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12.740 Paleoceanography
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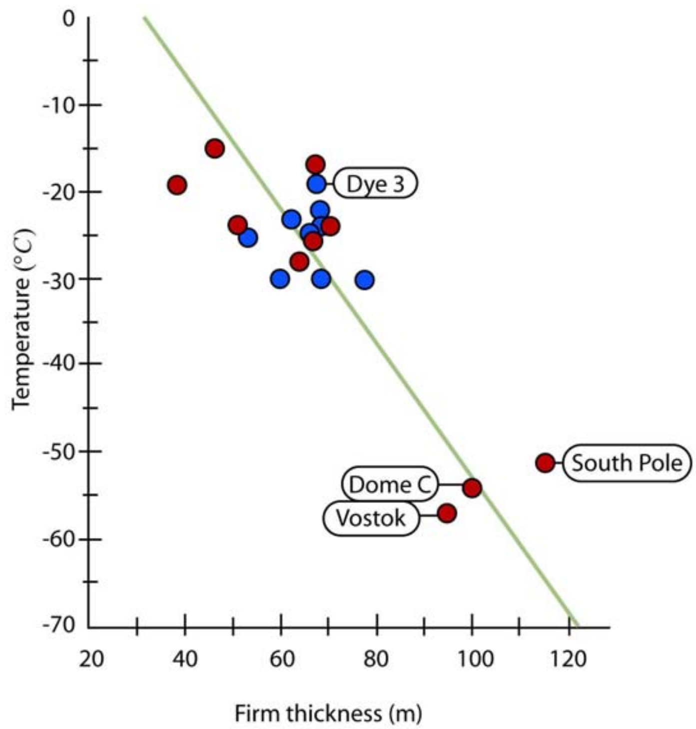
III. Atmospheric gas record in ice cores

A. Methodological issues; firn/ice transition; age of air; gravitational fractionation; bubble compression and relaxation; gas extraction; reactions with ice and/or water or solids; impurities.

1. Firn/ice transition: depth correlated with temperature due to effect of T on pressure sintering:



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)

2. "Gravitational equilibrium for isotope and perfect gas ratios is described by the Gibbs equation:" (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%, ^{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

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

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 seen in the atmosphere](Dalton, 1826; Gibbs, 1928).

3. Thermal diffusion: 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: $\delta^{15}N = \alpha_N \Delta T$ and $\delta^{40}Ar = \alpha_{Ar} \Delta T$ where α_N and α_{Ar} are the thermal diffusion coefficients for N_2 and Ar respectively.

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Please see:
Figure 2 in Severinghaus J. P., T. Sowers, E.J. Brook, R. B. Alley, and M. L. Bender. "Timing of abrupt climate change at the end of the Younger Dryas interval from thermally fractionated gases in polar ice." *Nature* 391 (1998): 141-146.

4. Methods of gas extraction: melting/freezing cycles for CO_2, N_2O; needle-crushing for CO_2.

B. CO_2

1. Vostok ice core CO_2:

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

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Please see:
Figure 3 in Vostok time series and insolation. *Nature* 399 (June 3, 1999).

2. Byrd ice core CO2

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Source: Staffelbach et al. (1991).

4. Taylor Dome Holocene CO_2 record

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Source: Indermühle et al. (1999).

C. $\delta^{18}O_2$

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

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

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

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

2. Gross Productivity and atmospheric oxygen residence time

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

source: Bender et al. (1985)

3. Terrestrial O_2 and $\delta^{18}O_2$ mass balance

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 ‰	

source: Bender et al. (1994)

