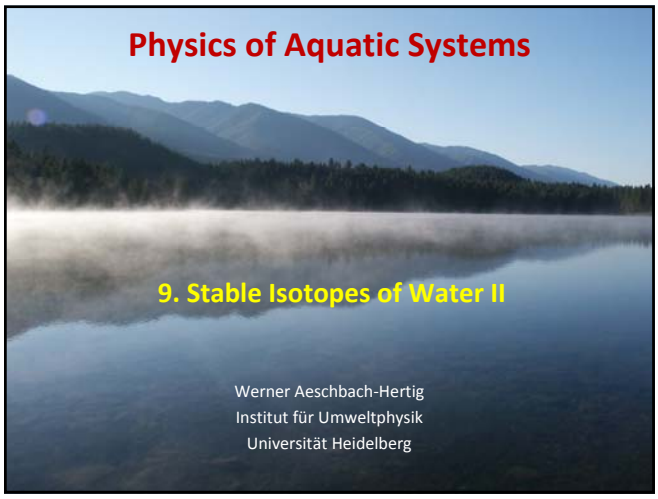
Physics of Aquatic Systems



9. Stable Isotopes of Water II

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Contents of Session 9: Isotopes of Water

9.1 Stable Isotopes of Water in the Hydrological Cycle
- Effects on stable isotopes in precipitation: Temperature, altitude, amount effect etc.

9.2 Applications of Stable Isotopes in Hydrology
- Stable isotopes as markers of water origin
- Stable isotopes in process studies

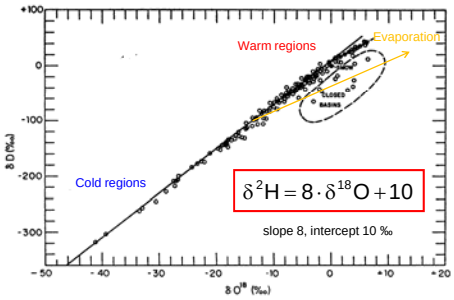
9.3 Applications of Stable Isotopes in Paleoclimatology
- Stable isotopes as paleoclimate proxies in ice, groundwater, speleothems, and sediments

Literature: Mook Vol. 2, ch. 3, 4; Vol. 3, ch. 2,4; Vol. 4, ch. 5

9.1 Stable Isotopes in the Hydrological Cycle

The Global Meteoric Water Line (GMWL)

Empirical Finding (Craig, 1961): Isotopic composition of worldwide precipitation, plotted as δ^2H versus $\delta^{18}O$ (in ‰), is strongly correlated

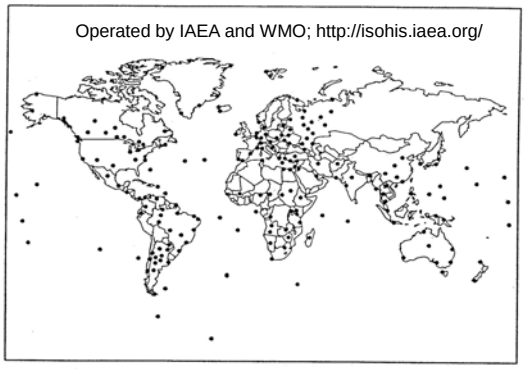


Harmon Craig (1926 – 2003)

H. Craig, 1961, Science 133: 1702-1703

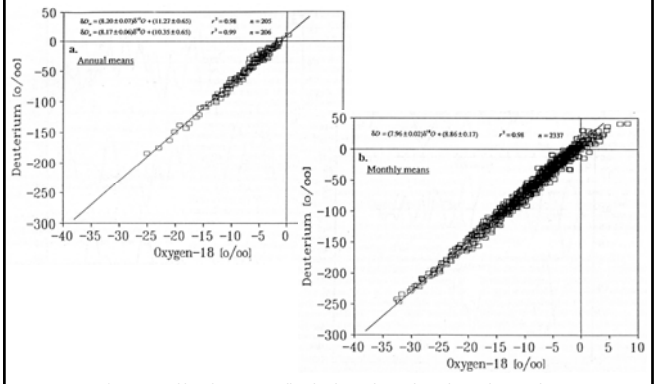
GNIP: Global Network of Isotopes in Precipitation

