a direct result of gravitational fractionation. The CO$_2$ and δO$_2$/N$_2$ trends reflect the fact that deeper samples are comprised of older air with less CO$_2$ and more O$_2$.

O$_2$/N$_2$ ratios reported here for Vostok increase smoothly with depth and, as expected, increase by an amount greater than that due to gravitational fractionation alone. O$_2$/N$_2$ ratios reported for firn air at the GRIP (Greenland) site [*Schwander et al.*, 1993] scatter considerably and, with one exception, increase by less than predicted for gravitation alone. Our improved results may reflect better drying of the samples and use of more appropriate vessels for storage.

Identifying anomalies in composition and their causes

There are a number of prominent anomalies in the data. CO$_2$ concentrations in 2 of the 4 surface samples, both 20 m samples, and flask 34 from 40 m depth are above the ambient atmospheric level of about 352.5 ppmV. O$_2$/N$_2$ values for the 20 and 40 m samples were also anomalous. The δ^{15}N of flask 34, from 40 m depth, is highly anomalous (- 0.099‰). The concentration of methane in flask 31, from 40 m depth, is 1.741 ppmV, about 0.04 ppmV higher than the ambient concentration over East Antarctica at the time of sampling. Other CH$_4$ results for Vostok firn air samples are highly consistent (J. Chappellaz, unpublished data).

Flask 34 contained anomalously high levels of water vapor and was not vacuum tight. Otherwise, we do not completely understand the origin of these anomalies. The air sampled at the surface and 20 m may have been incompletely dried; deeper samples were effectively dried cryogenically by the cold temperature of the firn itself. The 20 m samples were the first taken; procedures may have improved with experience. Future work will hopefully reveal the processes causing the anomalous compositions. We eliminate results for samples with anomalously high CO$_2$ concentrations from 0 m depth, 20 m depth, and flask 34 from 40 m depth from the ensuing discussion. We retain the data from flask 31, 40 m depth, but note that removing this sample brings our results into better agreement with the change in O$_2$ computed below assuming that the biosphere is in balance.
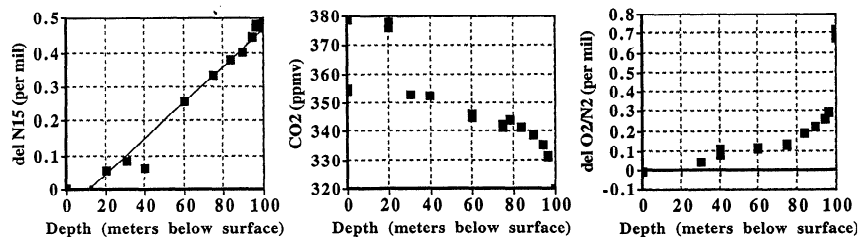

Figure 1. δ^{15}N of N$_2$, gravitationally corrected concentration of CO$_2$, and gravitationally corrected δO$_2$/N$_2$ vs. depth in firn air at Vostok Station, Antarctica. Note that the δO$_2$/N$_2$ value of the 20 m sample and the 101.8 m sample fall off scale and are not plotted. The line on the δ^{15}N - depth plot is the best - fit line through the data points at depths of 30.5, 60, 75, 83.5, 94.4 and 96.2 meters below surface having the slope predicted by the barometric equation (0.54 ‰ / 100 m).

The agreement between $\delta O_2/N_2$ analyses in air from the two flasks collected from 100 m depth is poor ($\pm$ 0.023 ‰). The gravitationally corrected $\delta O_2/N_2$ value measured at this depth, + 0.7 per mil, seems anomalously high. It is roughly equal to the estimated preindustrial value [Sowers et al., 1989] despite the fact that the CO_2 concentration, 318.5 ppmV, is well above the preindustrial CO_2 value. The samples at 100 mbs were collected near the base of the bubble closeoff zone. Flow was, accordingly, conductance limited, as indicated by a reduction of a factor of 3 in the pumping speed under similar sampling conditions as for the shallower samples. This conductance limitation did not result in mass dependent fractionation, but could have caused artifactual enrichment of O_2 in two ways. First, the sample might have been enriched in O_2 derived by diffusion of that gas through the rubber sleeve which was pressurized and inflated to seal the bottom of the hole. In this case, shallower samples would also have been contaminated, but at a lower level and also by a constant amount, since they were collected under identical conditions. Second, the sample might have been enriched in gas pumped out of bubbles which had closed very recently. The driving force would have been the pressure difference between gas in new bubbles, which is at hydrostatic pressure with respect to the overlying atmosphere, and lower pressures at the pump intake at the bottom of the hole. This suggestion derives from the observation that gases in ice core samples are depleted in O_2 with respect to N_2 [Sowers et al., 1989; Craig et al., 1988], probably because of configurational diffusion of O_2 through imperfections in ice having a dimension comparable to the molecular diameter of O_2 [Craig et al., 1988]. We neglect the results for the 100 m sample in the discussion below.

