Ice Core Paleoclimatology II: gases

12.740 Topic 6 Spring 2008
Processes and steps involved in transfer function, which relates concentrations in ice to those in the global atmosphere. Depth and age scales are for Greenland. Snow-to-firn transition is defined by metamorphism and grain growth; firn-to-ice transition is defined by pore closure.

Figure by MIT OpenCourseWare based on Neftel, et al., 1995.
Firn thickness vs. mean annual surface temperature

Plot of observed values of firn thickness at Arctic (Blue Circles) and Antarctic (Red Circles) polar-ice sites versus temperatures at a depth of 10m. Data are from Paterson ([3], p. 15). The firn temperatures are approximate mean annual surface temperatures on the ice sheets during snow accumulation. The linear fit is given by \( Z = -1.307T + 31.5 \).

Figure by MIT OpenCourseWare.
Adapted from source: Craig and Wiens (1996).
Gases in Ice Cores

- Bubbles seal off at the bottom of the firn layer, \( \sim 80-120 \text{ m} \)
- Hence gas is younger than the solid ice that contains it - the “gas age/ice age difference” depends on the accumulation rate
- Most gases are well mixed in atmosphere; so records from Antarctic and Greenland are nearly the same; features of the records can be used to correlate chronologies between hemispheres
- Gases that have been measured:
  - \( \text{CO}_2 \)
  - \( \text{O}_2 (^{18}\text{O}/^{16}\text{O} \text{ ratio, O}_2/\text{N}_2) \)
  - \( \text{CH}_4 \)
  - \( \text{N}_2\text{O} \)
Methods of extracting gases from ice

• Melting/freezing cycles, vacuum extraction:
  \[ \text{CH}_4, \text{N}_2\text{O}, \text{O}_2, \text{N}_2 \]

• Needle-crushing:
  \[ \text{CO}_2 \]
  (because \( \text{CO}_2 \) will be partially soluble in water and will react with ions, solid phase components, and contaminants)
Image removed due to copyright restrictions.

CO$_2$ During the last 450 kyr from the Vostok, Antarctica Ice Core

Image removed due to copyright restrictions.

CO$_2$ in the Byrd Ice Core

Image removed due to copyright restrictions.

Staffelbach et al. (1991)
CO$_2$ in the Taylor Dome Ice Core

Image removed due to copyright restrictions.

Indermühle et al. (1999)
δ¹⁸O of gaseous oxygen in ice cores (δ¹⁸O₂)

Dole Effect: δ¹⁸O₂ of atmosphere is +23.5‰ relative to SMOW.

a. Photosynthesis: H₂O + CO₂ = O₂ + CH₂O

\[ \delta^{18}O_{\text{photo}} = \delta^{18}O(\text{water}) + A \]

(where A is the kinetic isotope effect during photosynthesis)

where \( \delta^{18}O(\text{water}) = \delta^{18}O(\text{ocean}) + W \)

(where W is the weighted mean difference between the isotopic composition of the ocean and the water immediately used for respiration)

b. Respiration: O₂ + CH₂O = H₂O + CO₂

\[ \delta^{18}O_{\text{resp}} = \delta^{18}O₂ + B \]

(respiratory kinetic isotope fractionation)

c. At steady-state,

\[ \delta^{18}O₂ - \delta^{18}O (\text{ocean}) = W + A - B \]
δ¹⁸O of gaseous oxygen in ice cores (δ¹⁸O₂)

<table>
<thead>
<tr>
<th>Parameters for estimating the turnover time of atmospheric O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global atmospheric O₂ reservoir (GO₂R) = 3.7 × 10¹⁹ mol</td>
</tr>
<tr>
<td>Terrestrial net primary productivity (TNPP) = 5 × 10¹⁵ mol yr⁻¹</td>
</tr>
<tr>
<td>(refs 21, 22)</td>
</tr>
<tr>
<td>Terrestrial gross primary productivity (TGPP) = 2 × TNPP (ref. 23) = 10 × 10¹⁵ mol yr⁻¹</td>
</tr>
<tr>
<td>Marine primary productivity (MPP) = 2 × 10¹⁵ (ref. 24) - 10 × 10¹⁵ mol yr⁻¹ (refs 24, 25)</td>
</tr>
<tr>
<td>Global primary productivity (GPP) = (TGPP + MPP) = 12 × 10¹⁵ - 20 × 10¹⁵ mol yr⁻¹</td>
</tr>
<tr>
<td>Atmospheric O₂ turnover time = (GO₂R/GPP) = 3.1 - 1.9 kyr</td>
</tr>
</tbody>
</table>

Bender et al. (1985)
**$\delta^{18}O$ of gaseous oxygen in ice cores ($\delta^{18}O_2$)**