4. Marine O_2 and $\delta^{18}O_2$ mass balance

BENDER ET AL.: DOLE EFFECT IN THE VOSTOK ICE CORE

Table 1b. Marine Mass Balance of O_2 and $\delta^{18}O$ of O_2

Production term	Production ($x10^{15}$ moles/yr)	Reference
Marine gross production (=4 x seasonal net production)	12	*Keeling and Shertz* [1992]
Marine gross production - recycling within the ocean	10.6	
Process	**Isotope effect**	**Reference**
$\delta^{18}O$ of O_2 produced by marine photosynthesis		
$\delta^{18}O$ of marine photosynthetic O_2	0 ‰	
Discrimination against ^{18}O during marine respiration		
Average marine ε_R (applies to euphotic respiration)	20 ‰	*Kiddon et al.* [1993]
Effective ε_R for respiration below the euphotic zone	12 ‰	*Bender* [1990]
Equilibr. enrichment in $\delta^{18}O$ of O_2 in water w.r.t. air	0.7 ‰	*Benson and Krause* [1984]
Effective ε_R for marine respiration*	18.9 ‰	
Marine Dole effect	18.9 ‰	

* =0.95x(20 ‰-0.7 ‰)+0.05x12‰

source: Bender et al. (1994)

5. Byrd ice core

6. Vostok ice core

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Source: Sowers et al. (1993).

7. GISP2 ice core

D. CH_4

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Source: Chappelez et al. (1993).

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Please see:
Brook, et al. *Science* 273 (August 23, 1996): 1088.

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

E. O_2/N_2: relation to local insolation, use for time scale development.

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Please see:
Bender. *EPSL* 204 (2002): 275.

F. N_2O

IV. Other tracers in ice cores: dust (note Sr+Nd isotope work), ^{10}Be, volcanic ash, chemicals, crystal size in ice cores; atmospheric pressure of bubbles

A. Sea-salt, volcanic acid, and dust in Greenland ice cores

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Source: Hammer et al. (1985).

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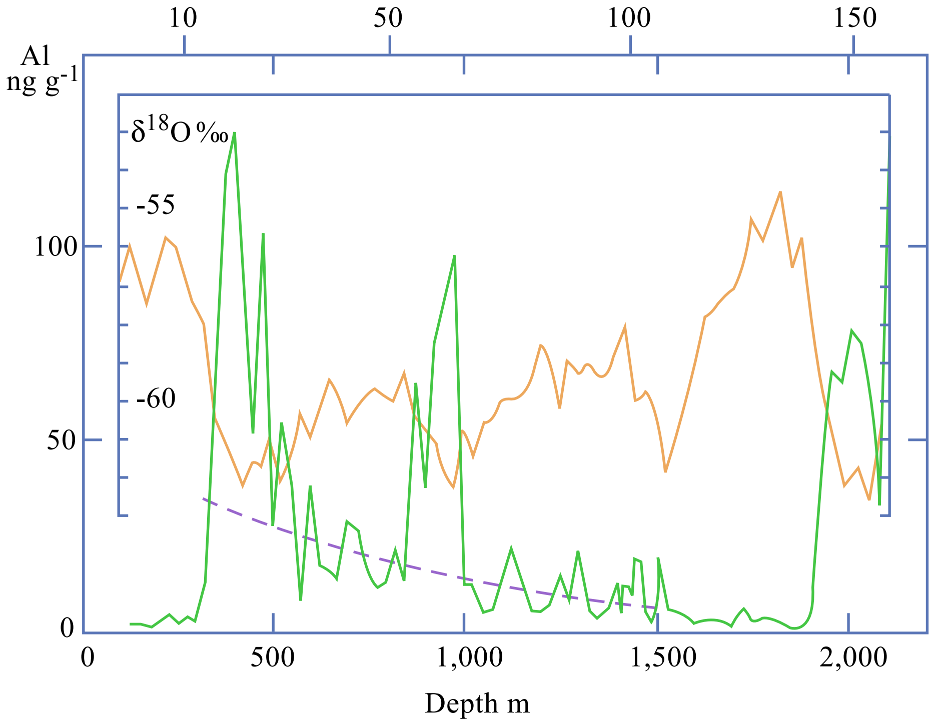
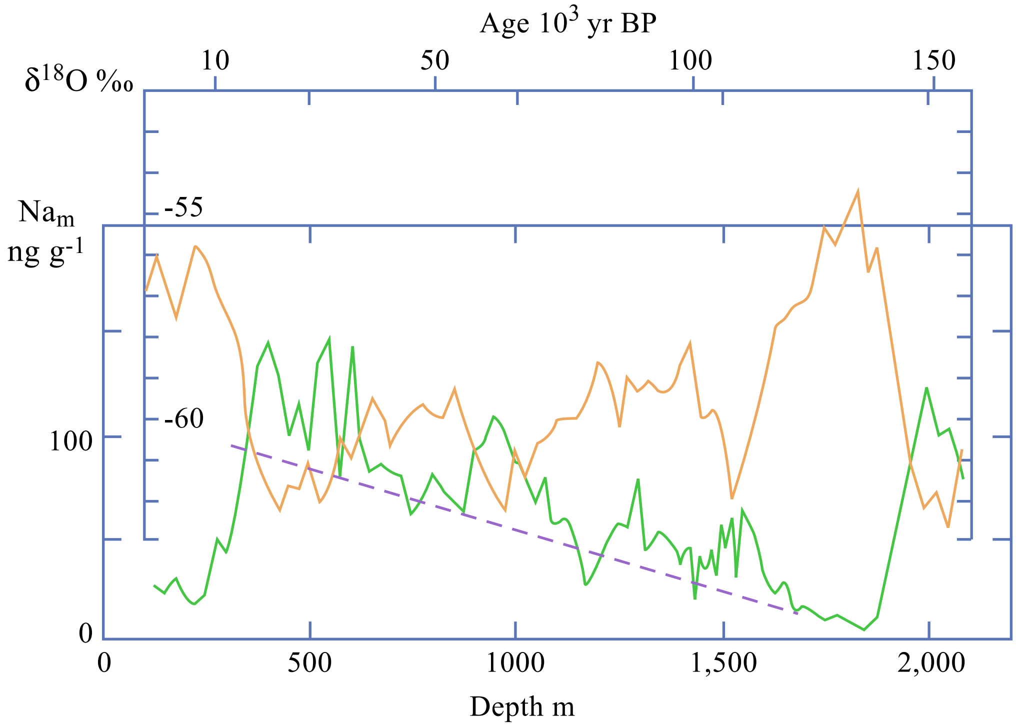
B. Seasalt and dust in the Vostok ice core



Al concentration as a function of real depth (green line). The climatic reference is given by $\delta^{18}O$ (yellow line). The lower dashed line represents the estimated background.

Figure by MIT OpenCourseWare. Adapted from de Angelis et al. (1987).



As previous figure, with Na_m instead of Al.

Figure by MIT OpenCourseWare. Adapted from de Angelis et al. (1987).

B. ^{10}Be

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C. Calcium in the GISP2 ice core: relation to "1500 year" climate cycle and Dansgaard/Oeschger events

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Source: Mayewski et al. (1997).

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Source: Mayewski et al. (1997).