Operated by IAEA and WMO; http://isohis.iaea.org/



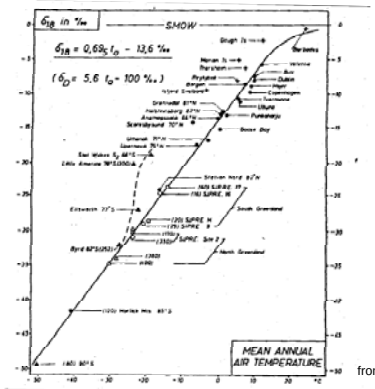
from Rozanski et al., 1993, In: Climatic Change in Continental Isotopic Records

GMWL from GNIP Data



from Rozanski et al., 1993, In: Climatic Change in Continental Isotopic Records

Temperature Effect



Relationships between temperature T (in °C) and $\delta^{18}O$ (in ‰):

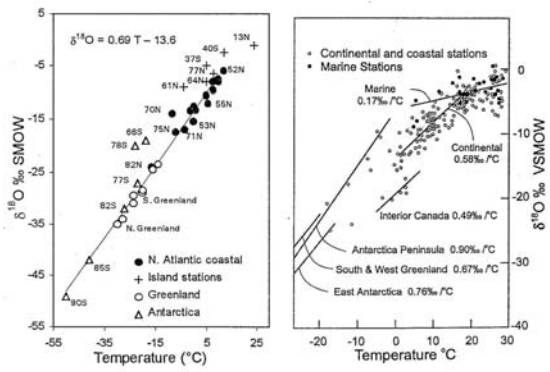
Dansgaard (1964):
$\delta^{18}O = 0.695T - 13.6$

Yurtsever (1975):
$\delta^{18}O = 0.521T - 15.0$

Slope ≈ 0.6 ‰ °C^{-1}

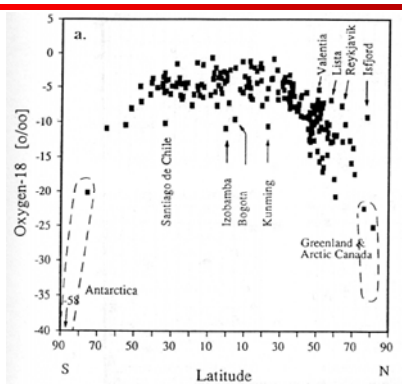
from Dansgaard, 1964, Tellus 16: 436-468

Temperature Effect



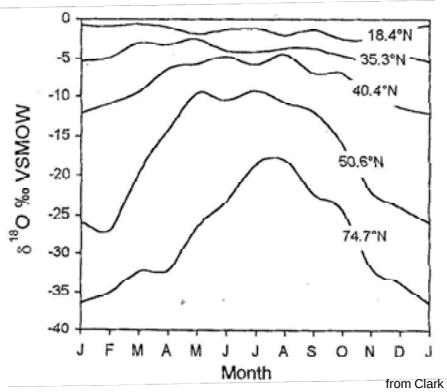
from Rozanski et al., 1993, In: Climatic Change in Continental Isotopic Records

Latitude Effect



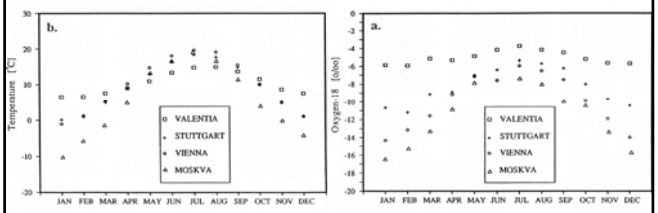
from Rozanski et al., 1993, In: Climatic Change in Continental Isotopic Records

Seasonal Effect



from Clark & Fritz, 1997

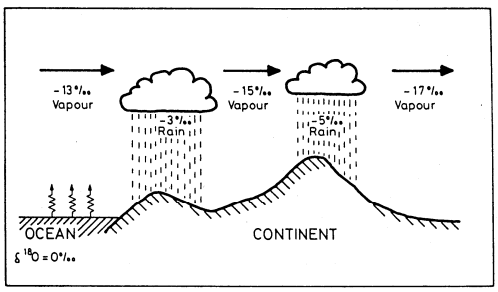
Seasonal Effect



from Rozanski et al., 1993, In: Climatic Change in Continental Isotopic Records

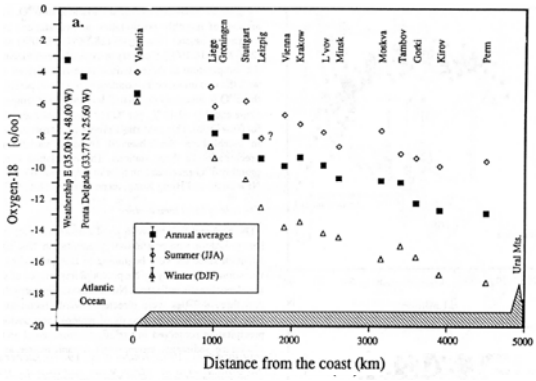
Continental Effect

Rainout of oceanic water vapour: Increasing depletion of precipitation



from Siegenthaler, 1997, In: Lectures in Isotope Hydrology

Continental Effect

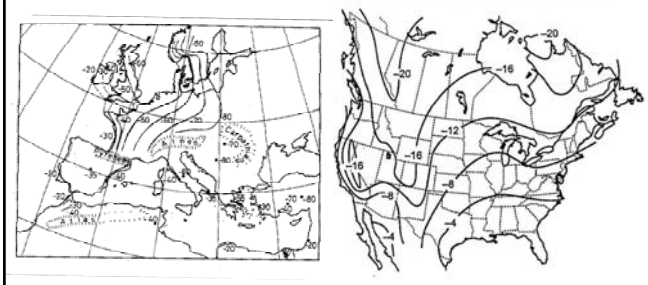


from Rozanski et al., 1993, In: Climatic Change in Continental Isotopic Records

Continental Effect

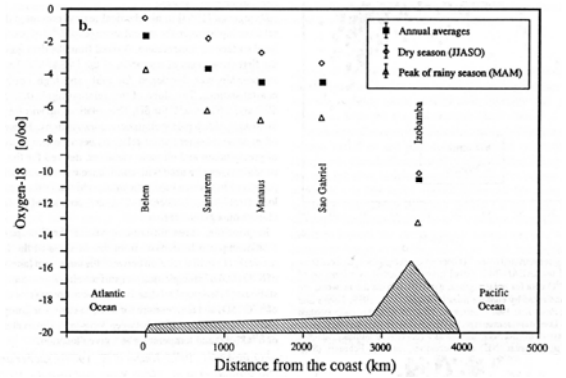
δ^2H in precipitation

Weighted mean $\delta^{18}O$ in precipitation



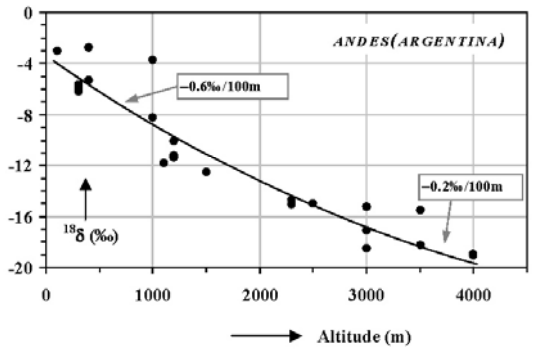
Clark & Fritz, 1997

Altitude Effect



from Rozanski et al., 1993, In: Climatic Change in Continental Isotopic Records

Altitude Effect



from Mook, 2001

Slope of Altitude Effect

Simple estimate:

Lapse rate: dT/dz ≈ -0.5 °C/100m

Temperature effect: $d\delta^{18}O/dT \approx 0.6$ ‰/°C

Altitude effect: $d\delta^{18}O/dz \approx -0.3$ ‰/100m

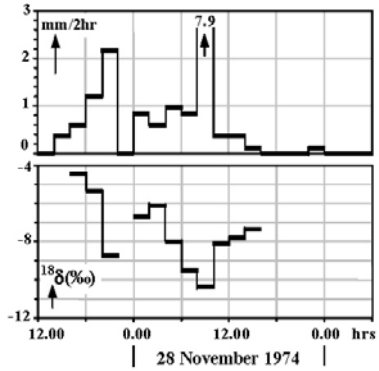
Table 3 -1 Range of values for the $\delta^{18}O$-altitude gradient in different studies

Site	Region	Altitude (m asl)	Gradient (‰ per 100 m) $\delta^{18}O$	δ^2H	Reference
Jura Mountains	Switzerland	500-1200	-0.2		Siegenthaler et al., 1983
Black Forest	Switzerland	250-1250	-0.19		Dubois and Flück, 1984
Mont Blanc	France	2000-5000	-0.5*	-4	Moser and Stichler, 1970
Coast Mountains	British Columbia	250-3250	-0.25		Clark et al., 1982
Piedmont	Western Italy	500-2000	-0.31	-2.5	Bortolami, 1979
Dhofar Monsoon	Southern Oman	0-800	-0.10		Clark, 1987
Saiq Plateau	Northern Oman	400-2000	-0.20		Stanger, 1986
Mount Cameroun	West Africa	0-4095	-0.155		Fontes and Olivry, 1977

* Calculated from δ^2H using a slope of 8.

from Clark & Fritz, 1997

Amount Effect



Light/early rainfall tends to be enriched compared to heavy rainfall.

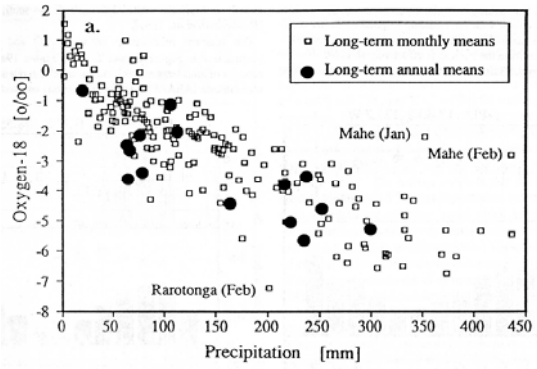
Negative correlation of $\delta^{18}O$ with rain intensity

In part due to evaporation of falling rain drops.

Important effect in tropical regions!

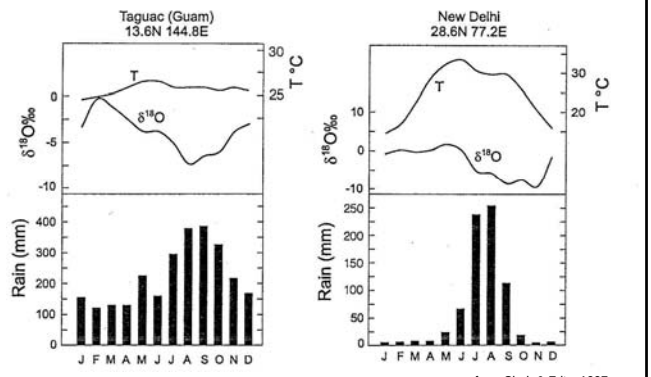
from Mook, 2001

Amount Effect



from Rozanski et al., 1993, In: Climatic Change in Continental Isotopic Records

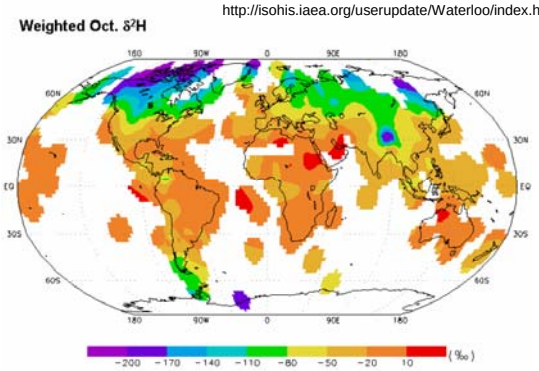
Amount Effect



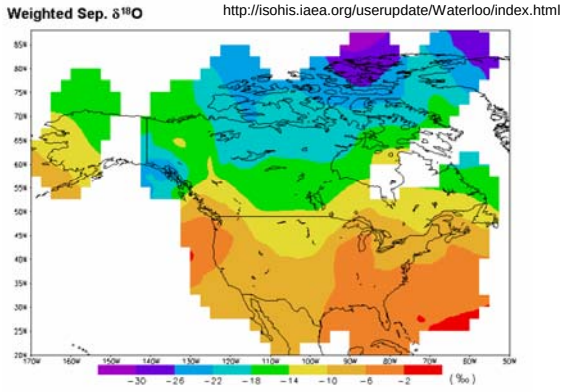
from Clark & Fritz, 1997

Global Distribution of Stable Isotopes

http://isohis.iaea.org/userupdate/Waterloo/index.html



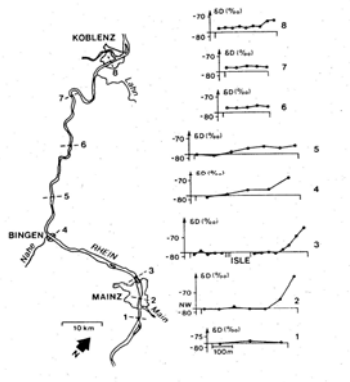
Global Distribution of Stable Isotopes



9.2 Applications of Stable Isotopes in Hydrology

1. **Stable isotopes as "colour":**
   - Trace water masses with specific isotopic signature
   - Quantify mixing between different water masses
   - Hydrograph separation

Mixing Between Rivers



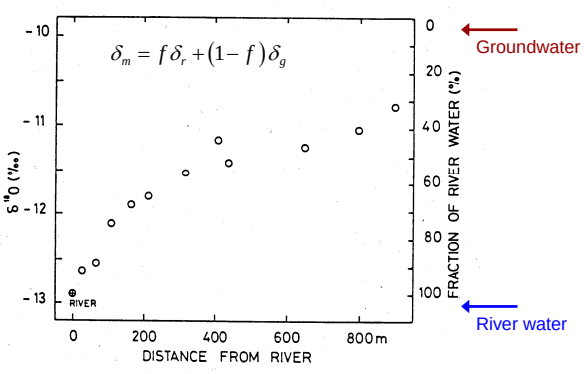
Cross-sections through Rhine:

Slow lateral mixing with tributaries

Why do tributaries have higher $\delta^{18}O$ than the Rhine?

Altitude effect! (lower catchment)

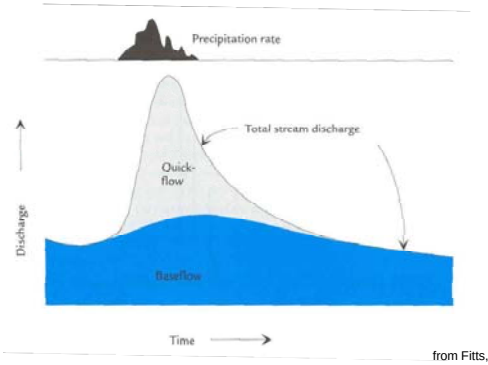
Mixing of River Water and Groundwater



from Siegenthaler, 1997, In: Lectures in Isotope Hydrology

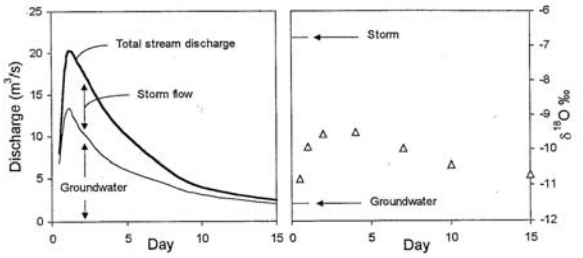
Hydrograph Separation

Separation of peak in discharge into fresh rain water and groundwater



from Fitts, 2002

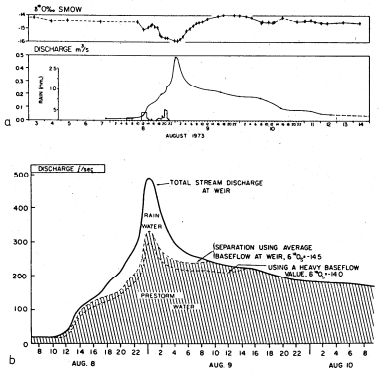
Hydrograph separation using stable istopes



$$\left\{ \begin{array}{l} Q_{total} = Q_{groundwater} + Q_{rain} \\ Q_t \cdot \delta_t = Q_g \cdot \delta_g + Q_r \cdot \delta_r \end{array} \right\} \quad \Rightarrow \quad Q_g = Q_t \left(\frac{\delta_t - \delta_r}{\delta_g - \delta_r} \right)$$

from Clark & Fritz, 1997

Hydrograph separation using stable istopes

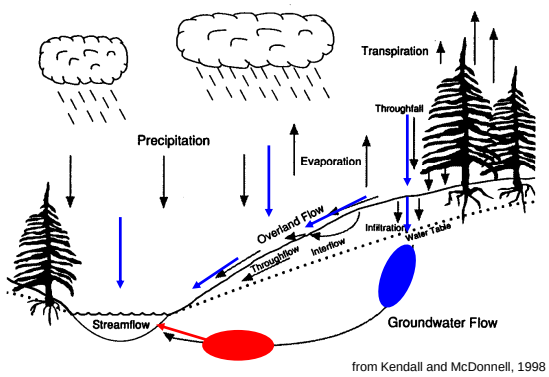


Result:
Prestorm ground-water contributes strongly to storm discharge

"Push effect"

from Siegenthaler, 1997, In: Lectures in Isotope Hydrology

Components of Runoff



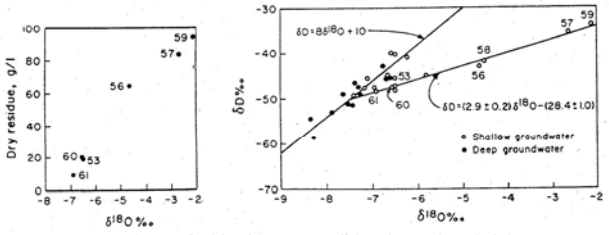
from Kendall and McDonnell, 1998

Applications of Stable Isotopes in Hydrology

2. **Stable isotopes as process tracers:**
   - Identify processes that affect the isotopic signature
   - Trace isotope fractionating processes
   - Trace transport and exchange processes

Origin of Saline Groundwaters in Arid Regions

What is the origin of the high salinity of samples 56, 57, 59?



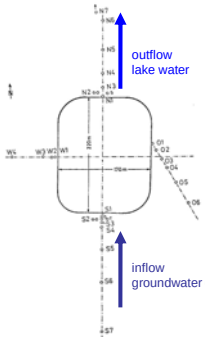
from Gonfiantini et al., In: Isotope techniques in groundwater hydrology 1974, IAEA

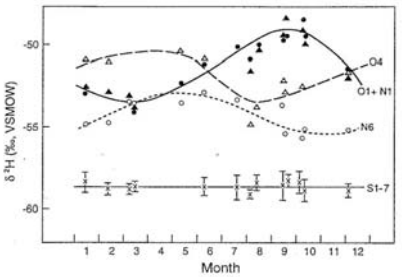
Evaporation!

Evaporation lines have low (< 8) slope in δD-$\delta^{18}O$ plots

Lake – Groundwater Interaction and Dating

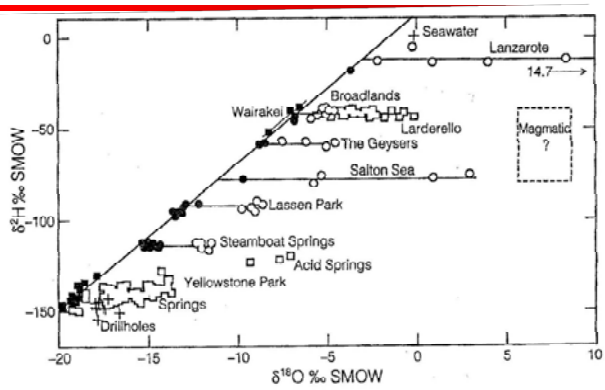
Delay and damping of seasonal variations in groundwater





from Stichler & Moser, In: Isotope Hydrology 1979, IAEA

Water- Rock Interaction



from Clark & Fritz, 1997

9.3 Stable Isotopes in Paleoclimatology

Stable isotopes as paleoclimate proxies:

- Reconstruct paleotemperature (T effect)
- Reconstruct paleoprecipitation (amount effect)

Archives:

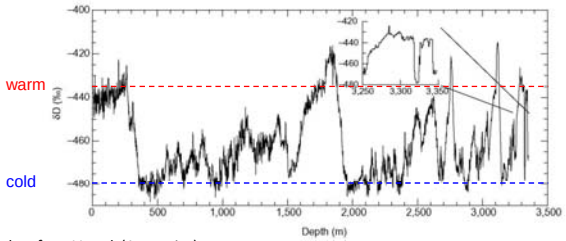
A) Stored precipitation
- Ice (polar ice sheets, glaciers)
- Groundwater

B) Carbonates (Oxygen in CO_3)
- Carbonate shells of foraminifera etc. in sediments
- Stalagmites, corals

Example 1: Ice Cores

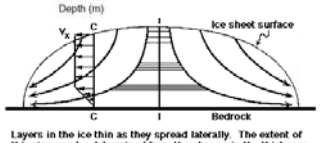
- Polar ice sheets and alpine glaciers are archives of precipitation
- Stable isotopes ($\delta^{18}O$, $\delta^{2}H$) in ice are proxies for temperature
- Dating is possible by layer counting and flow models
- Records of > 400 kyr obtained from > 3000 m cores in Antarctica

Stable Isotopes in Polar Ice Cores



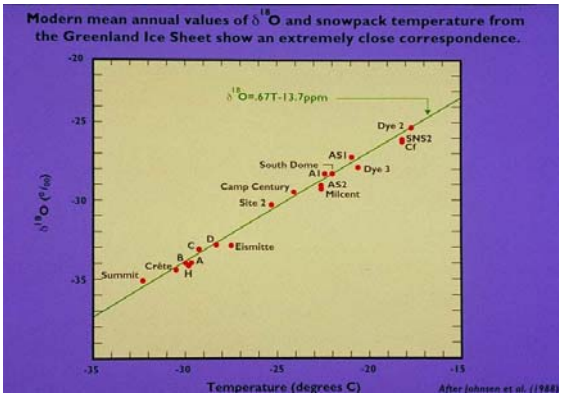
Raw data from Vostok (Antarctica), Petit et al., Nature 1999, 399:429-436

Dating by layer counting (upper part) and by ice flow model (lower part) (from Broecker, 1995)

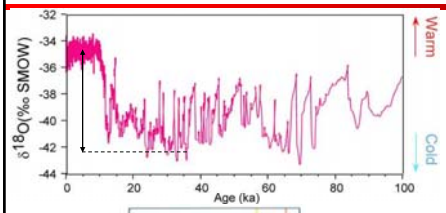


Layers in the ice thin as they spread laterally. The extent of thinning can be determined from the change in the thickness of seasonal couplets.

Calibration of $\delta^{18}O$ Thermometer in Ice



How Cold was the Ice-Age in Greenland?

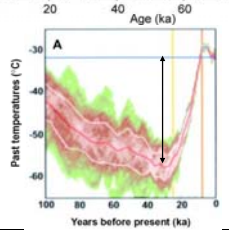


Stable Isotopes

$\Delta\delta^{18}O \sim 8$ ‰

Slope: 0.67 ‰/°C

$\Delta T \sim 12$ °C



Borehole Temperatures

$\Delta T \sim 23$ °C

Mismatch by factor of 2!

ΔT had been underestimated

Dahl-Jensen et al., 1998, Science 282: 268-271

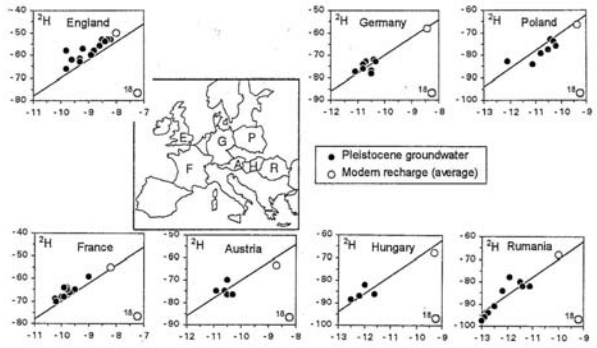
Slopes of δ-T relationship

- Spatial (latitudinal) slope (temperature effect):
  - Annual means, same time, different places
- Temporal (seasonal) slope (seasonal effect):
  - Monthly means, different times, same place
- Needed for palaeotemperature reconstruction:
  - Longterm temporal slope
  - Annual means, different times, same place

Example 2: Groundwater

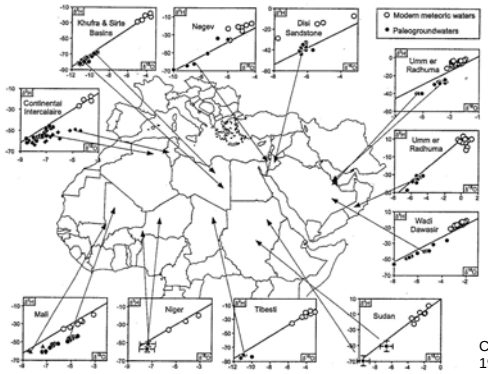
- Aquifers are archives of precipitation
- Stable isotopes ($\delta^{18}O$, $\delta^{2}H$) in water are proxies for temperature
- Dating by ^{14}C on dissolved inorganic carbon (DIC)
- Records of > 30 kyr obtained from many aquifers

Stable Isotopes in Palaeogroundwaters



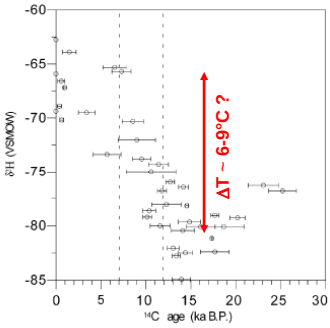
from Clark & Fritz, 1997

Stable Isotopes in Palaeogroundwaters



Clark & Fritz, 1997

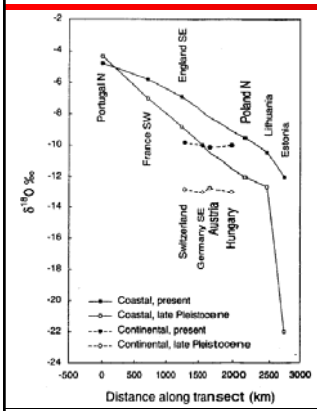
Stable Isotopes in China



- North China Plain
- strong isotope signals

Zongyu et al., 2003. Appl. Geochem. 18: 997–1009.

PALAEAUX: Stable Isotopes in European Aquifers

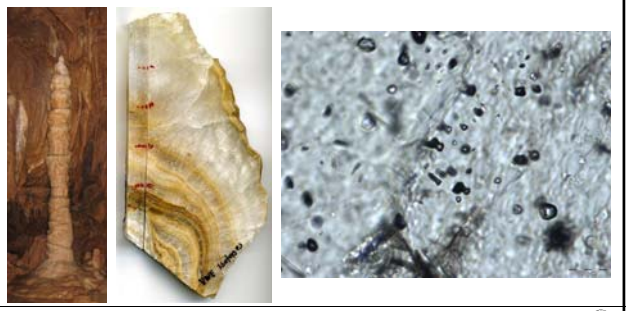


- Combination of effects:
  - temperature
  - continentality
  - ice volume
- Calibration is necessary

Loosli et al., 2001. Geol. Soc. Special Publ., Vol. 189, pp. 193-212.

Example 3: Stalagmite Fluid Inclusions

- Speleothems are archives of (carbon in) precipitation
- Stable isotopes in water & carbonate: proxies for T and precip.
- Dating: Th/U, up to ~ 300 kyr



Formation & Isotope Composition of Stalagmites

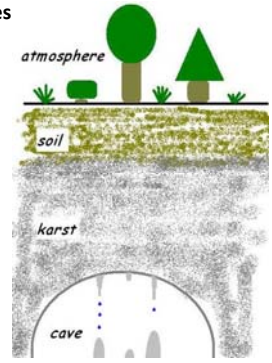
Carbonate Species

pCO_2 air

pCO_2 soil >> pCO_2 air
CO_2 dissolution

$CaCO_3$ dissolution

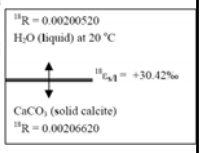
pCO_2 air
CO_2 degassing
$CaCO_3$ precipitation
stalagmite formation



Modified from J. Fohlmeister

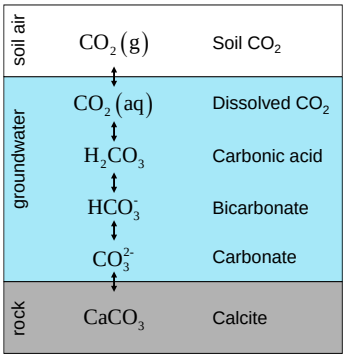
Oxygen Isotopes

$\delta^{18}O$ water (VSMOW)
(precipitation, soil water, groundwater, drip water)



$\delta^{18}O$ carbonate (VPDB)

Carbonate Geochemistry



$$CO_2(g) \leftrightarrow CO_2(aq)$$

$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$$

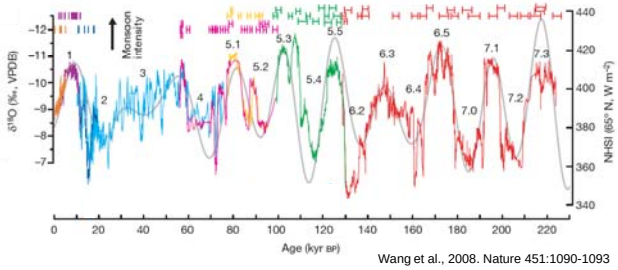
$$\varepsilon_{c/w}^{eq} = \varepsilon(T) \approx 30\ ