

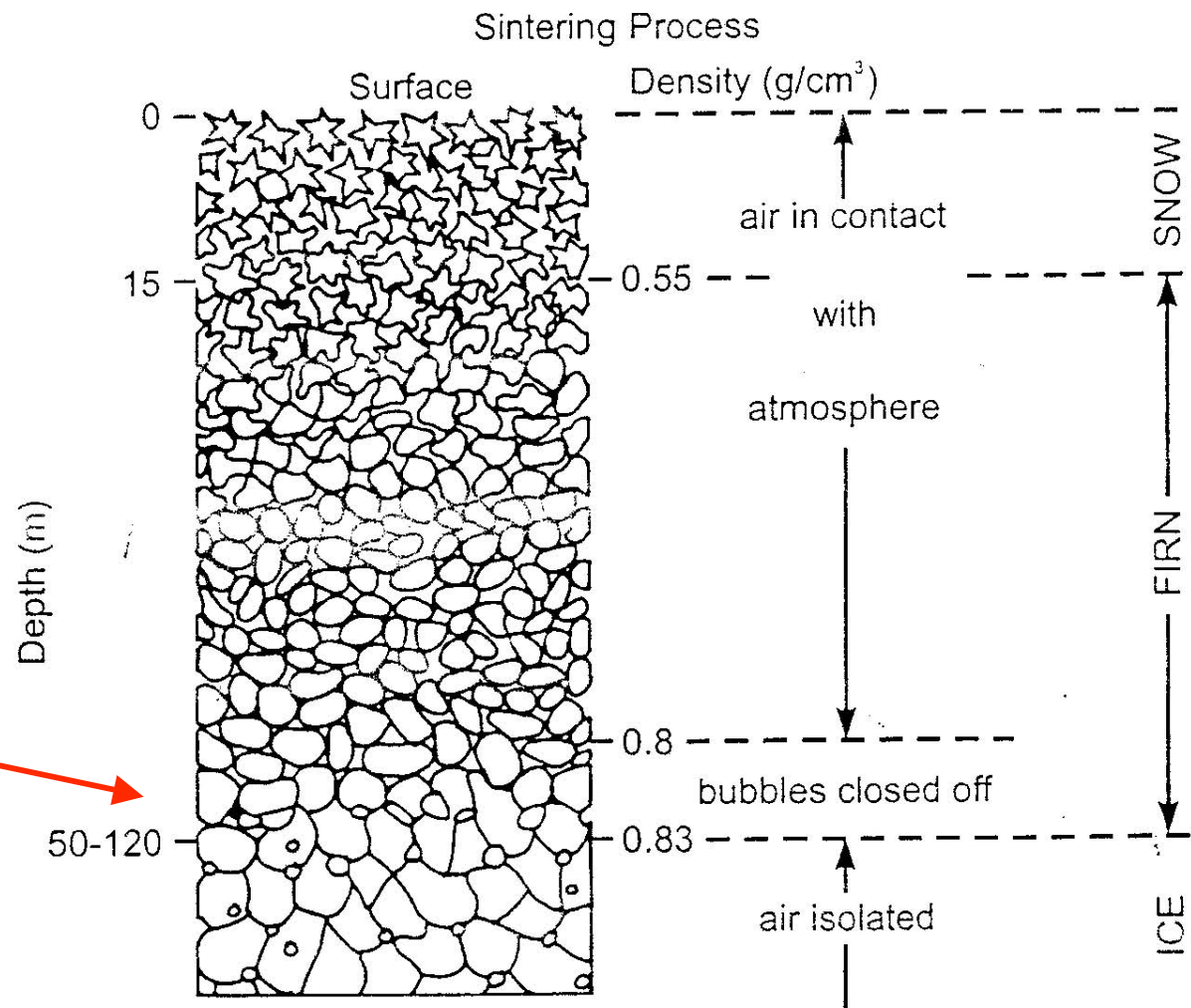
# Records of gases and impurities in ice cores

**Greenhouse gases**  
**Atmospheric dust**  
**Major ions, organic acids, heavy metals**  
**Volcanic deposits**

**Lecture # 31**

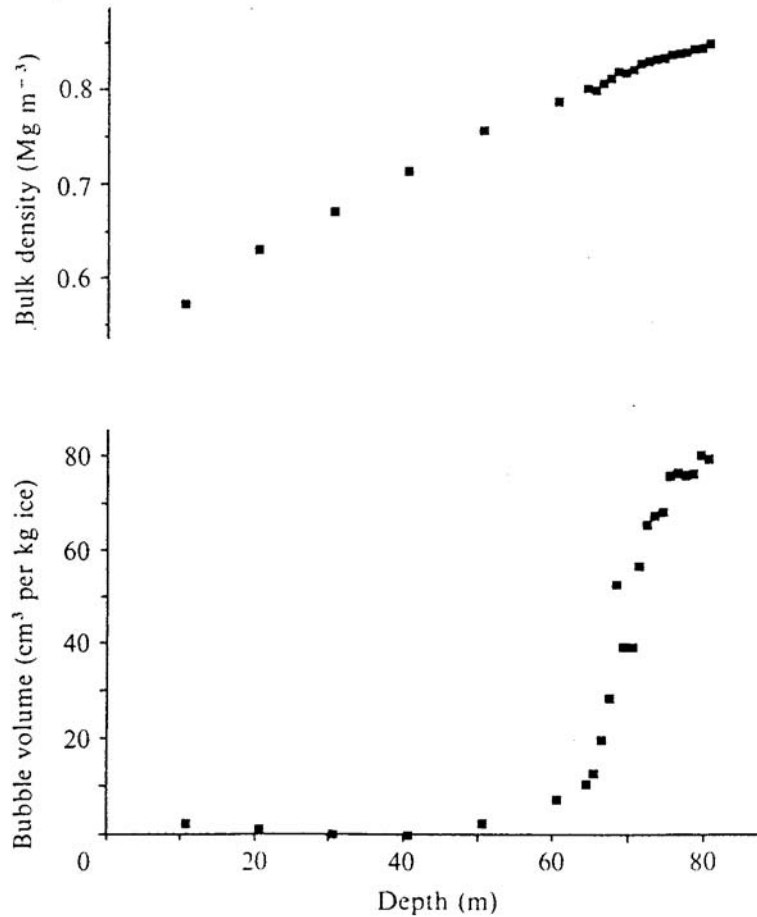
**Thorsteinn Thorsteinsson**

**Age difference between air in bubbles and enclosing ice up to 2500 yr in Antarctica at present.**



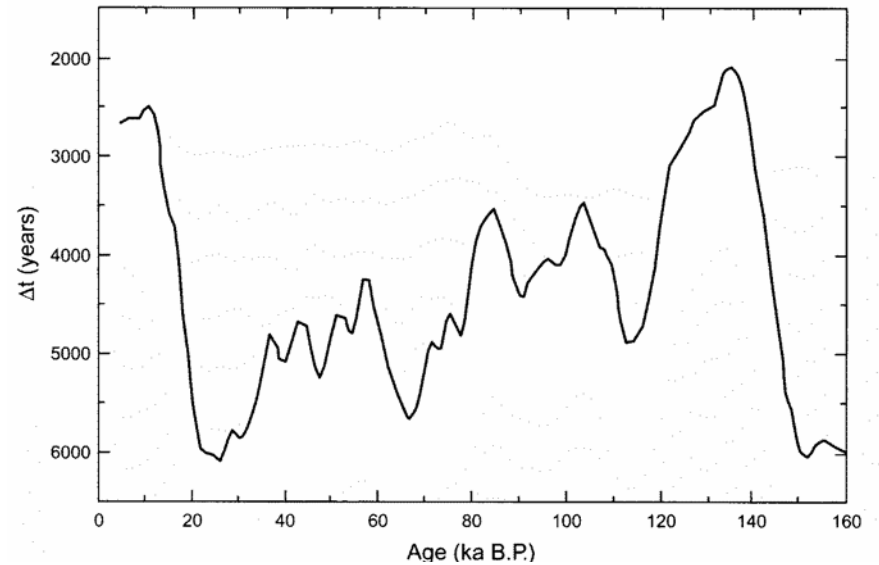
**Trapping of air in glacier ice (Greenland/Antarctica)**

**Depth of bubble close-off depends on accumulation rate and temperature.**



**Density and bubble volume vs. depth at Siple Station, Antarctica**

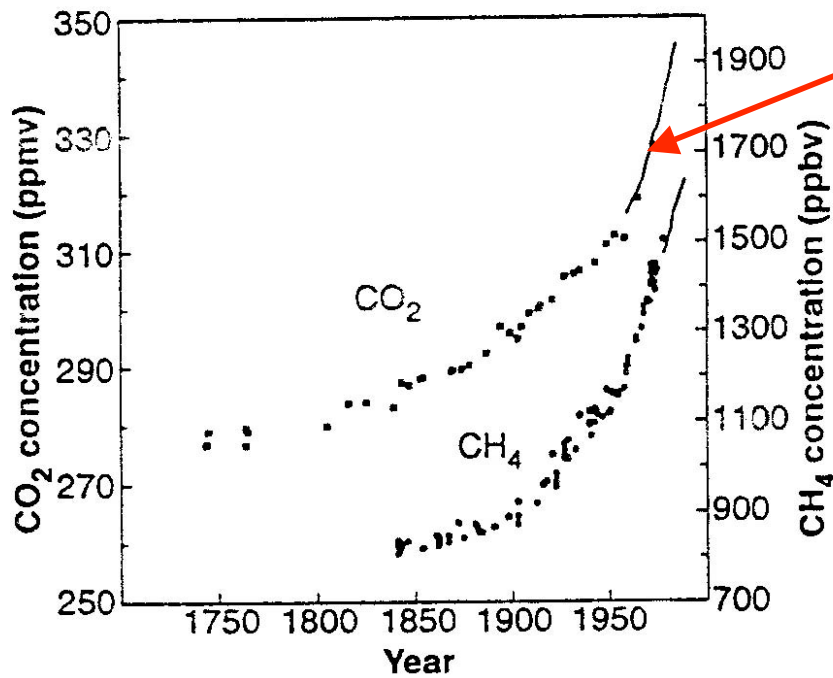
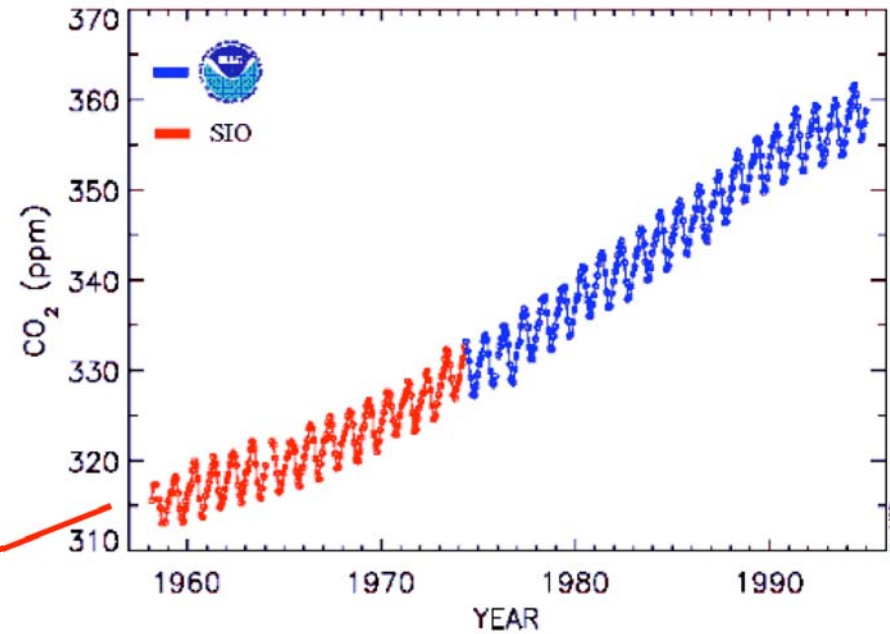
**Not all bubbles close at the same time.**



**Vostok: 0-160 ka BP**

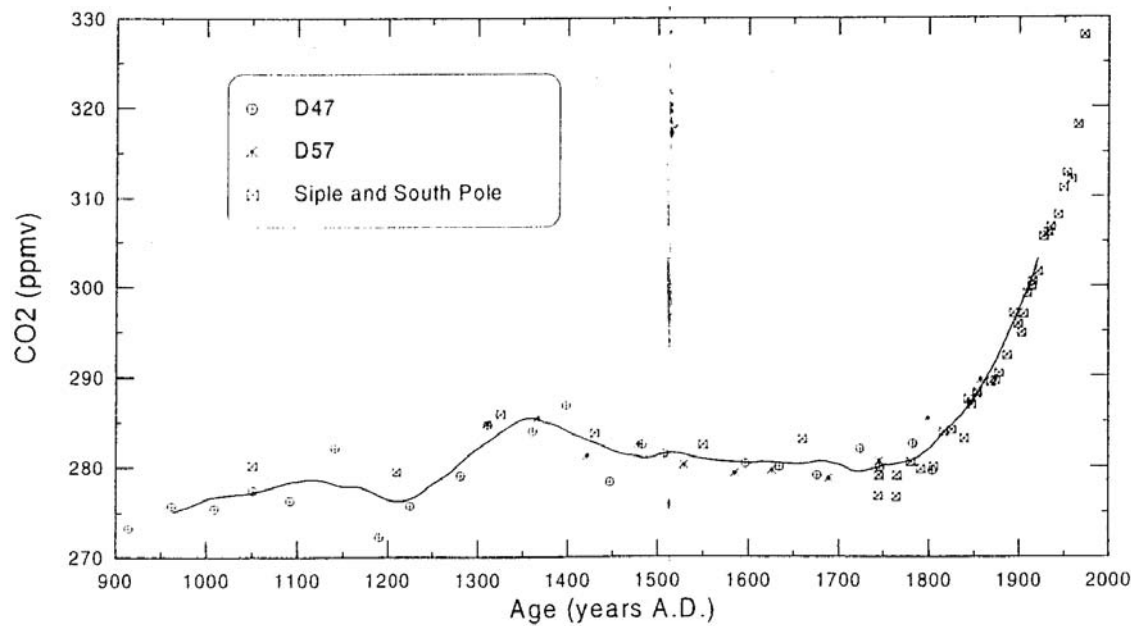
**Modelled age difference between ice and air in bubbles.**

