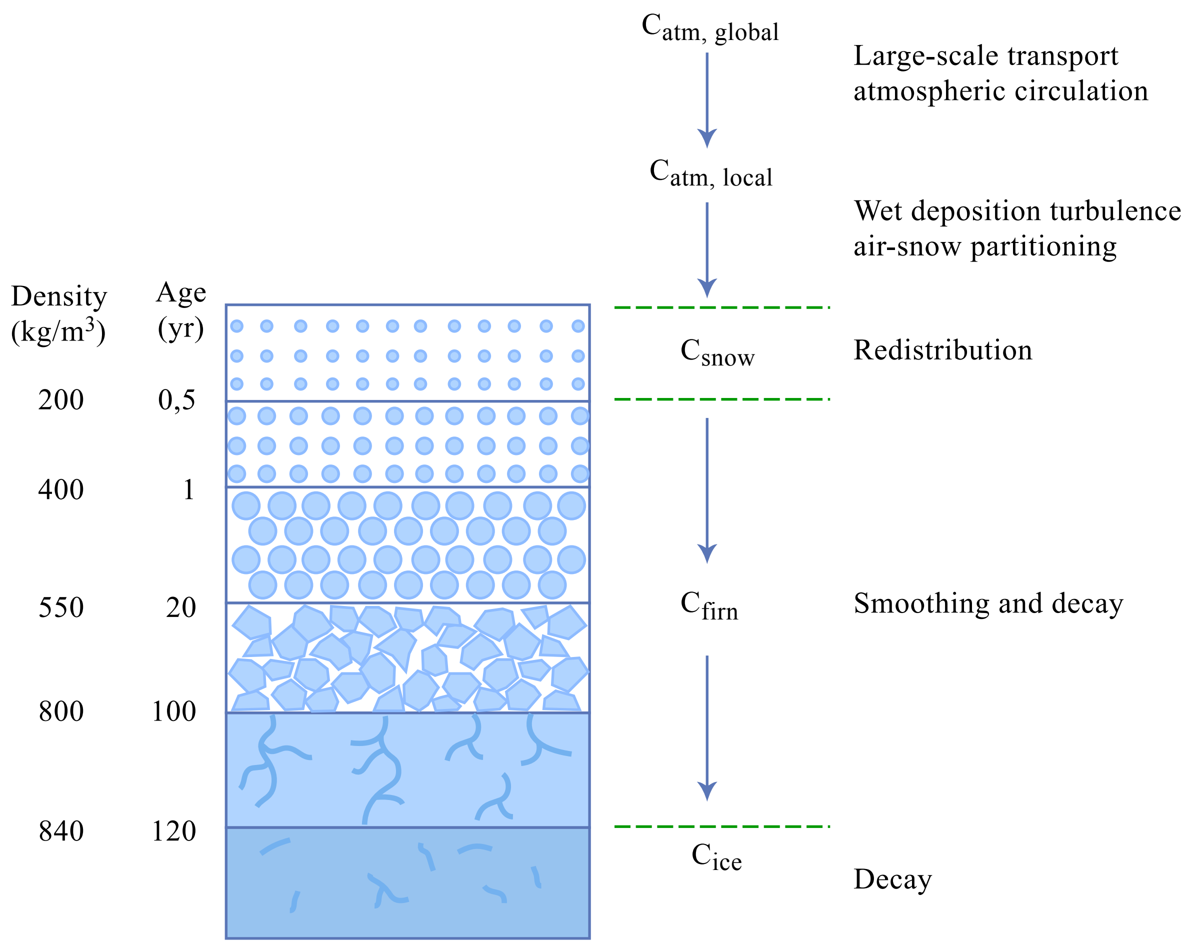
12.740 Paleoceanography
Spring 2008

Ice Core Paleoclimatology II: gases

12.740 Topic 6 Spring 2008

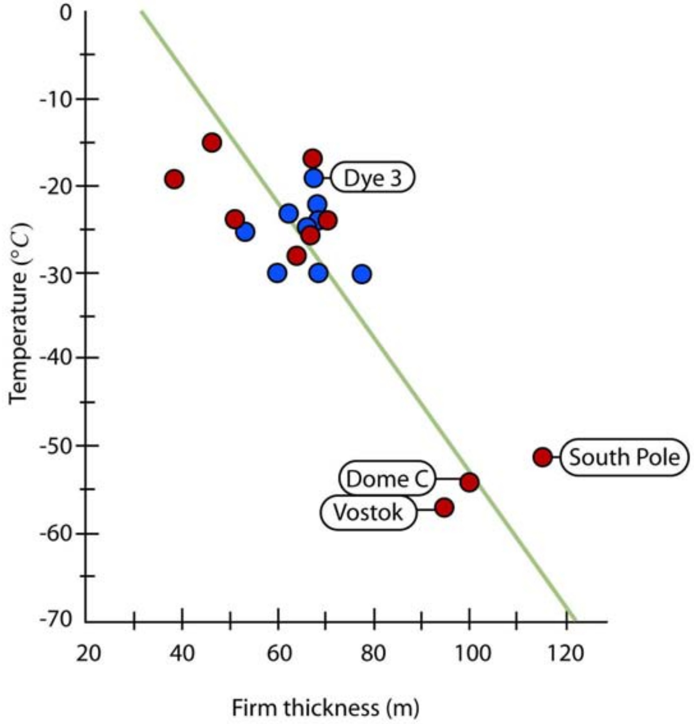
Snow -> Firn -> Ice transition



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 $Z = -1.30T + 31.5$.

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, ~80-120 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:
  - CO_2
  - O_2 ($^{18}O/^{16}O$ ratio, O_2/N_2)
  - CH_4
  - N_2O

Methods of extracting gases from ice

- Melting/freezing cycles, vacuum extraction:

  CH_4, N_2O, O_2, N_2

- Needle-crushing:

  CO_2

  (because CO_2 will be partially soluble in water and will react with ions, solid phase components, and contaminants)

CO_2 in the Vostok Ice Core

Image removed due to copyright restrictions.

Jouzel, Barnola et al. (1987) Nature 329:403 Nature 329:408.

CO_2 During the last 450 kyr from the Vostok, Antarctica Ice Core

Image removed due to copyright restrictions.

Petit et al (1999) in Kump (2002) *Nature*, 419:188-190.

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)

$\delta^{18}O$ of gaseous oxygen in ice cores ($\delta^{18}O_2$)

Dole Effect: $\delta^{18}O_2$ of atmosphere is +23.5‰ relative to SMOW.

a. Photosynthesis: $H_2O + CO_2 = O_2 + CH_2O$

$$\delta^{18}O_2(\text{photo}) = \delta^{18}O(\text{water}) + A$$

(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: $O_2 + CH_2O = H_2O + CO_2$

$\delta^{18}O_2(\text{resp}) = \delta^{18}O_2 + B$ (respiratory kinetic isotope fractionation)

c. At steady-state,

$$\delta^{18}O_2 - \delta^{18}O\ (\text{ocean}) = W + A - B$$

$\delta^{18}O$ of gaseous oxygen in ice cores ($\delta^{18}O_2$)

Parameters for estimating the turnover time of atmospheric O_2

Global atmospheric O_2 reservoir (GO_2R) = 3.7×10^{19} mol
Terrestrial net primary productivity (TNPP) = 5×10^{15} mol yr^{-1} (refs 21, 22)
Terrestrial gross primary productivity (TGPP) = 2 × TNPP (ref. 23) = 10×10^{15} mol yr^{-1}
Marine primary productivity (MPP) = 2×10^{15} (ref. 24)–10×10^{15} mol yr^{-1} (refs 24, 25)
Global primary productivity (GPP) = (TGPP + MPP) = 12×10^{15}–20×10^{15} mol yr^{-1}
Atmospheric O_2 turnover time = (GO_2R/GPP) = 3.1–1.9 kyr

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

Production term		Production	Reference
Gross production excluding photorespired O_2 (GPP)		14.1	*Farquhar et al.* [1993]
Gross production including photorespiration (14.1/0.69)		20.4	*Farquhar et al.* [1980]
Process	**Fraction of respiratory O_2 consumption**	**Isotope effect**	**Reference**
$\delta^{18}O$ of terrestrial photosynthetic O_2 w. r. t. SMOW		4.4 ‰	*Farquhar et al.* [1993]
Discrimination against O^{18} during respiration			
Dark respiration	59%	18.0	*Guy et al.* [1992, 1993]
Mehler reaction	10%	15.1	*Guy et al.* [1992]
Photorespiration	31%	21.2‰	*Guy et al.* [1992]
Flux weighted terrestrial respiratory isotope effect, excluding dark respiration		18.7‰	
Equilibrium enrichment in $\delta^{18}O$ of leaf water w. r. t. air		+0.7‰	*Benson and Krause* [1984]
Terrestrial respiratory isotope effect (= 18.7‰-0.7‰)		18.0‰	
Terrestrial Dole effect		22.4 ‰	

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}Kr should be enriched over ^{36}Ar by 1.28%, and ^{15}N is enriched over ^{14}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

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

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 $\delta^{18}O_2$, use $\delta^{15}N$ 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)

Image removed due to copyright restrictions.