**Table 1a. Terrestrial Mass Balance of $O_2$ and $\delta^{18}O$ of $O_2$**

<table>
<thead>
<tr>
<th>Production term</th>
<th>Production</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gross production excluding photorespired $O_2$ (GPP)</td>
<td>14.1</td>
<td>Farquhar et al. [1993]</td>
</tr>
<tr>
<td>Gross production including photorespiration (14.1/0.69)</td>
<td>20.4</td>
<td>Farquhar et al. [1980]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process</th>
<th>Fraction of respiratory $O_2$ consumption</th>
<th>Isotope effect</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^{18}O$ of terrestrial photosynthetic $O_2$ w. r. t. SMOW</td>
<td></td>
<td>4.4 %o</td>
<td>Farquhar et al. [1993]</td>
</tr>
<tr>
<td>Discrimination against $O^{18}$ during respiration</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dark respiration</td>
<td></td>
<td>59%</td>
<td>Guy et al. [1992, 1993]</td>
</tr>
<tr>
<td>Mehler reaction</td>
<td></td>
<td>10%</td>
<td>Guy et al. [1992]</td>
</tr>
<tr>
<td>Photorespiration</td>
<td></td>
<td>31%</td>
<td>Guy et al. [1992]</td>
</tr>
<tr>
<td>Flux weighted terrestrial respiratory isotope effect, excluding dark respiration</td>
<td></td>
<td>18.7 %o</td>
<td></td>
</tr>
<tr>
<td>Equilibrium enrichment in $\delta^{18}O$ of leaf water w. r. t. air</td>
<td></td>
<td>+0.7 %o</td>
<td>Benson and Krause [1984]</td>
</tr>
<tr>
<td>Terrestrial respiratory isotope effect ($= 18.7% - 0.7%$)</td>
<td></td>
<td>18.0 %o</td>
<td></td>
</tr>
<tr>
<td>Terrestrial Dole effect</td>
<td></td>
<td>22.4 %o</td>
<td></td>
</tr>
</tbody>
</table>
But: we must make a correction for gravitational fractionation in firn

Gibbs equation for gravitational equilibrium for isotope and perfect gas ratios (Craig and Wiens, 1996):

\[
\frac{R}{R_o} = \exp \left[ \frac{gz(\Delta M)}{RT} \right]
\]

e.g. in a 100m diffusive firn layer, \(^{84}\text{Kr}\) should be enriched over \(^{36}\text{Ar}\) by 1.28%, and \(^{15}\text{N}\) is enriched over \(^{14}\text{N}\) by ~0.4‰.

The driving processes are a balance between gravitational forcing (forcing heavier isotopes to underlay lighter isotopes), and random molecular diffusion, working against the gradient established by gravity.

The result can be derived from the barometric equation

\[
P = P_o \exp \left[ \frac{Mgza}{RT} \right]
\]

describing the pressure of a gas above the surface of the earth that would be observed if molecular diffusion was the dominant mode of vertical transport [i.e., no turbulent diffusion, as occurs in the real atmosphere](Dalton, 1826; Gibbs, 1928).

So for \(\delta^{18}\text{O}_2\), use \(\delta^{15}\text{N}\) to make a correction.
$\delta^{18}O_2$ in the Vostok ice core, compared to the marine $\delta^{18}O$ record

Image removed due to copyright restrictions.

Sowers et al. (1993)
$\delta^{18}O_2$ in the GISP2 ice core, compared to Vostok

Image removed due to copyright restrictions.
Image removed due to copyright restrictions.

Image removed due to copyright restrictions.
CH$_4$ comparison between GRIP and Vostok

Brook et al. (1996)
Science 273:

Image removed due to copyright restrictions.
GRIP/Byrd CH$_4$ comparison

Image removed due to copyright restrictions.

Blunier, T. and E. Brook (2001) Timing of millennial-scale climate change in Antarctica and Greenland during the last glacial period, Science 291:109-112. Figure 1.
“Thermal diffusion” fractionation during transient events

During a sudden warming, where the surface is warmer than the bottom of the firn layer, the cold bottom end is enriched in heavier isotopes:

\[ \delta^{15}\text{N} = a_N D_N T \]

and

\[ \delta^{40}\text{Ar} = a_{\text{Ar}} D_{\text{Ar}} T \]

where \( a_N \) and \( a_{\text{Ar}} \) are the thermal diffusion coefficients for \( \text{N}_2 \) and \( \text{Ar} \) respectively.
GISP2
$\delta^{15}N$ record

Image removed due to copyright restrictions.

Nature 391 (8 January 1998). Figure 1.
Comparison of $\delta^{15}$N and $\delta^{40}$Ar

Severinghaus et al. (2003) GCA 67:325

Implies 11±3 degree abrupt warming

Image removed due to copyright restrictions.
Borehole T modeled from δ¹⁸O with changing δ¹⁸O-T slopes

Image removed due to copyright restrictions.