The question is whether the factor(s) responsible for the anomalous O_2/N_2 values at 100 m have influenced the O_2/N_2 ratios between 30 and 96 m. If the enrichment were due to loss from new bubbles, samples from depths less than 90 m would have been unaffected, since there are no isolated bubbles at shallower depths. If diffusion through the bladder were the O_2 source, all samples would have been affected. However, the enrichment would have been similar for all samples above 100 m depth, since conditions of collection were identical. The artifactual enrichment would have undoubtedly contributed to scatter, but would not have caused a systematic error in the slope. The O_2 enrichment for the 100 m sample would have been greater (in agreement with observation), since it was collected at a low flow rate.

In the following discussion we consider data for 11 selected samples taken between 30.5 and 96.2 m depth.

Discussion

$\delta^{15}N$ in the selected samples increases with the slope predicted by the barometric equation (Fig. 1). The sample at 40 m depth is an exception; its $\delta^{15}N$ is anomalous by 0.08 ‰. The x-axis intercept of the regression line constrained to have the predicted slope is at 13 m depth, suggesting that the firn is well mixed by convection to this level.

The gravitationally corrected CO_2 concentration at 96.2 m depth is 330.1 ppmV, corresponding to that in air at South Pole in 1977 [Trends, 1991], approximately 14 years before sample collection at Vostok. The O_2 concentration in air at the base of the firn should then be approximately equal to the

atmospheric value about 10.8 years (= 14 years x D_{CO_2}/D_{O_2}) prior to collection, or in early 1980. We scale the "age" in this manner because the time required for a gas at the base of the firn to equilibrate with a changed atmospheric concentration is inversely proportional to its diffusivity.

The change in the O_2 concentration of air between 96.2 m and the shallowest integral sample (at 30.5 m depth) is 0.254 ‰. Assuming that the sample at 30.5 m has a composition similar to that of overlying air at the time of collection and that the sample at 96.2 m depth represents the O_2 concentration of air 10.8 years earlier, we estimate that the atmospheric O_2/N_2 ratio decreased by 0.254 ‰ in the 10.8 years prior to January, 1991. During this time, combustion of fossil fuels consumed enough O_2 to lower the O_2/N_2 ratio of air by about 0.194 ‰. This value is calculated by multiplying the total amount of coal, lignite, crude petroleum and natural gas combusted during this period [Trends '91] by the ratio of the number of moles of O_2 consumed per mole of fuel combusted for each fuel [Keeling, 1973]. Thus the increase measured in the $\delta O_2/N_2$ ratio near the base of the firn at Vostok is in within 25 % of that calculated from the rate of O_2 consumption by the burning of fossil fuels during the last 10.8 years.

A more rigorous approach to interpreting the downcore change in CO_2 concentration and $\delta O_2/N_2$ of firn air at Vostok Station involves examining the covariation of $\delta O_2/N_2$ with CO_2. In Fig. 2, we plot gravitationally corrected values of $\delta O_2/N_2$ vs. CO_2 concentration. We also plot the covariation of CO_2 and $\delta O_2/N_2$ calculated from the observed atmospheric CO_2 concentration and the change in the $\delta O_2/N_2$ of air that would have occurred as a function of time, calculated assuming that the atmospheric O_2 concentration varied only because of fossil fuel O_2 consumption ("Balanced biosphere" curve). The balanced biosphere curve is calculated from the model of Schwander et al. [1993] assuming that the diffusivity - porosity curve at Vostok is the same as that measured by Schwander et al. [1988] for the Siple ice core. We have done a simple sensitivity test that shows that the slope of calculated curves of O_2/N_2 vs. CO_2 are sensitive to the relative
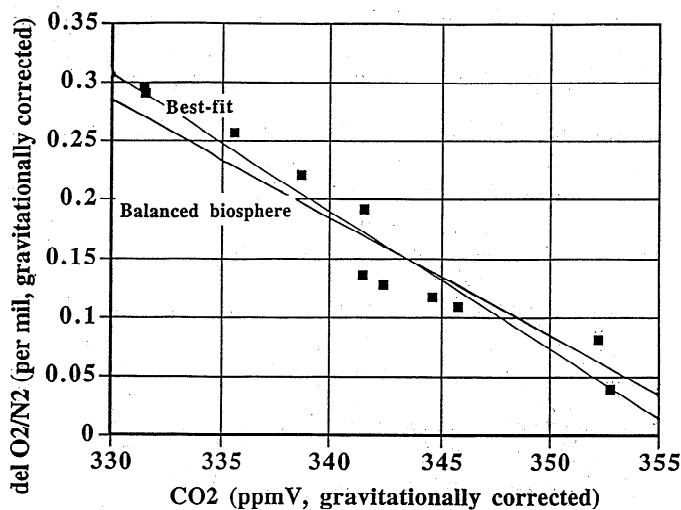

Figure 2. Gravitationally corrected $\delta O_2/N_2$ vs. gravitationally corrected CO_2 concentration. The linear regression line through the data is shown. Also plotted is the line representing the slope of O_2/N_2 vs. CO_2 (both gravitationally corrected) calculated assuming that the land biosphere is in balance and using the firn air diffusion model of Schwander et al. [1993].

Table 1. Recent estimates of CO_2 uptake by the ocean and the land biosphere. The sum of the two terms differs slightly from one work to another because the estimates are for slightly different time periods. Units: gigatons C per year.

Citation	Ocean	Land bios.
Keeling et al. [1989]	2.3	0.5
Tans et al. [1990]	0.3-0.8	1.5-2.0
Quay et al. [1991]	1.5	0.6
Sarmiento and Sundquist [1992]	1.8±0.7	
Sarmiento et al. [1991]	1.9	~0
Keeling and Shertz [1992]	2.5±1.7	0.2±1.7
This paper	3.8±1.5	-1.3±1.5

diffusivities of the gases only, and not to their absolute values as a function of depth.

The model predicts a nearly linear variation of $\delta O_2/N_2$ with CO_2 concentration. The slope of the balanced biosphere curve is - 0.0100 ‰/ppmV CO_2. We estimate the uncertainty in this calculated slope as about 10 %. This uncertainty derives from 2 sources: uncertainty in the rates of fossil fuel consumption and related ratios of O_2 utilization per mole of fuel combusted [Keeling et al., 1993], and uncertainties in the relative diffusivities of CO_2 and O_2 in the firn.

The best-fit slope of the observed $\delta O_2/N_2$ vs. CO_2 plot is - 0.0117 ± 0.0010 ‰/ppmV. This slope is 17 % higher than that of the balanced biosphere line (-0.0100 ± 0.0010 ‰/ppmV) but overlaps it within the uncertainties.

O_2 consumption in excess of that due to fossil fuels implies net consumption of O_2 by the terrestrial biosphere. The magnitude of the excess, 17 ± 20 % of the fossil fuel O_2 demand, corresponds to a CO_2 source from the terrestrial biosphere of 1.3 ± 1.5 Gt carbon/yr. This value is calculated assuming an average rate of fossil fuel CO_2 production of 5.6 Gt/yr during the time accessed by our studies and a stoichiometric ratio of 1.05 moles of O_2 consumed per mole of CO_2 produced during conversion of the land biosphere to CO_2. The corresponding oceanic CO_2 sink would be about 3.8 ± 1.5 Gt carbon/yr.

A number of recent studies have estimated these fluxes from different approaches (Table 1). Our large uncertainties preclude the possibility that we can presently use our firn air data to improve on other recent estimates of anthropogenic carbon fluxes. However, future studies of the composition of air in the firn at different sites on polar ice sheets, using improved sampling methods, may allow one to constrain anthropogenic O_2 uptake and anthropogenic carbon fluxes during recent decades with much better accuracy. Such studies would thus complement ongoing studies of the distribution of O_2/N_2 in air, which will lead to estimates of anthropogenic carbon fluxes in the present and future.

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