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

Vostok CO_2, T (δD), CH_4, $\delta^{18}O_2$, June 65°N insolation

Image removed due to copyright restrictions.

Figure 3. Vostok time series and insolation. Nature, 3 June 1999, Vol 399.

CH_4 in the GRIP ice core

Image removed due to copyright restrictions.

Chappelez et al. (1993)

Image removed due to copyright restrictions.

CH_4 comparison between GRIP and Vostok

Brook et al. (1996)

Science 273:

GRIP/Byrd CH_4 comparison

Image removed due to copyright restrictions.

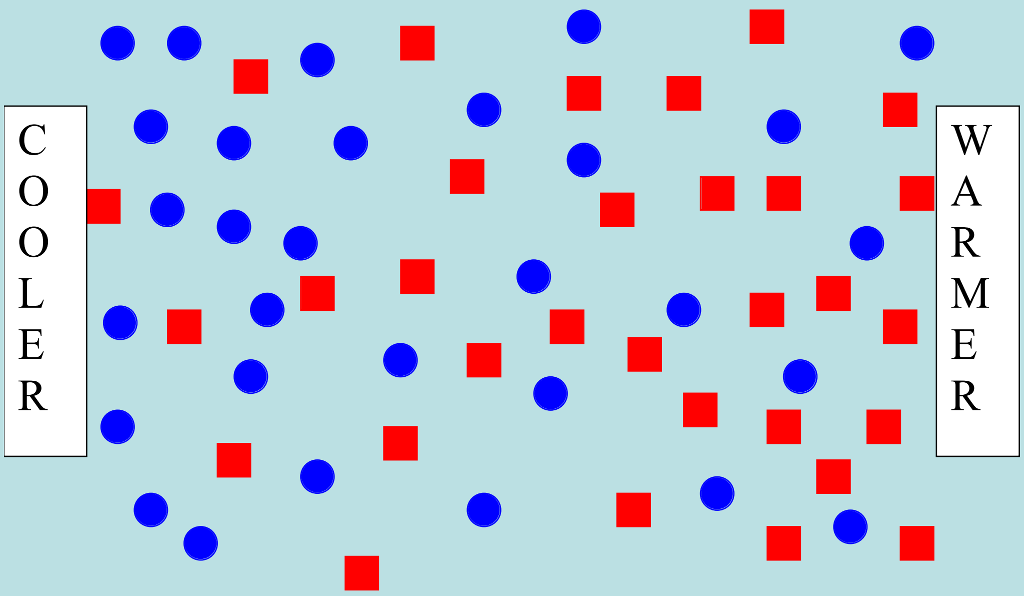
Blunier, T. and E. Brook (2001) Timing of millennial-scale climate change in Antarctica and Greenland during the last glacial period, Science 291:109-112. Figure 1.

"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: $\delta^{15}N = a_N D_N T$

and $\delta^{40}Ar = a_{Ar} D_{Ar} T$

where a_N and a_{Ar} are the thermal diffusion coefficients for N_2 and Ar respectively



GISP2
$\delta^{15}N$ record

Image removed due to copyright restrictions.

Nature 391 (8 January 1998). Figure 1.

Image removed due to copyright restrictions.

Comparison of $\delta^{15}N$ and $\delta^{40}Ar$

Implies 11±3 degree abrupt warming

Severinghaus et al. (2003) GCA 67:325

Borehole T modeled from $\delta^{18}O$ with changing $\delta^{18}O$-T slopes

Image removed due to copyright restrictions.

Science 270 (20 October 1995). Figures 2 and 3.

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)
Geophys. Res. Lett.
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.

CO_2 During the last 450 kyr from the Vostok, Antarctica Ice Core

Image removed due to copyright restrictions.

Petit et al (1999) in Kump (2002) *Nature*, 419:188-190.

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

Image removed due to copyright restrictions.

Vostok CO_2, T (δD), CH_4, $\delta^{18}O_2$, June 65°N insolation

Image removed due to copyright restrictions.

Figure 3. Vostok time series and insolation. Nature, 3 June 1999, Vol 399.

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.

Earth and Planetary Science Letters 204 (2002) 275–289

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 paleoatmospheric 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

(65°N)

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

Dome Fuji climate record on O_2/N_2 time scale

Image removed due to copyright restrictions.

Kawamura et al. (2007)

Nature 448:912-917

Reading (1)

* Barnola, J.M., Raynaud, D., Korotkevitch, Y.S. and Lorius, C., 1987. Vostok ice core: a 160,000-year record of atmospheric CO2. Nature, 329:408-414.

* Bender M. L. (2002) Orbital tuning chronology for the Vostok climate record supported by trapped gas composition. Earth Planet. Sci. Lett. 204, 275-289.

* Bender, M., T. Sowers, M.-L. Dickson, J. Orchardo, P. Grootes, P. Mayewski, and D.A. Meese, Climate correlations between Greenland and Antarctica during the past 100,000 years, Nature, 372, 663-666, 1994a.

Bender, M., T. Sowers, and L. Labeyrie, The Dole effect and its variations during the last 130,000 years as measured in the Vostok ice core, Glob. Biogeochem. Cyc., 8, 363-376, 1994b.

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

Boyle, E.A. (1997) Cool tropical temperatures shift the global d18O-T relationship: an explanation for the Ice Core δ18O / borehole thermometry conflict?, Geophys. Res. Lett. 24:273-276.

Craig H., Horibe Y. ,and Sowers T. (1988) Gravitational separation of gases and isotopes in polar ice caps. Science. 242, 1675-1678.

Cuffey, K.M., G.D. Clow, R.B. Alley, M. Stuiver, E.D. Waddington, and R.W. Saltus, Large Arctic Temperature Change at the Wisconsin-Holocene Glacial Transition, Science, 270, 455-458, 1995.

Dahl-Jensen, D., K. Mosegaard, et al. (1998). “Past temperatures directly from the Greenland ice sheet.” Science 282: 268-271.

Dansgaard W., Johnsen S. J., Clausen H. B. ,and C.C. Langway J. (1971) Climatic record revealed by the Camp Century Ice Core. In Late Cenozoic Ice Ages (ed. K. K. Turekian), Vol. pp. 37-56. Yale University Press.

Grootes P. M., Stuiver M., White J. W. C., Johnsen S., and Jouzel J. (1993) Comparison of oxygen isotope records from the GISP2 and GRIP Greenland ice cores. Nature 366, 552-554.

Hammer, C.U., Clausen, H.B. and Tauber, H., 1986. Ice-core dating of the Pleistocene/Holocene boundary applied to a calibration of the 14C time scale, Radiocarbon. 28:284-291.

Hammer C. U., Clausen H. B., Dansgaard W., Neftel A., Kristinsdottir P. ,and Johnson E. (1985) Continuous impurity analysis along the Dye 3 deep core. In Greenland Ice Core: Geophysics, Geochemistry, and the Environment (ed. C. C. LangwayJr., H. Oeschger and W. Dansgaard), Vol. 33, pp. 90-94. Am. Geophys. Union.

Herron M. M. , and Langway Jr. C. C. (1985) Chloride, nitrate, and sulfate in the Dye 3 and Camp Century, Greenland ice cores. In Greenland Ice Core: Geophysics, Geochemistry, and the Environment (ed. C. C. LangwayJr., H. Oeschger and W. Dansgaard), Vol. 33, pp. 77-84. Am. Geophys. Union.*Jouzel, J., Raisbeck, G., Benoist, J.P., Yiou, F., Lorius, C., Raynaud, D. and J.R. Petit, N.I. Barkov, Y.S. Kortkevitch, and V.M. Kotlyakov, 1989. A comparison of deep Antarctic ice cores and their implications for climate between 65,000 and 15,000 years ago. Quat. Res., 31:135-150.

Indermühle A., Stocker T. F., Joos F., Fischer H., Smith H. J., Wahlen M., Deck B., Mastroianni D., Tschumi J., Blunier T., Meyer R., and Stauffer B. (1999) Holocene carbon-cycle dynamics based on CO2 trapped in ice at Taylor Dome, Antarctica. Nature 398, 121-126.

* Jouzel J., Lorius C., Petit J. R., Genthon C., Barkov N. I., Kotlyakov V. M. ,and Petrov V. M. (1987) Vostok ice core: a continuous isotope temperature record over the last climatic cycle (160,000 years). Nature. 329, 403-408.

* Jouzel J., Barkov N. I., Barnola J. M., Bender M., Chappellaz J., Genthon C., Kotlyakov V. M., Lipenkov V., Lorius C., Petit J. R., Raynaud D., Raisbeck G., Ritz C., Sowers T., Stievenard M., Yiou F. ,and Yiou P. (1993) Extending the Vostok ice-core record of paleoclimate to the penultimate glacial period. Nature. 364, 407-412.

* Kawamura K., Parrenin F., Lisiecki L., Uemura R., Vimeux F., Severinghaus J. P., Hutterli M. A., Nakazawa T., Aoki S., Jouzel J., Raymo M. E., Matsumoto K., Nakata H., Motoyama H., Fujita S., Goto-Azuma K., Fujii Y., and Watanabe O. (2007) Northern Hemisphere forcing of climatic cycles in Antarctica over the past 360,000 years Nature 448, 912-917.

Reading (2)

Landais, A., J. Jouzel, V. Masson-Delmotte, N. Caillona (2005) Large temperature variations over rapid climatic events in Greenland: a method based on air isotopic measurements, C.R. Geoscience 337:947–956.

Legrand M., Feniet-Saigne C., Saltzman E. S., Germain C., Barkov N. I. ,and Petrov V. N. (1991) Ice-core record of oceanic emissions of dimethylsulphide during the last climate cycle. Nature. 350, 144-146.

Mayewski, P.A., L.D. Meeker, M.S. Twickler, S.I. Whitlow, Q. Yang, W.B. Lyons, and M. Prentice (1997) Major features and forcing of high-latitude northern hemisphere atmospheric circulation using a 110,000-year-long glaciochemical series, J. Geophys. Res. 102:26345-26366.

Mulvaney R., Wolff E. W. ,and Oates K. (1988) Sulfuric acid at grain boundaries in Antarctic ice. Nature. 331, 247-249.

* Neftel, A., Oeschger, H., Staffelbach, T. and Stauffer, B., 1988. CO2 record in the Byrd ice core 50,000-5,000 years BP. Nature, 331:609-611.

Neftel, A., Moor, E., Oeschger, H. and Stauffer, B., 1985. Evidence from polar ice cores for the increase in atmospheric CO2 in the past two centuries. Nature, 315:45-47.

Schwander J. ,and Stauffer B. (1984) Age difference between polar ice and the air trapped in its bubbles. Nature. 311, 45-47.

Severinghaus J. P., Sowers T., Brook E. J., Alley R. B., and Bender M. L. (1998) Timing of abrupt climate change at the end of the Younger Dryas interval from thermally fractionated gases in polar ice. Nature 391, 141-146.

Shoji H. ,and Langway Jr. C. C. (1985) Mechanical properties of fresh ice core from Dye 3, Greenland. In Greenland Ice Core: Geophysics, Geochemistry, and the Environment (ed. C. C. LangwayJr., H. Oeschger and W. Dansgaard), Vol. 33, pp. 39-48. Am. Geophys. Union.

Shuman, C. A., R. B. Alley, et al. (1995). “Temperature and accumulation at the Greenland Summit: Comparison of high-resolution isotope profiles and satellite passive microwave brightness temperature trends.” J. Geophys. Res. 100: 9165-9177.

Ram M. ,and Gayley R. I. (1991) Long-range transport of volcanic ash to the Greenland ice sheet. Nature. 349, 401-404.

* Sowers, T., Bender M., Labeyrie L., Martinson D., Jouzel J., Raynaud D., Pichon J. J. ,and Korotkevich Y. S. (1993) A 135,000-year Vostok-Specmap common temporal framework. Paleoceanogr. 8, 699-736.

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

Zielinksi G. A., Mayewski P. A., Meeker L. D., Whitlow W., and Twickler M. S. (1996) Potential atmospheric impact of the Toba mega-eruption ~71,000 years ago. Geophys. Res. Lett. 23, 837-840.

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.