Mauna Loa Monthly Mean Carbon Dioxide

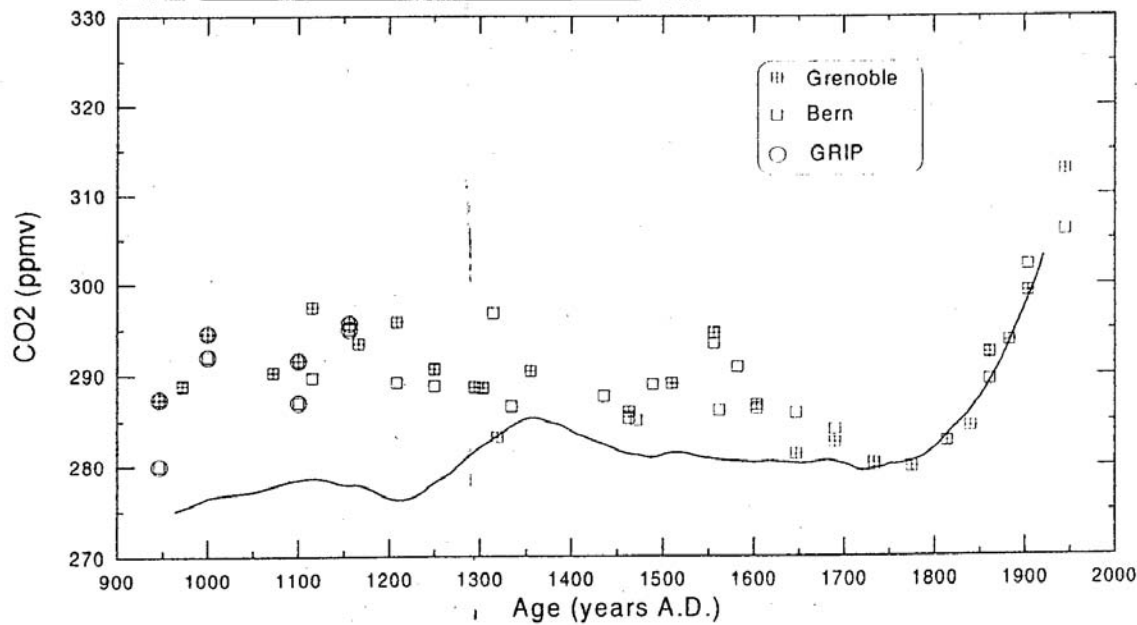


Reconstruction of the CO<sub>2</sub> and CH<sub>4</sub> increases since preindustrial time (Siple and DE08 shallow ice cores).

Good agreement with Mauna Loa curve!

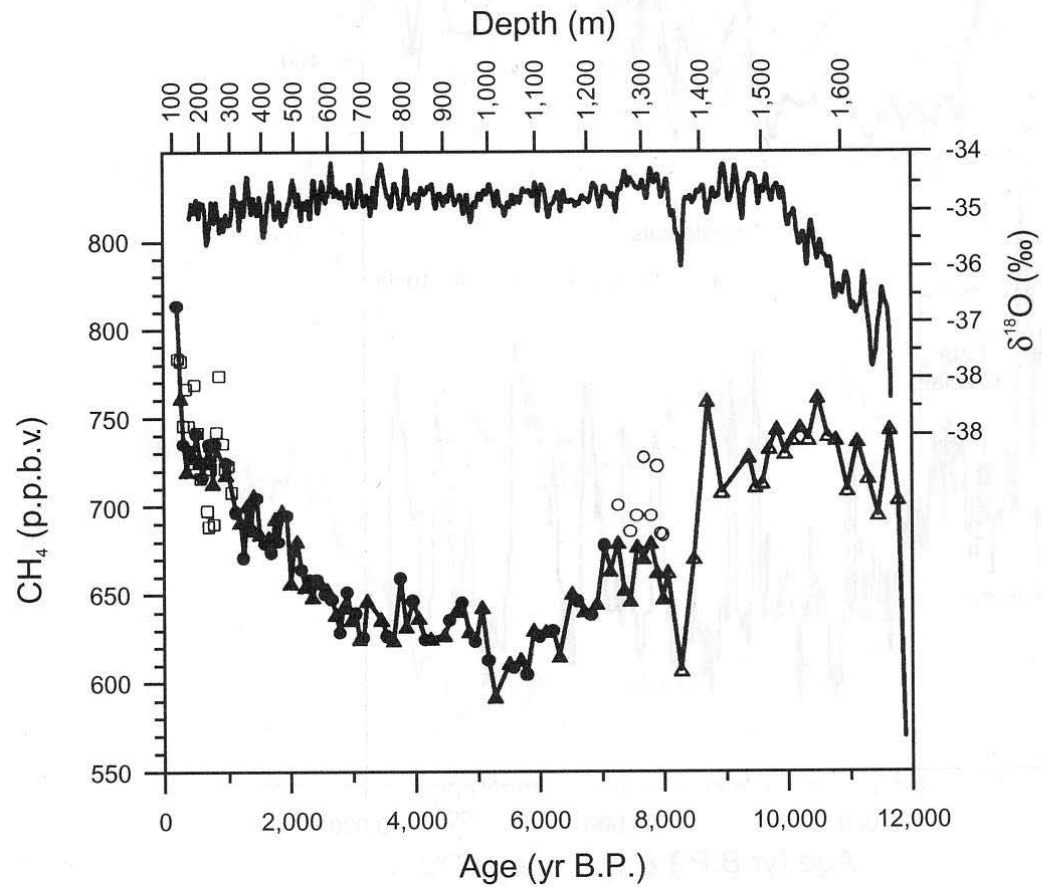


**CO<sub>2</sub> over last 1000 years from Antarctic cores.**

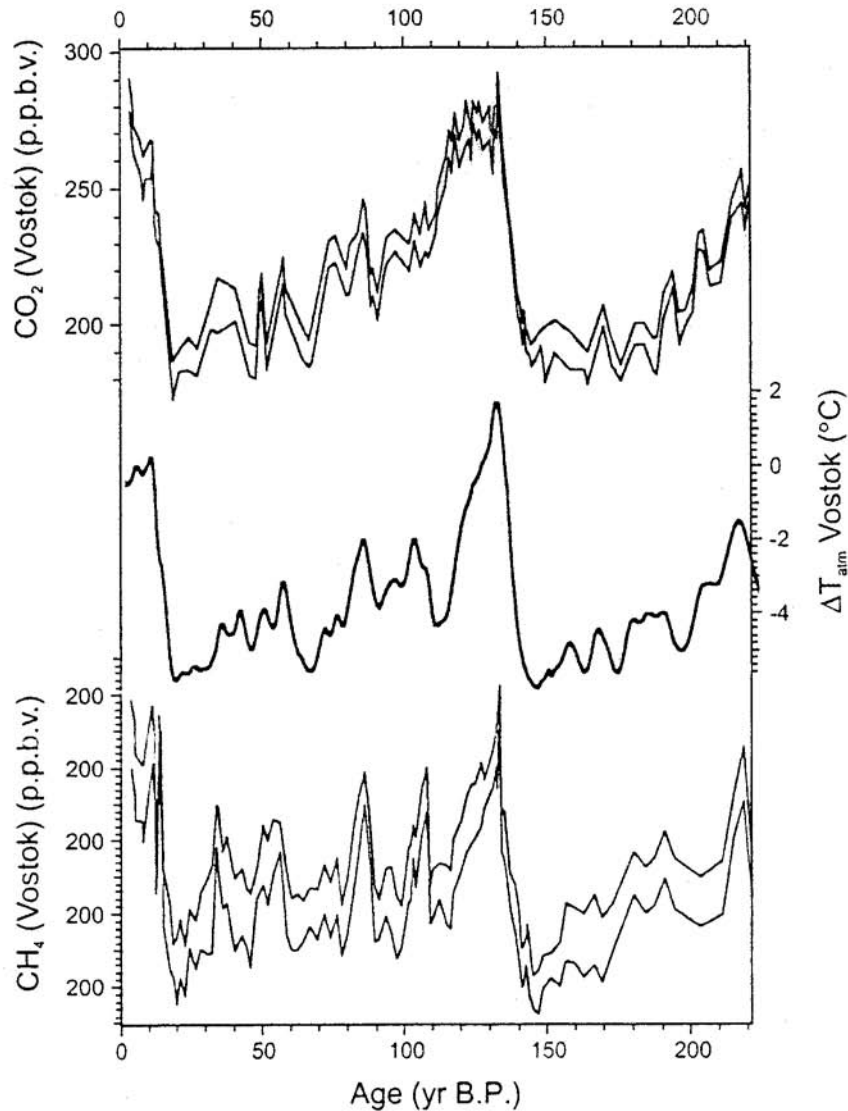


**CO<sub>2</sub> over last 1000 years from Greenland cores, compared with Antarctic curve.**

***In situ* production of CO<sub>2</sub> in Greenland ice!**



**FIGURE 5.33** Methane levels in the GRIP ice core (Summit, Greenland) during the last 12,000 yr. A pronounced drop in  $\delta^{18}\text{O}$  at  $\sim 8250$  (calendar years) B.P. corresponds to a sudden reduction in  $\text{CH}_4$ . The decline in  $\text{CH}_4$  to  $\sim 5200$  B.P. is related to a reduction in tropical wetlands. The subsequent  $\text{CH}_4$  increase is ascribed to high-latitude peatland expansion (Blunier *et al.*, 1995).

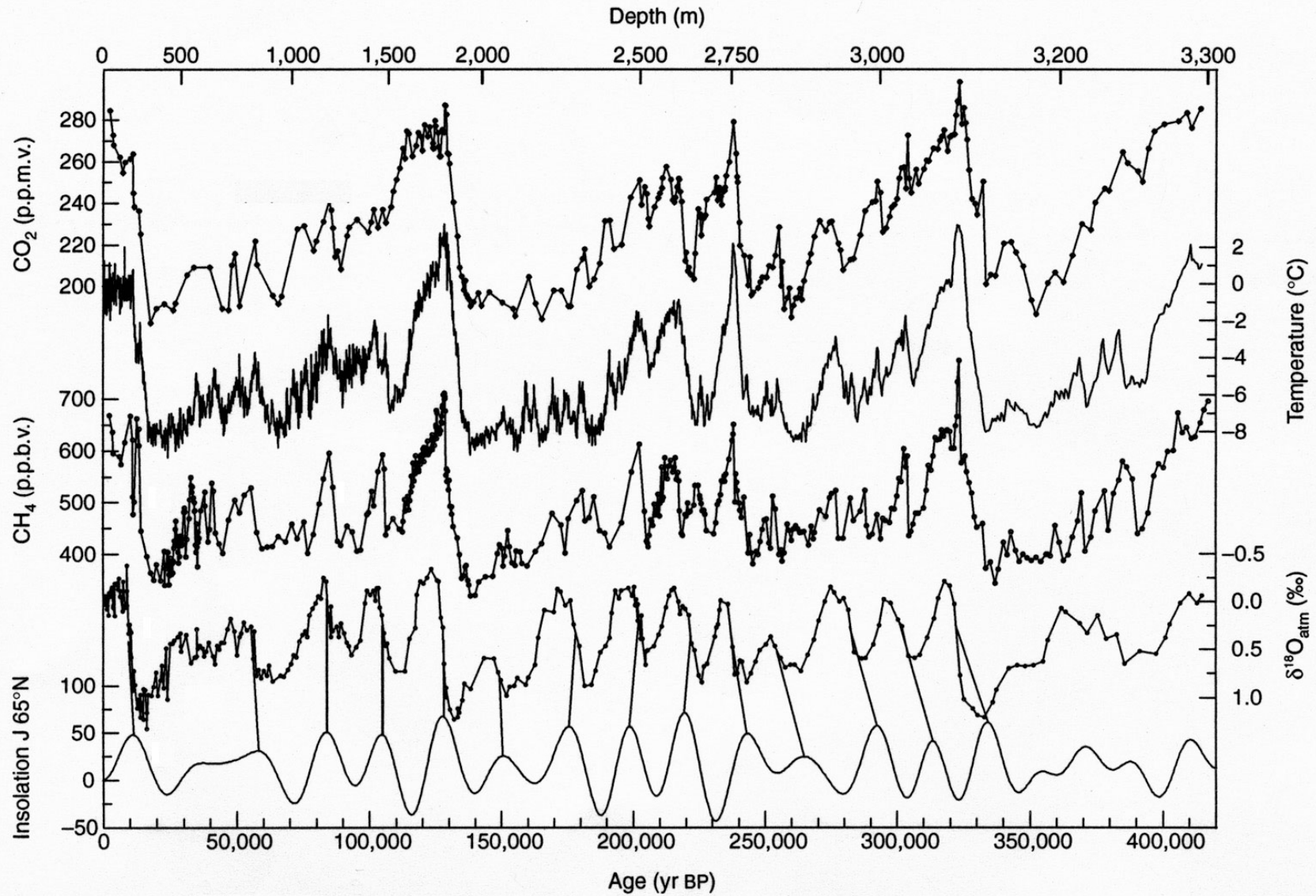


Vostok 0-220 kyr BP

Glacial-interglacial  
temperature variation ~7 °C

**FIGURE 5.32** The Vostok record of changes in the concentration of carbon dioxide (top) and methane (bottom) with temperature *above the surface inversion* expressed as differences from present. Temperatures are estimated from changes in  $\delta D$ . The difference in age between the air and the enclosing ice has been taken into consideration, as have changes in this value, with variations in accumulation rate over time (Jouzel *et al.*, 1993b).