GRIP borehole temperature Monte-Carlo inversions

Image removed due to copyright restrictions.
Shift in intercept of LGM $\delta^{18}$O-T relationship due to cool tropical/subtropical temperatures?

Image removed due to copyright restrictions.

Boyle (1999)
24:273-276
Alternative:

Suppose it just didn’t snow in central Greenland during the LGM winter (too cold, too dry, wrong storm track pathways…). Then $\delta^{18}O$ of the ice would only reflect summer $T$, not the mean annual $T$ (M. Werner et al., 2000, Geophys. Res. Lett. 27:723)

Best guess as of now: the source vapor temperature matters somewhat, but the discrepancy is dominated by low winter snowfall. So LGM annual temperatures in Greenland were ~ a factor of two lower than “modern spatial calibration $\delta^{18}O$” indicates. It is argued that Antarctic cores don’t show this effect.
CO₂ During the last 450 kyr from the Vostok, Antarctica Ice Core

$\delta^{18}O_2$ in the GISP2 ice core, compared to Vostok

Image removed due to copyright restrictions.
Vostok CO$_2$, T ($\delta$D), CH$_4$, $\delta^{18}$O$_2$, June 65°N insolation

Image removed due to copyright restrictions.

GRIP/Byrd CH$_4$ comparison

Image removed due to copyright restrictions.

Blunier, T. and E. Brook (2001) Timing of millennial-scale climate change in Antarctica and Greenland during the last glacial period, Science 291:109-112. Figure 1.
Do Antarctic climate events match Greenland climate events?

Image removed due to copyright restrictions.

Figure 2. Nature 444 (9 November 2006): 196.
Orbital tuning chronology for the Vostok climate record supported by trapped gas composition

Michael L. Bender*

Department of Geosciences, Princeton University, Princeton, NJ 08544 USA

Received 4 April 2002; accepted 19 July 2002

Abstract

We present data on the O$_2$/N$_2$ ratios of trapped gas samples for the entire length of the Vostok climate record. As in other cores, O$_2$/N$_2$ ratios in these samples are less than the atmospheric ratio, by a small and variable amount, because O$_2$ is selectively excluded during the gas trapping process, and because O$_2$ is also preferentially lost in poorly preserved core samples. Samples younger than 150 ka have large and variable O$_2$ depletions. Samples older than 200 ka have O$_2$/N$_2$ ratios that replicate well and vary smoothly with depth. We plot O$_2$/N$_2$ ratios of well replicated samples older than 160 ka, using a chronology derived by matching the $\delta^{18}$O of paleatmospheric O$_2$ ($\delta^{18}$O$_{atm}$) to northern hemisphere June insolation. On this timescale, O$_2$/N$_2$ varies coherently with local (78°S) summertime insolation. Based on time series analysis of the O$_2$/N$_2$ record and the dynamics of snow metamorphism at the surface, we conclude that summertime insolation influences physical properties of ice grains that control the degree of O$_2$ exclusion during bubble closeoff. O$_2$/N$_2$ in Vostok is thus arguably a property that records local summertime insolation and can be used to test independent chronologies for the core. We show that the $\delta^{18}$O$_{atm}$ chronology, supported by the coincidence of O$_2$/N$_2$ ratios with insolation, is also compatible with recent radiometric dating of corals from high sea stands. We further successfully test the $\delta^{18}$O$_{atm}$ tuning chronology by showing that it predicts a chronology for the GISP2 core which is essentially indistinguishable from the standard GISP2 chronology and, therefore, in excellent agreement with the radiometric chronology of Hulu Cave, China. An accurate chronology for the Vostok ice core is now in place.
O$_2$/N$_2$ measurements on Vostok Ice Core

Image removed due to copyright restrictions.

Bender (2002) EPSL, Vol 204, Page 275. Figure 1.
Bender Vostok O$_2$/N$_2$ $\delta^{18}$O$_2$ orbitally-tuned timescale

Image removed due to copyright restrictions.

Bender (2002) EPSL.
Vostok climate records on $O_2/N_2$ timescale

Image removed due to copyright restrictions.

Bender (2002) EPSL, Vol 204, Page 275. Figure 3.
Dome Fuji
O$_2$/N$_2$ record

Image removed due to copyright restrictions.

Kawamura et al. (2007)
Nature 448:912-917
Image removed due to copyright restrictions.

Kawamura et al. (2007)
Nature 448:912-917


Blunier, T. and E. Brook (2001) Timing of millennial-scale climate change in Antarctica and Greenland during the last glacial period, Science 291:109-112


* Sowers, T., and M. Bender, Climate records covering the last deglaciation, Science, 269, 210-214, 1995.


Also note: a volume of joint GISP2/GRIP results were published in JGR vol. 102 (1997, #C12 pp. 26315-26886). Many worthwhile results and summaries are contained within.