E. Methanesulfonic acid (dimethyl sulfide product)

1. Marine organisms produce DMSP (dimethylsulfoniopropionate:

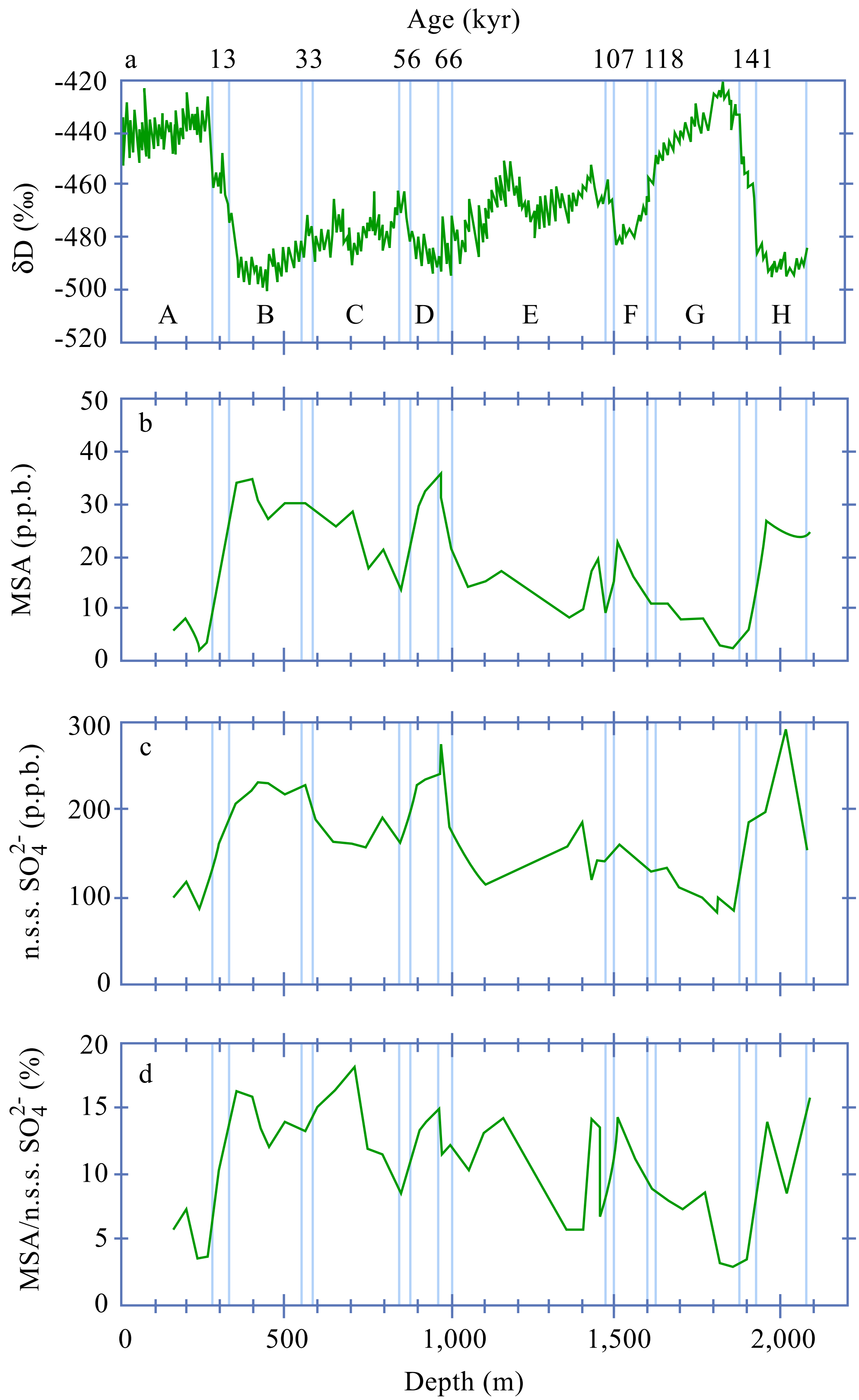
CH_3
\
$S^+-CH_2-CH_2-COO^-$
/
CH_3

this is converted to DMS [$(CH_3)_2S$] when they are munched up.

2. DMS is volatile and goes into the atmosphere

3. DMS is oxidized in the atmosphere to two byproducts with a "branch ratio": sulfuric acid (H_2SO_4) and methanesulfonic acid (MSA: CH_3SO_3H). Cycle is complex with many intermediates; branch ratio appears to depend mainly on temperature (low MSA:nss$SO_4^=$ at warmer temperatures)

4. The products are transported to the ice and recorded there as non-sea-salt sulfate (nss $SO_4^=$) and MSA.



Depth profiles of a, δD, b, MSA, c, non-seasalt sulphate and d, the ratio of MSA to non-seasalt sulphate in the Vostok ice core. Upper and lower stage boundaries are marked by vertical lines. (δD is deuterium isotope profile)

Figure by MIT OpenCourseWare. based on Legrand et al., 1991 source: Legrand et al. (1991)

F. Chemicals: other major ions and trace elements

d. GRIP borehole Monte-Carlo simulations Dahl-Jensen et al. (1998)

e. How to resolve this discrepancy?

i. Seasonality of precipitation (less snow in LGM winter)?

ii. Shifted O18-T relationship due to cool tropics?

H. Other indicators

1. Nd-Sr isotopes: argues that Greenland LGM dust came from Asia

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Source: Grousset, Biscaye et al.

V. The last 1000 years: Little Ice Age and Medieval Warm Period

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Please see:
Figure 3 in Dansgaard W., S. J. Johnsen, H. B. Clausen, and C.C. Langway J. "Climatic record revealed by the Camp Century Ice Core." In *Late Cenozoic Ice Ages*. Edited by K. K. Turekian. Yale University Press, 1971, pp. 37-56.

VI. Rapid climate change in ice cores: Younger Dryas, interstadials, etc.

- A. Younger Dryas and Bolling-Allerod
- B. Interstadials
- C. Synchroneity of rapid climate events

VIII. The ice core time scale: relative and absolute stratigraphy, accuracy and precision

- A. The players
  1. layer-counting (hoar frost layers, dust layers, O18 cycles, chemical signals
  2. $\delta^{18}O_2$
  3. CH_4
  4. ^{10}Be
  5. correlations to other climate records
- B. The state of the art, 1998
  1. Absolute chronology
     - a. Ice core layer counting at GISP2 appears to be the winner for precision and accuracy for the past ~40,000 years. It is consistent with $\delta^{18}O_2$ but offers more precision. Beyond that period, it becomes increasingly less objective and inaccurate.
       - i. a possible competitor in this interval is the calibrated radiocarbon record linked to key climate events. The accuracy ultimately should be the same or better, but problems in sorting out atmospheric D14C variability and phase leads and lags make it more problematical.
     - b. $\delta^{18}O_2$ links us to the marine chronology prior to that time (the marine chronology being constrained by coral 230Th/U dates correlated to foraminiferal d18O and "orbital tuning"
  2. Relative chronologies
     - a. $\delta^{18}O_2$ links ice cores between the two hemisphere with a relative precision of a few hundred to several thousands of years.
     - b. detailed CH_4 records can correlate ice cores between the hemisperes to several decades to several hundredds of years, given sufficient temporal resolution of the core and sampling.

c. ^{10}Be provides one or two absolute spikes that can test the accuracy the chronology provided by the above methods, and perhaps allow for a quicker homing in. If, as now seems very likely, the ^{10}Be spikes are linked to fluctuations in the earth's magnetic field, it may also allow a link to chronologies in marine sediments and continental materials.

d. correlation to other highly resolved climate records (e.g. ice $\delta^{18}O$ compared to gray scale of Cariaco Trench varved sediments, bioturbation index of Santa Barbara Nasin sediments) is useful, but carries inherent uncertainty regarding the phase relationships (some events may lead, others may lag, even though linked to the same system. For example: maximum summer warmth lags maximum incoming radiation by several months...)

e. Volcanic ash: Ram and Gayley (1991) observed a volcanic ash shard layer 1950 m depth in the Dye 3 ice core which they suggested was the same as a marine ash layer observed by Ruddiman and Glover (1972) - hence linking the marine and ice core chronologies at ~57 kyrBP.

f. Acidity links Indonesian marine record to central Greenland ice core? (can we be sure that this volcanic eruption was in fact Toba and not some other volcano?)

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Please see:
Figure 1 in Zielinksi G. A., P. A. Mayewski, L. D. Meeker, W. Whitlow, and M. S. Twickler. "Potential atmospheric impact of the Toba mega-eruption ~71,000 years ago." *Geophys Res Lett* 23. (1996): 837-840.

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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.