From R. Bradley, *Paleoclimatology* (p. 170)



**The 420,000 year record from Vostok.**

## Chemistry of ice cores

- Soluble impurities (major ions)
- Heavy metals
- Organic acids

### A few examples:

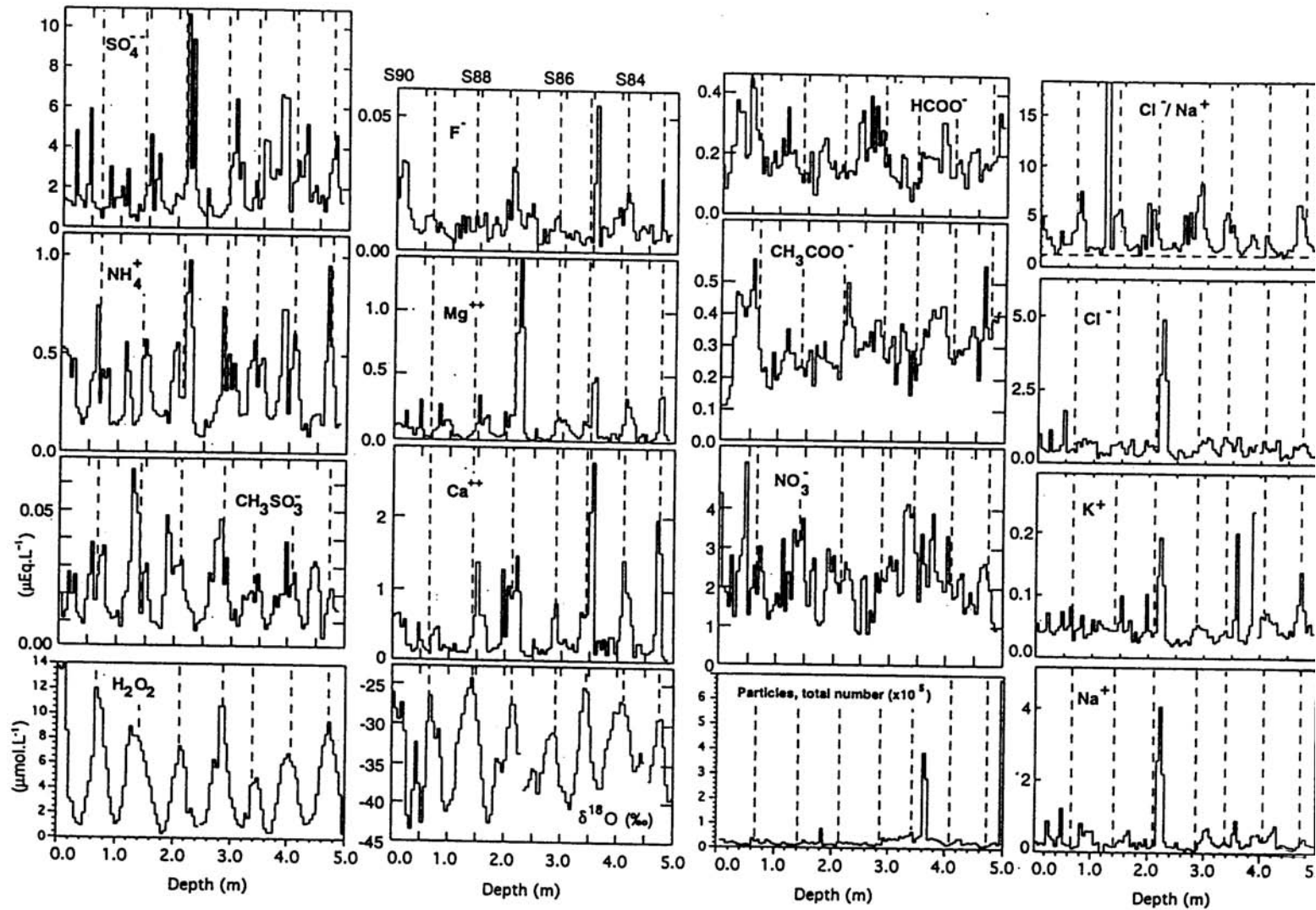
**Sulphate ( $\text{SO}_4^{2-}$ )** – formed by oxidation of  $\text{SO}_2$  in the atmosphere.  
Sources of  $\text{SO}_2$ : Volcanic eruptions, forest fires, fossil fuel combustion.  
Also marine and continental sources.

**Chloride ( $\text{Cl}^-$ )** – marine aerosol, also contributions from volcanism and pollution

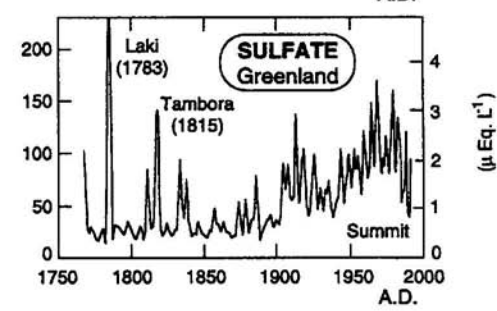
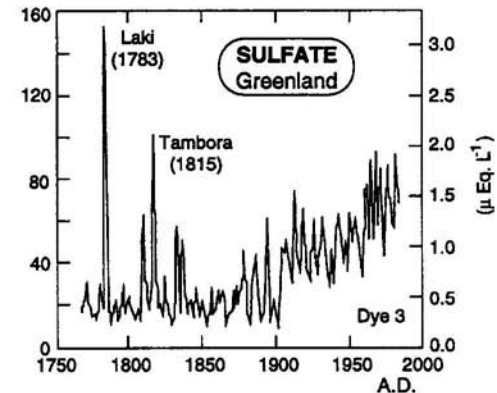
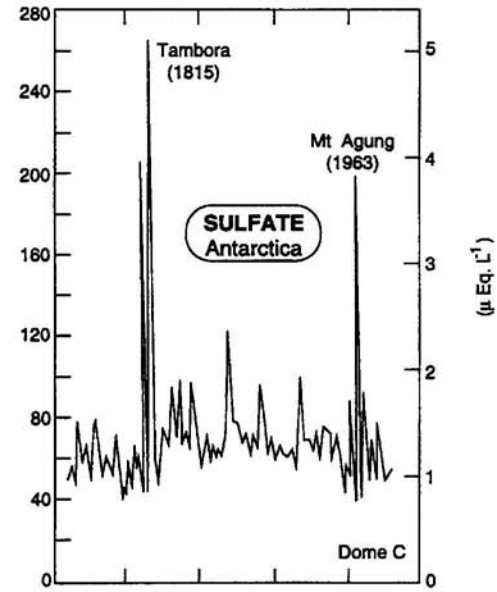
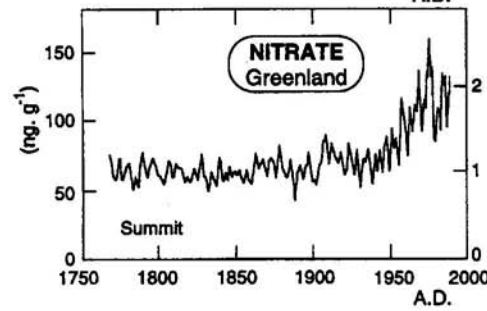
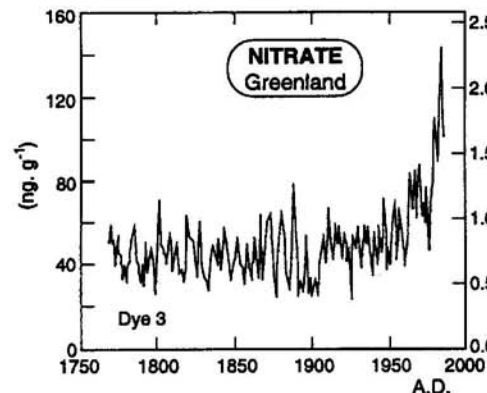
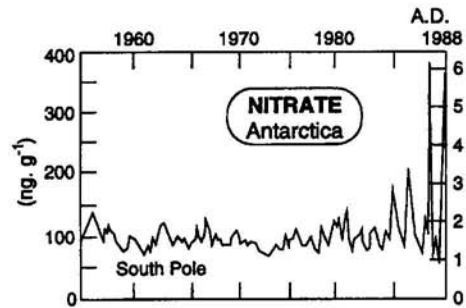
**Nitrate ( $\text{NO}_3^-$ )** – formed by oxidation of  $\text{NO}$  and  $\text{NO}_2$ .  
Sources of  $\text{NO}$  and  $\text{NO}_2$ : Reactions during lightning and due to cosmic radiation, organic processes in soil, burning of fossil fuels.

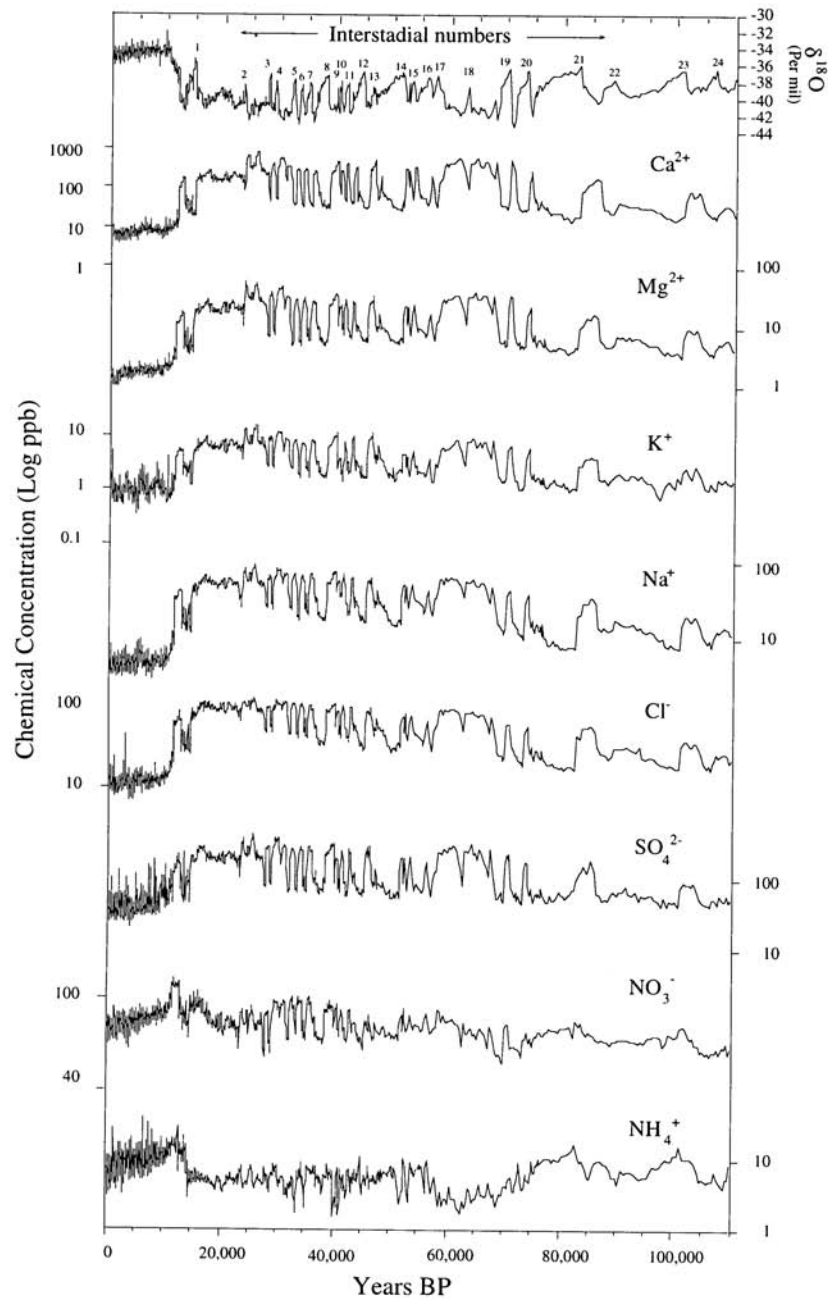
**Calcium ( $\text{Ca}^{2+}$ )** – Mainly of continental origin, transported with dust.

# Seasonal variation in impurity concentrations in a 5 m snowpit at Summit, Greenland.



# Anthropogenic increase in nitrate and sulphate seen in Greenland data.





**GISP2 core, Greenland:**

**Elevated concentrations of marine and continental impurities during the last glacial period.**

**Dansgaard-Oeschger cycles seen in most impurity records.**

Atmospheric dust, originating mainly in the Gobi desert, central Asia, is transported to Greenland.

Dust particle size:  $< 0.1 - 10 \mu\text{m}$

Typical concentrations:

Holocene: **0.1 mg dust /kg ice**

Wisconsin: **1-10 mg /kg**

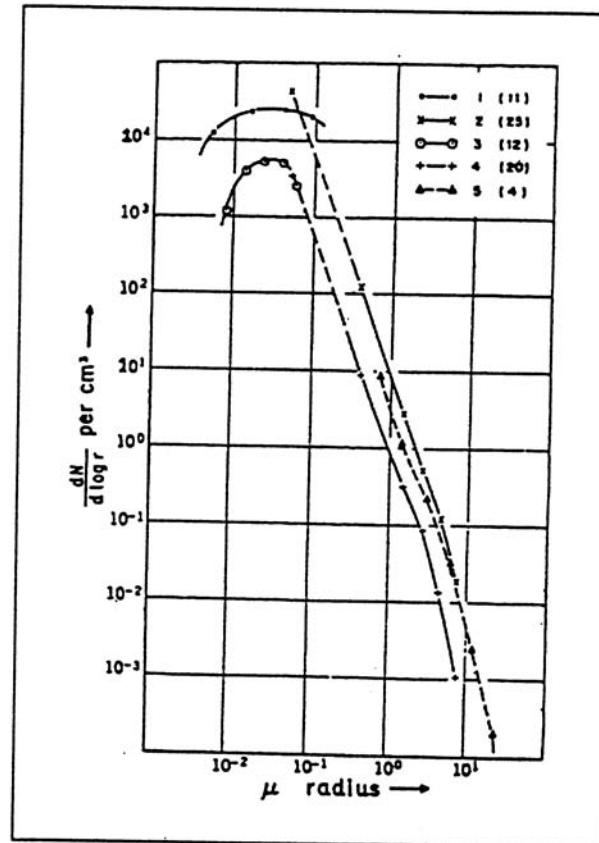
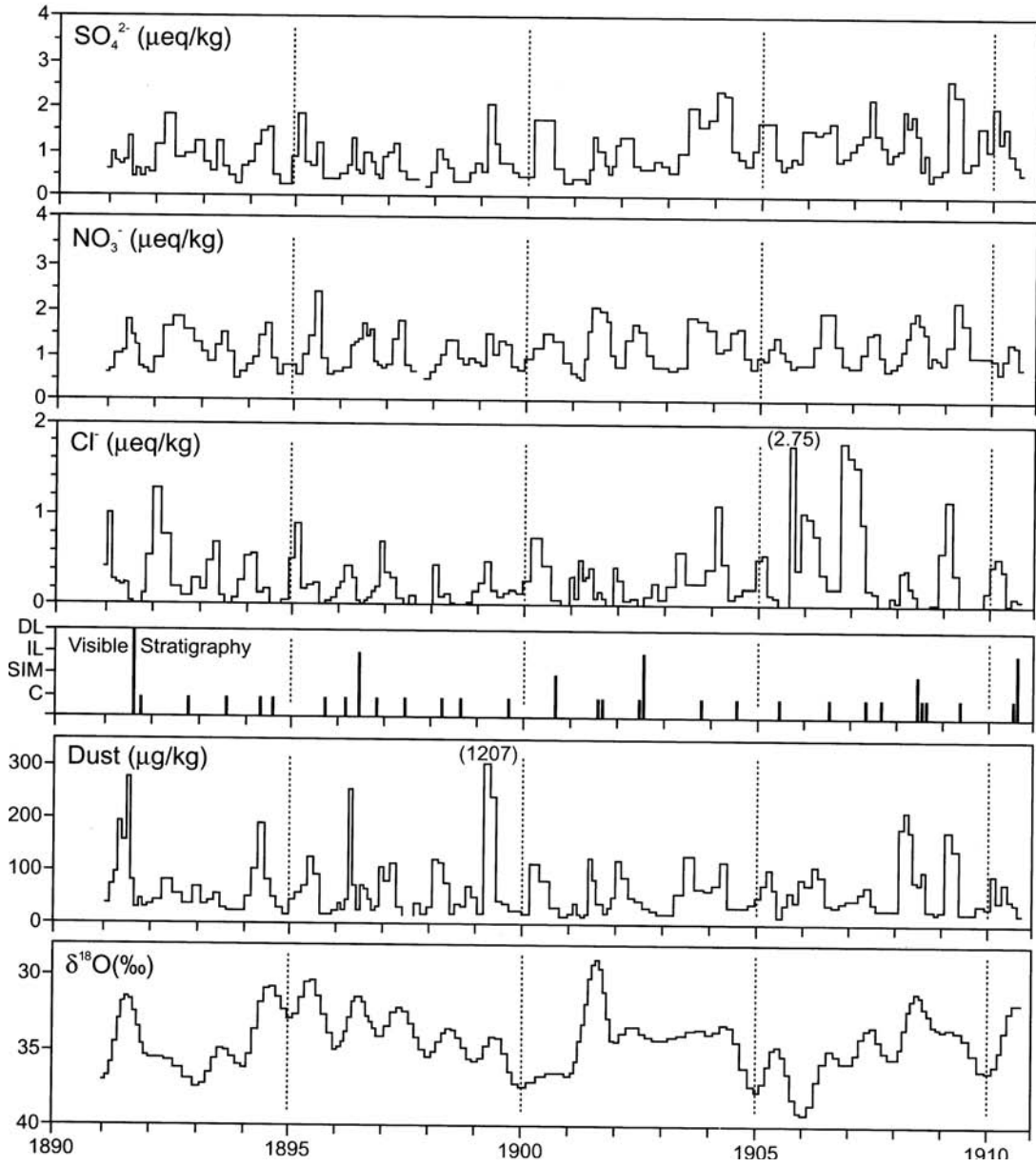
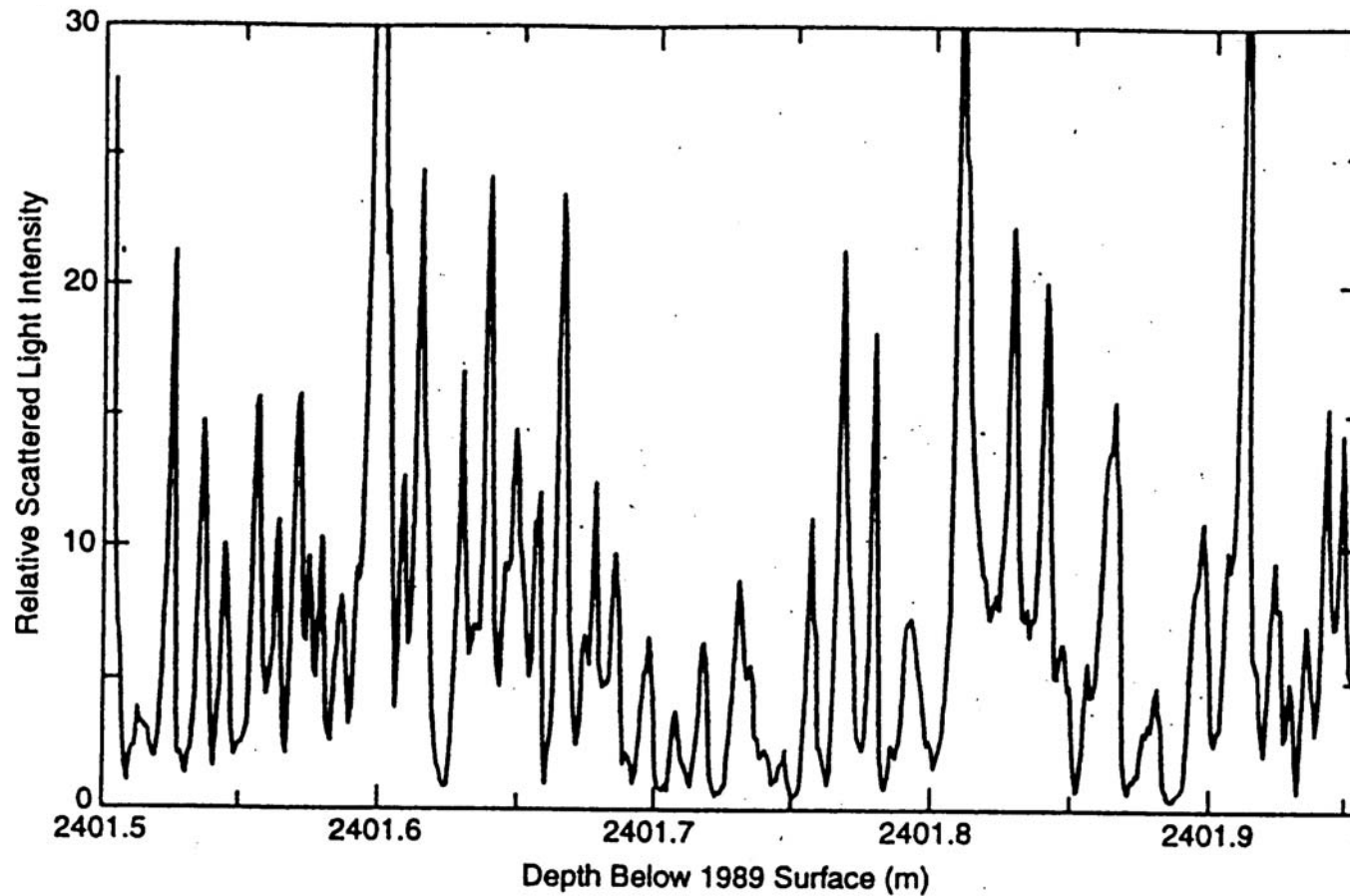


Figure 3: Average size distributions of natural aerosols. Curves 1,2,5 from Frankfurt am Main. Curves 3,4 from Zugspitze 3000m a.s.l. (From Junge, 1963)

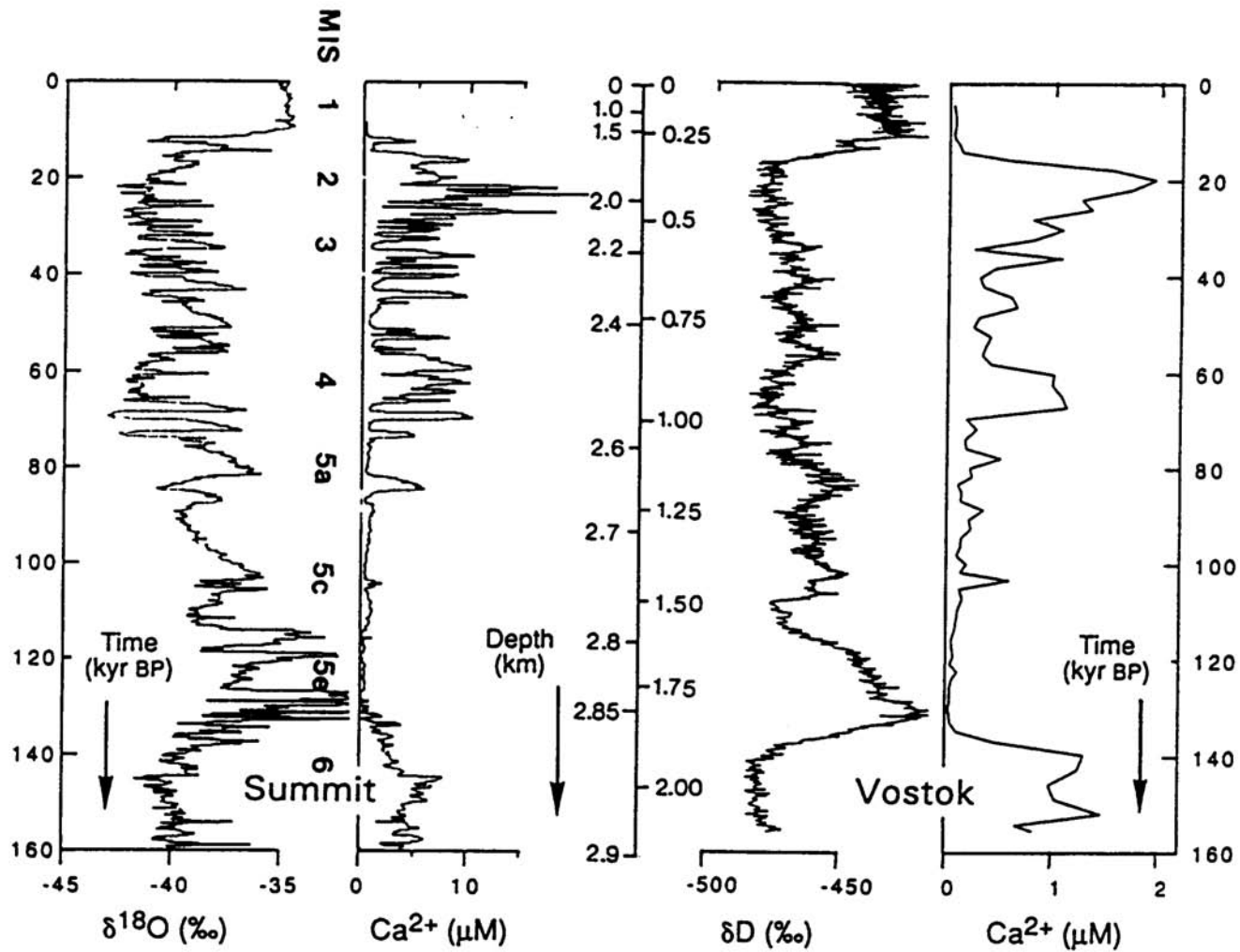


Spring peak





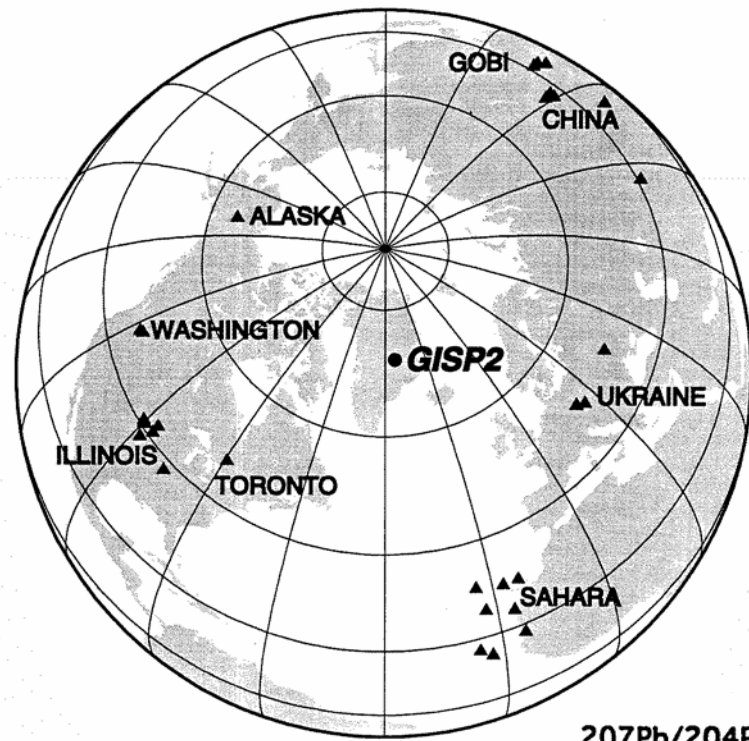
**~35 spring peaks in dust in a 45 cm section at 2400 m depth in the GISP2 core, Greenland. Age: ~50,000 years.**



**Calcium (proxy for dust) records from GRIP and Vostok, compared with  $\delta^{18}\text{O}$ .**

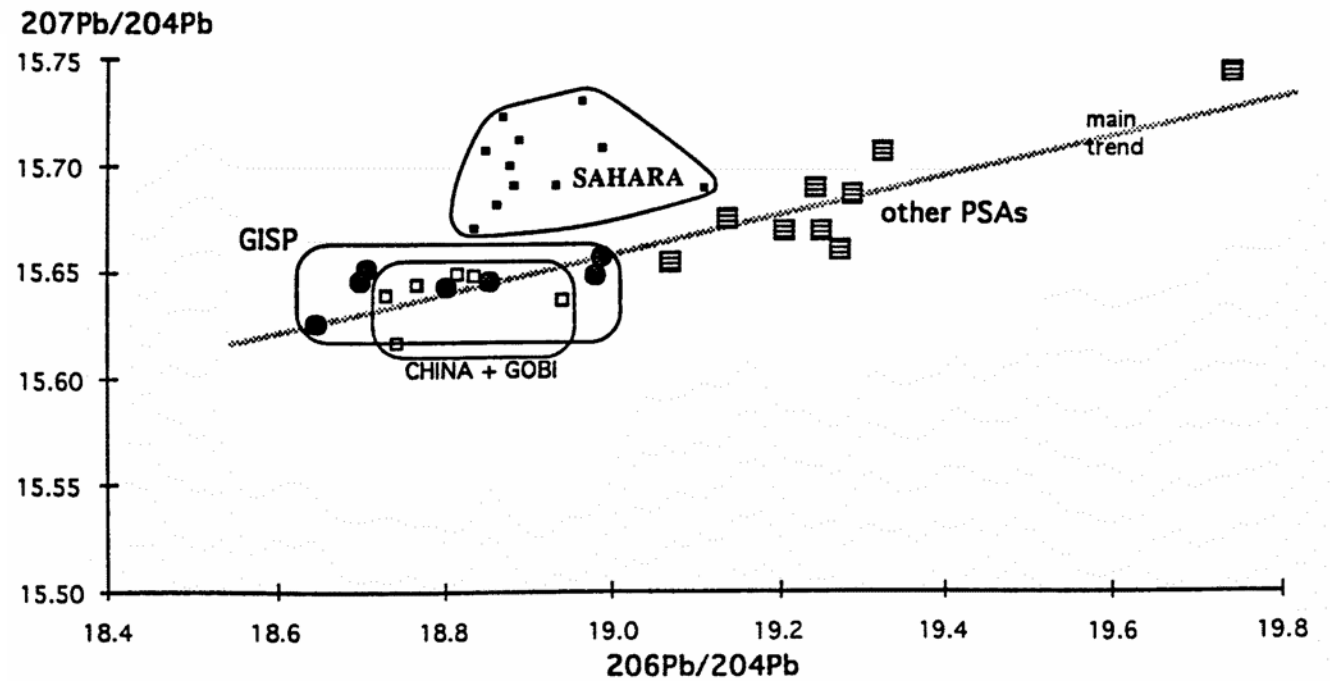
**Greenland: Dust from Gobi desert**

**Antarctica: Dust from Patagonia**



P. Biscaye et al. (1997):  
Study confirming the Gobi origin  
of Greenland dust

PSA = Possible  
Source Area



# Electric conductivity measurements on ice cores

ECM method

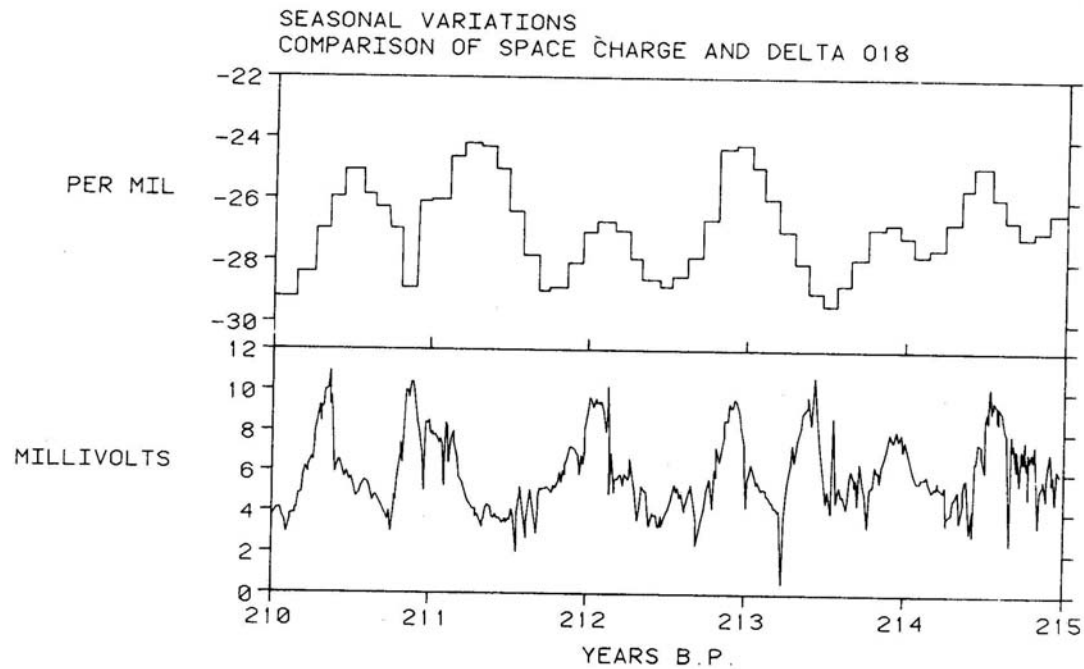
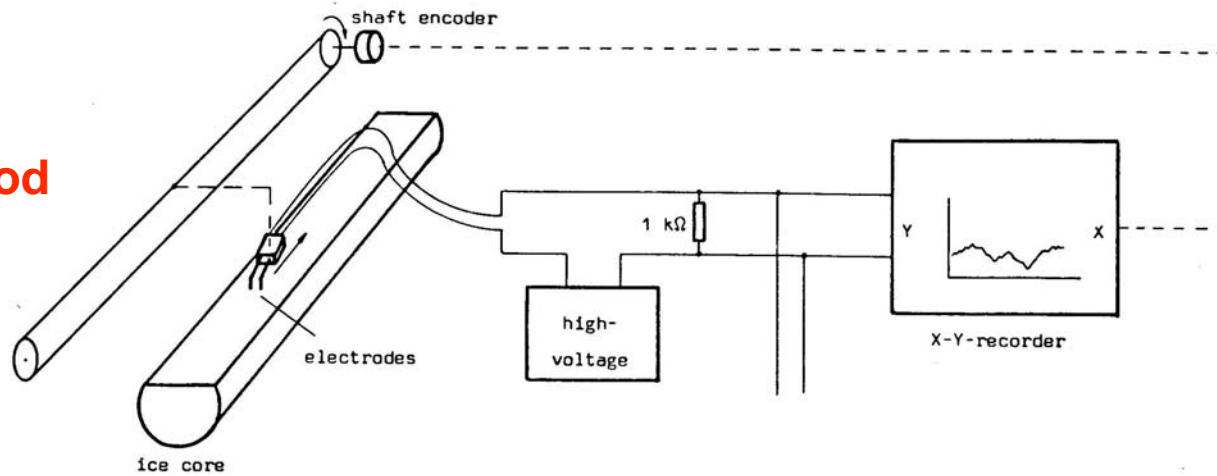


Fig. 4. Comparison of the seasonal features in the ECM signal and the  $\delta^{18}\text{O}$  record.

$$H^+ = 0.045i^{1.73} \mu\text{eq/kg}$$

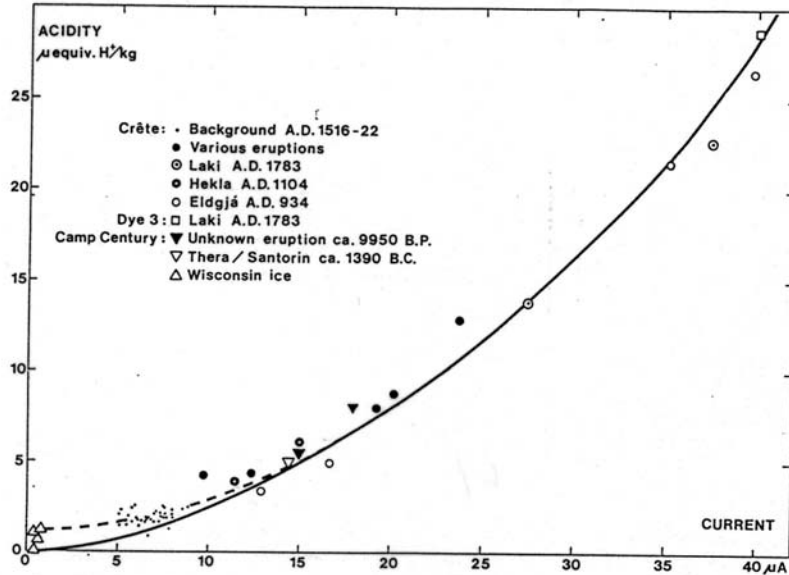


Fig. 2. Square-law relationship of acidity to current. Currents higher than 10  $\mu\text{A}$  only occur when the ice is doped by acid fall-out of volcanic origin. Solid line: proposed calibration curve. Broken line:  $H^+$  concentration including c. 50% surplus  $\text{CO}_2$  effect.

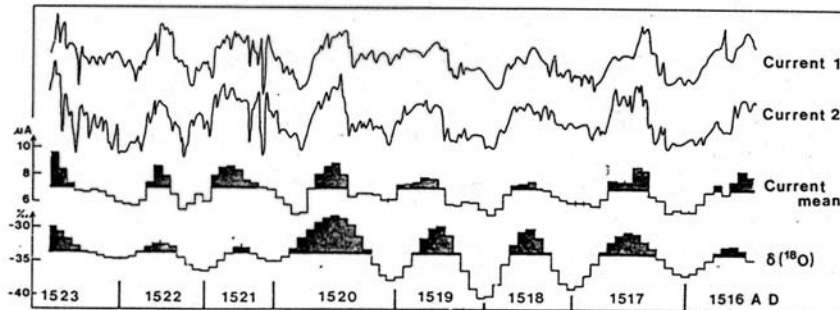
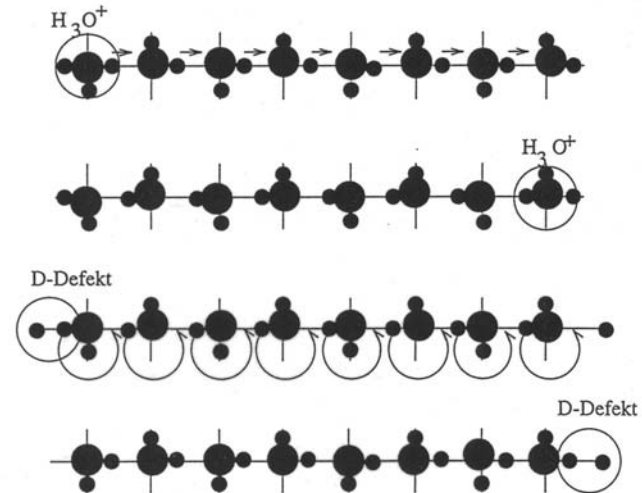


Fig. 3. Top section: Current profiles (1 and 2) measured on two different segments of the same increment of the Crête ice core. Mid section: Mean of currents 1 and 2 plotted with a resolution averaging twelve samples per annual layer. Lower section:  $\delta(^{18}\text{O})$  profile with the original annual cycles re-established by Johnsen's (1977) deconvolution technique. The time scale is determined by counting such cycles downwards from the surface.

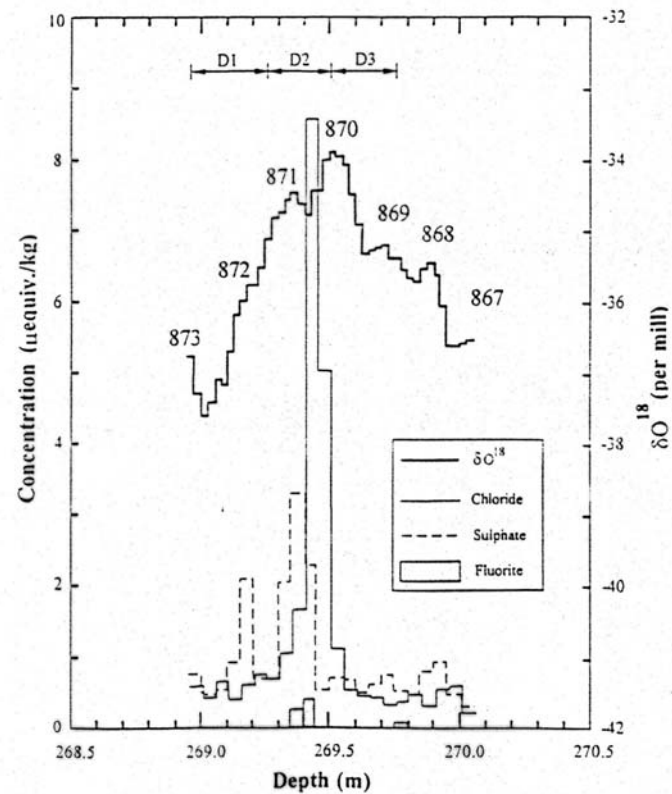
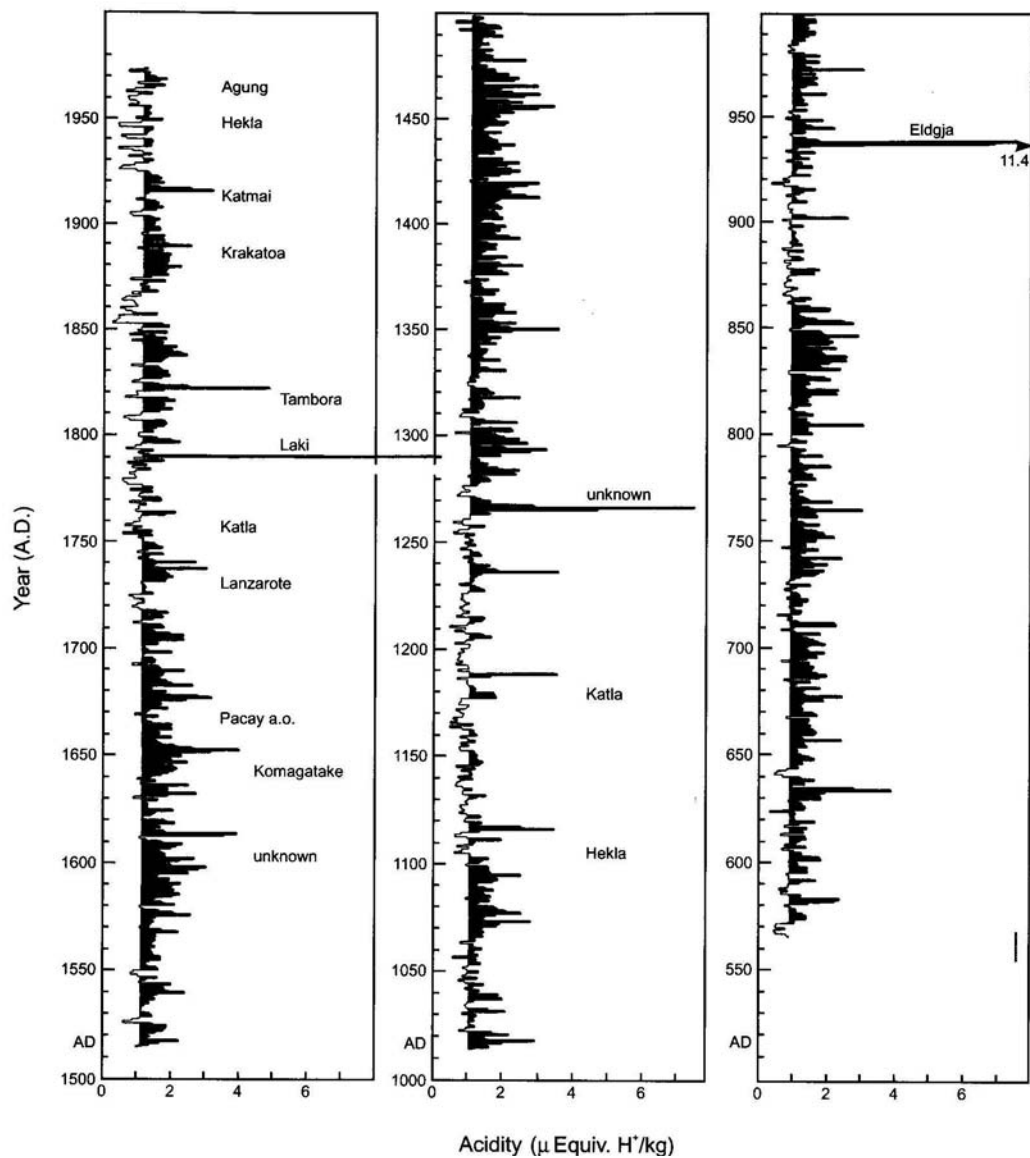
Hammer et al., 1980)

Calibration curve:

Acidity vs. current

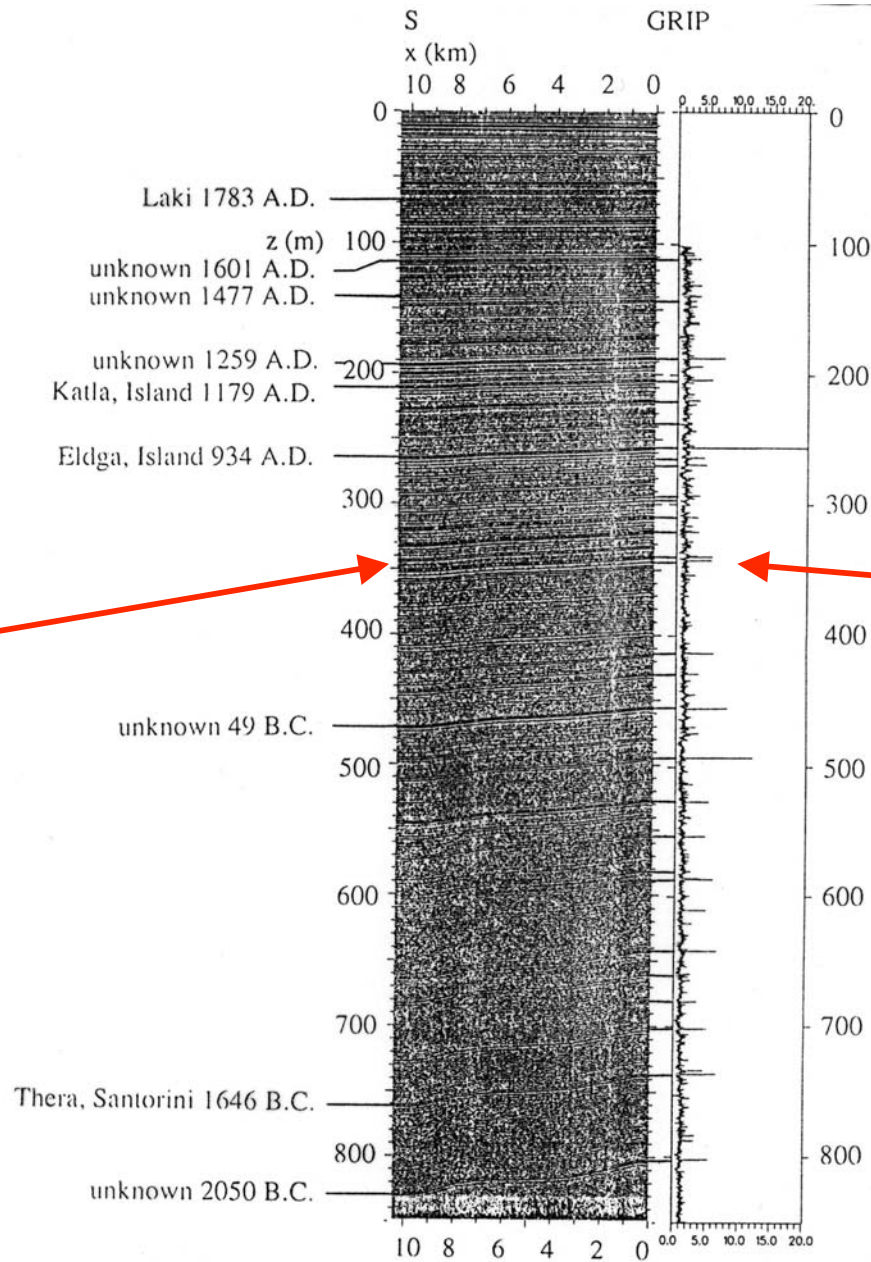


Protons are the charge carriers in pure ice



**The Settlement layer in Iceland (871 AD).**

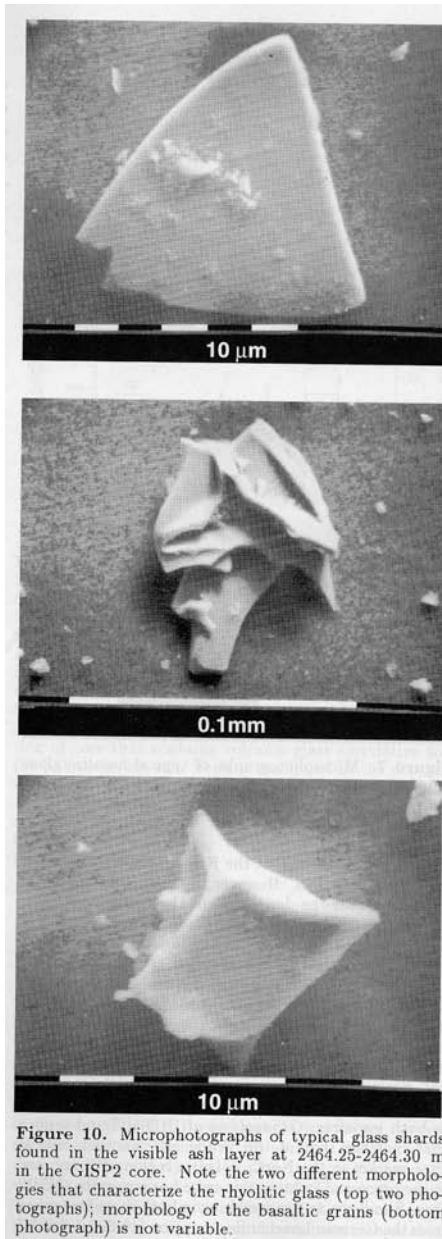
**ECM record of volcanism 570-1970 AD**



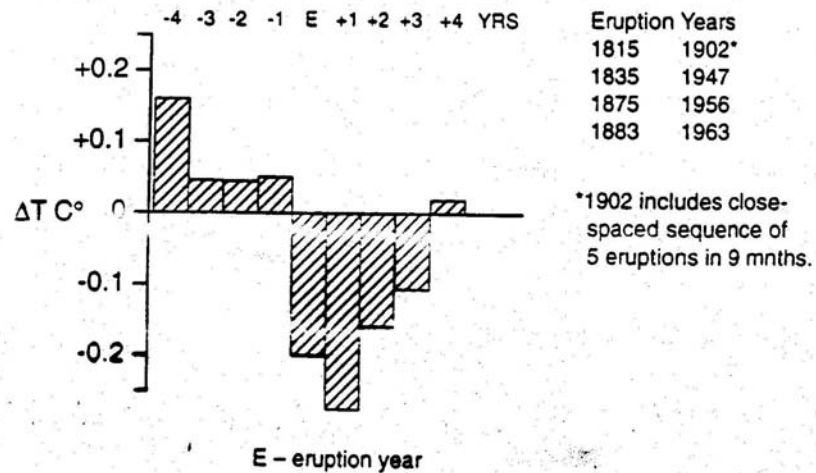
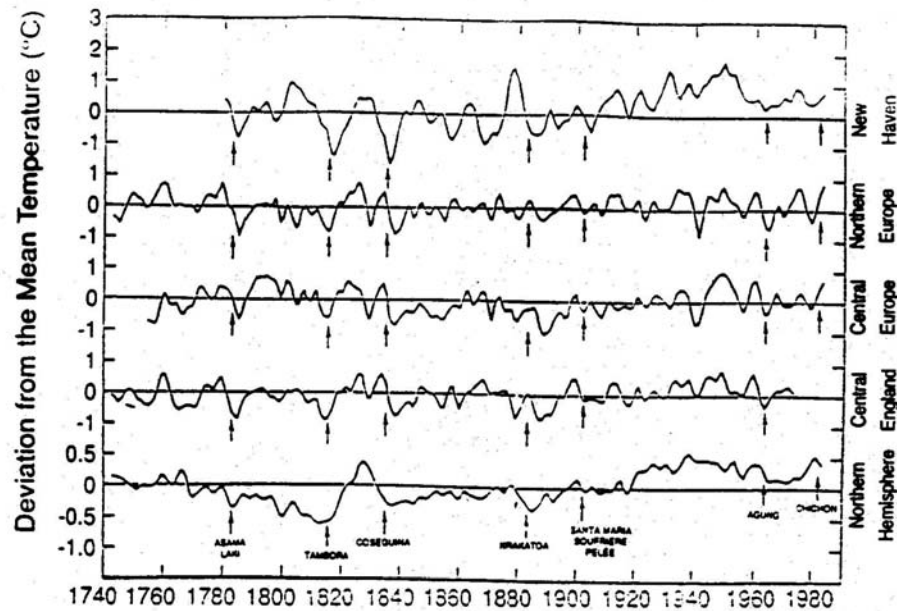
**Radio echo sounding reflectors**

**GRIP ECM record**

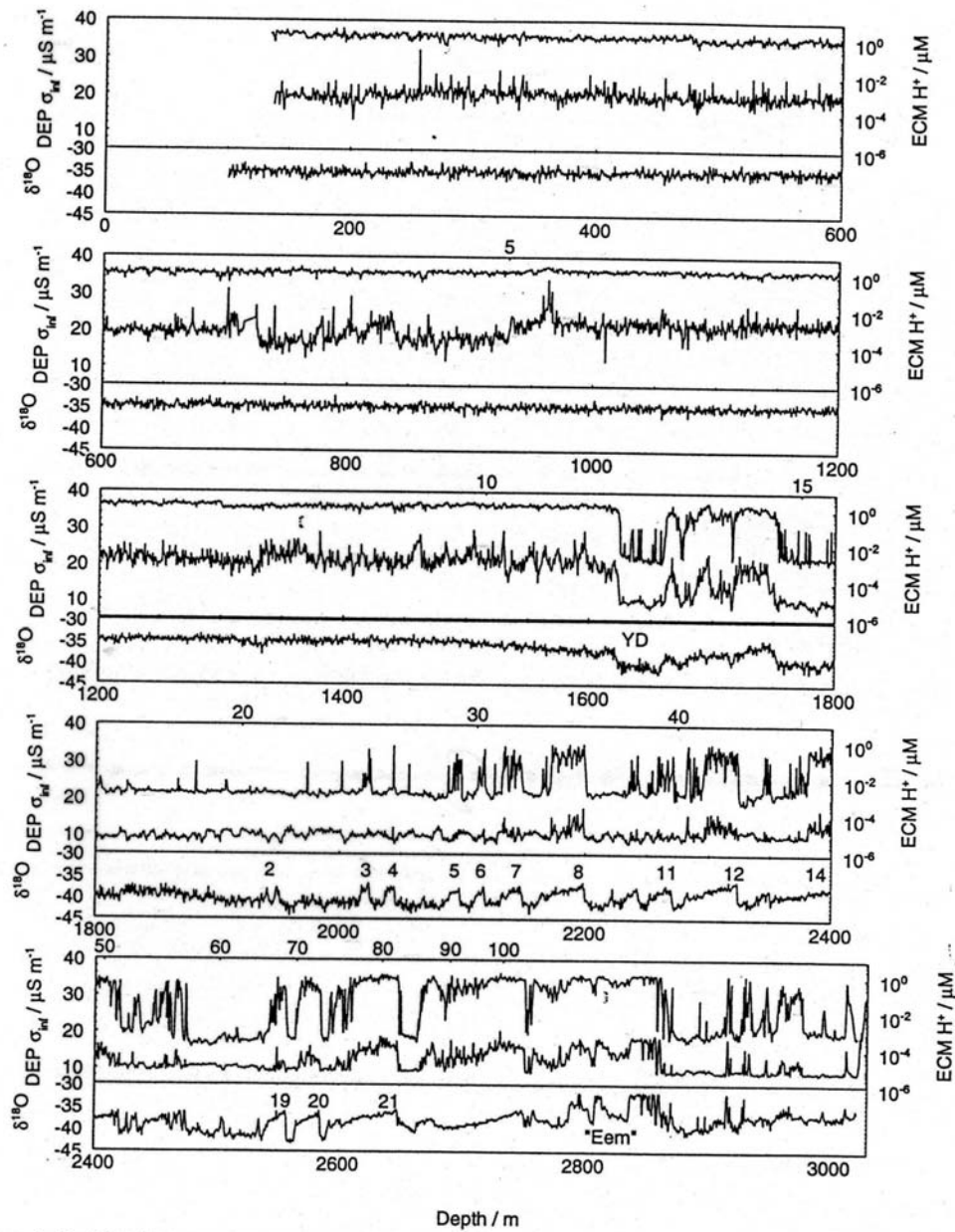
**Particles of volcanic ash (tephra)  
found at 2464 m depth in the GISP 2  
core – age 53,000 years BP.**



**From Zielinski et al., 1997**

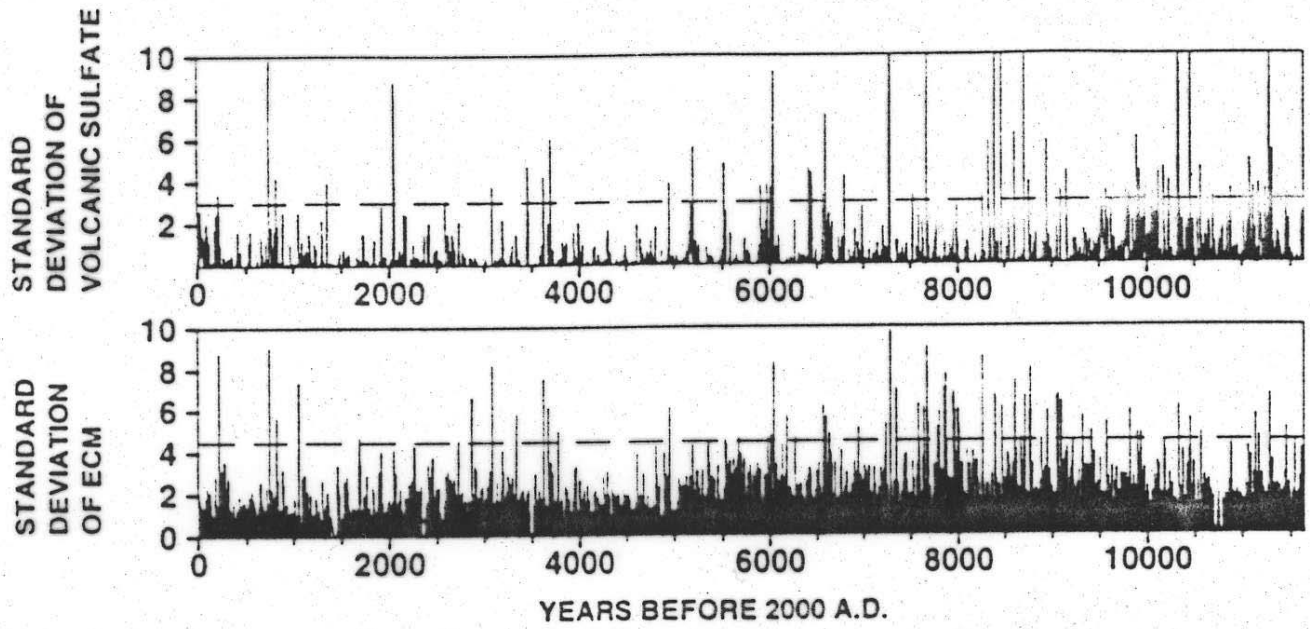


Large volcanic eruptions during the past centuries lead to slight cooling of the atmosphere for a few years.



Lower conductivity in ice from the glacial period.

Higher dust concentrations during the glacial period,  $\text{Ca}^{2+}$  neutralizes acids.



**GISP2, Greenland: ECM and volcanic sulfate during the Holocene.**

**High level of volcanic activity early in the Holocene – formation of large shield volcanoes in Iceland.**

**Skjaldbreið – W. Iceland  
Formed ~ 8000 BP**



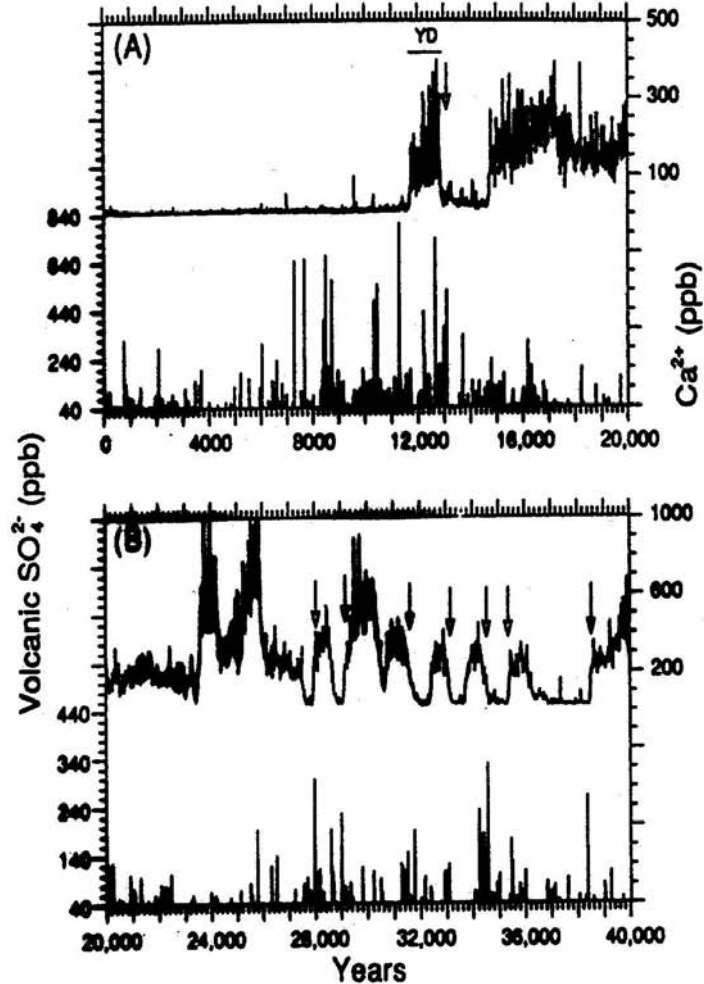
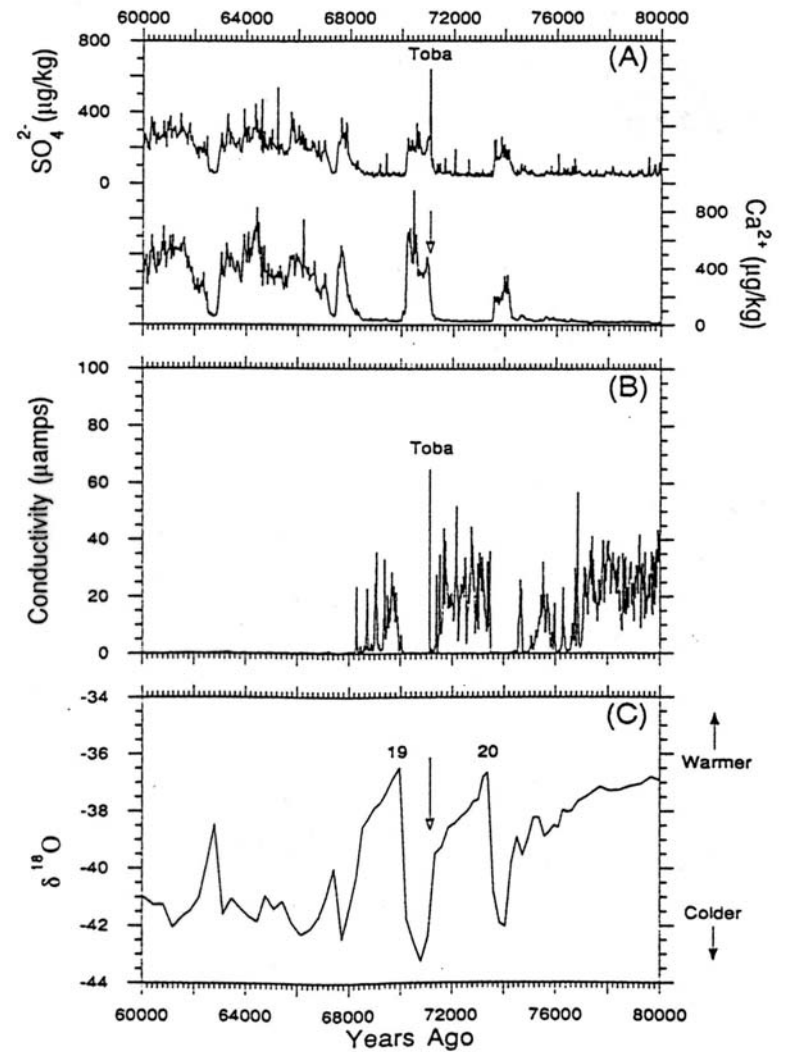
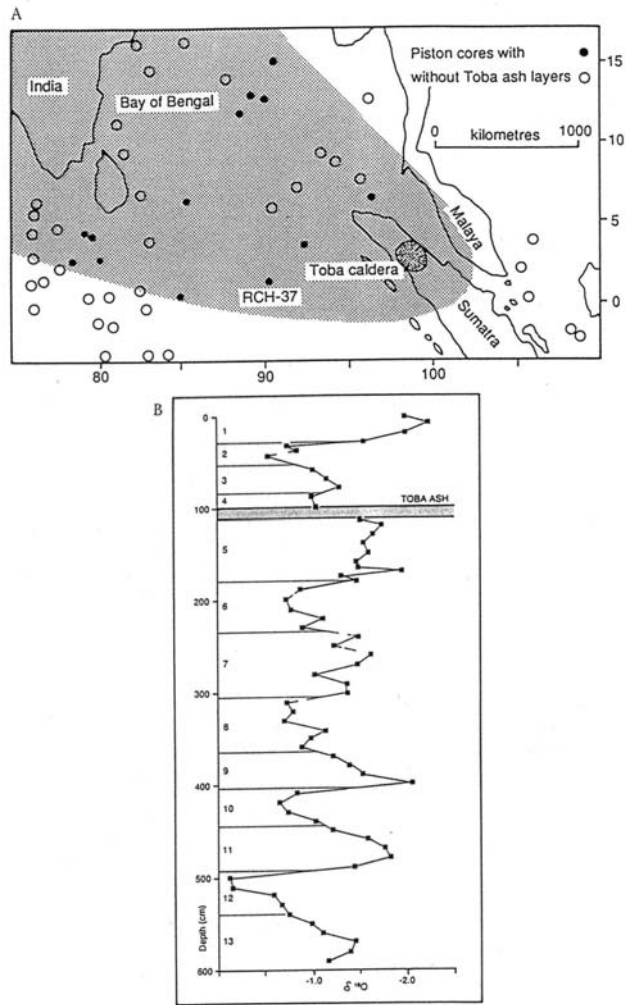


FIG. 2. Comparison between  $\text{Ca}^{2+}$  time series, a proxy for changing climatic conditions (Mayewski *et al.*, 1994), and volcanic  $\text{SO}_4^{2-} > 40$  ppb from EOF-5 time series for the past 20,000 yr (A) and, for the period between 40,000 and 20,000 years ago (B). The Younger Dryas interval is noted by YD. Arrows indicate stadal/interstadial transitions that are characterized by a large number of volcanic signals or a very large signal. High  $\text{Ca}^{2+}$  concentrations reflect colder climatic conditions, whereas low  $\text{Ca}^{2+}$  concentrations reflect warmer climatic conditions. Note changes in scale between each plot for both ion species.

Volcanic sulfate and calcium  
(climate indicator) – last  
40,000 years in the GISP2 core.

Zielinski *et al.*, 1997.

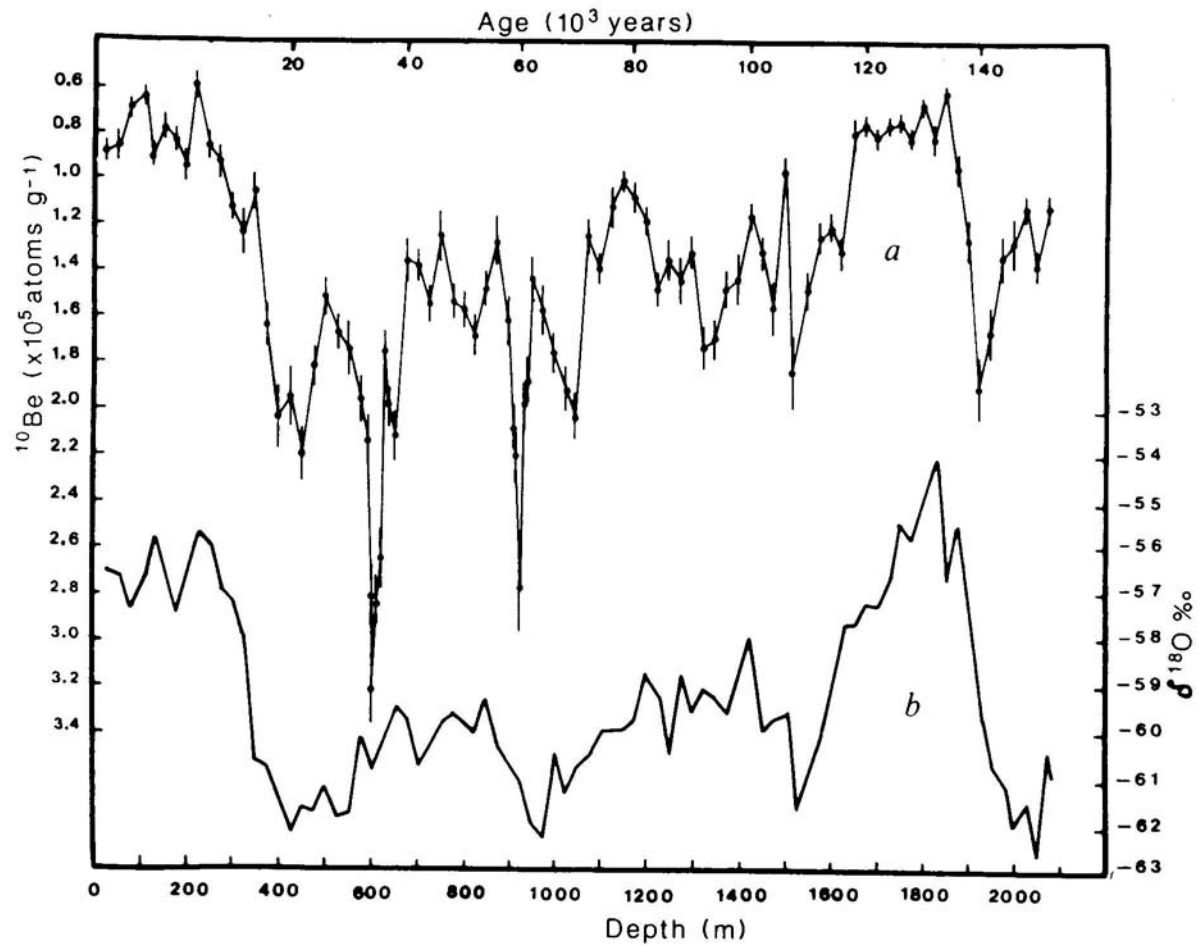


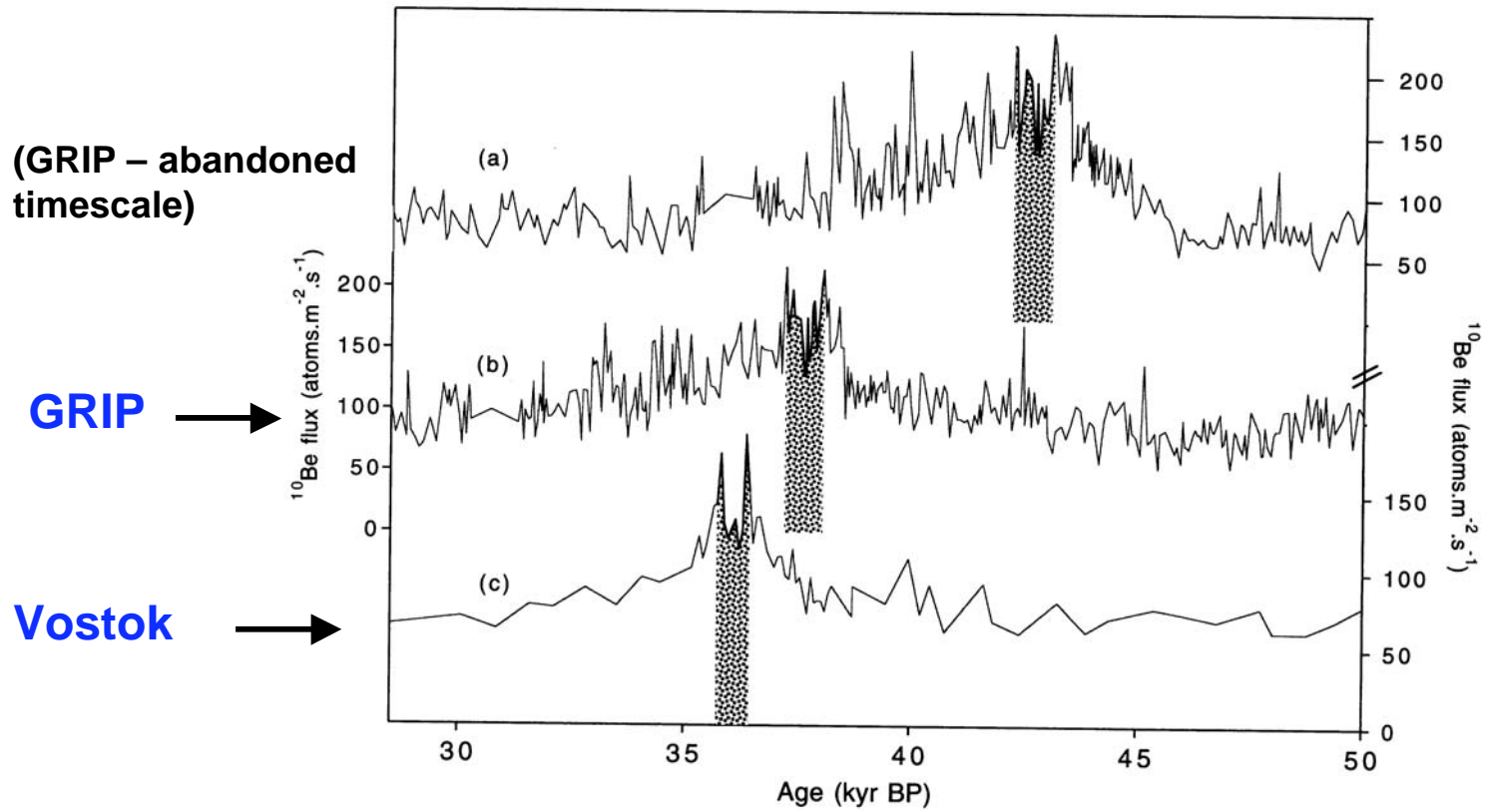
**Toba eruption ~70,000 years ago**

Figure 1. Time series of (A)  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  concentrations, (B) electrical conductivity (ECM), and (C)  $\delta^{18}\text{O}$  from the GISP2 ice core for the period between 60,000 and 80,000 years ago. Arrows show timing of Toba aerosols as related to non-volcanic  $\text{Ca}^{2+}$  and  $\delta^{18}\text{O}$  records. Interstadial events 19 and 20 in (C) from Dansgaard et al. [1993].

From Zielinski et al.

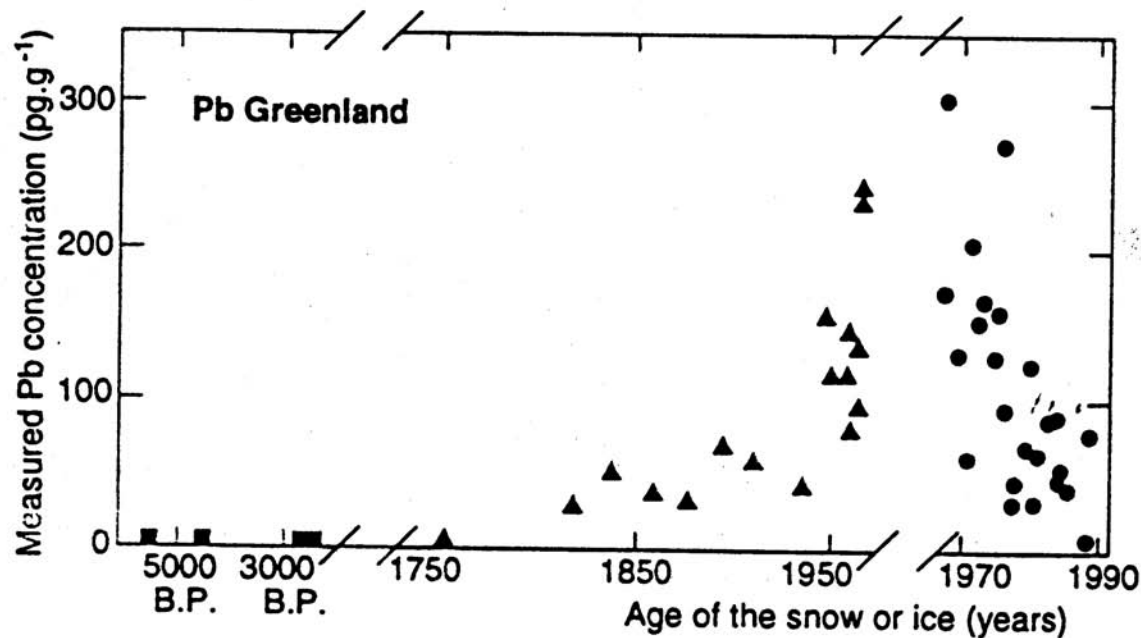
The  $^{10}\text{Be}$  peaks in the Vostok core, ~35 ka and ~60 ka BP





The 35 ka BP peak in  $^{10}\text{Be}$  is also seen in Greenland cores

Data from Greenland on lead pollution of the atmosphere forced us to switch to unleaded gasolin!



**Figure 9.** Trend in Pb concentrations of Greenland snow layers for the time period 1750–1989. Circles represent data from *Boutron et al.* [1991] in Summit (central Greenland), triangles represent data from *Murozumi et al.* [1969] in northwest Greenland snow, and squares are data from *Murozumi et al.* [1969] and *Ng and Patterson* [1981] in Greenland Holocene ice. Adapted from *Boutron et al.* [1994, Figure 5b] with kind permission from Elsevier Science Ltd., Oxford, England.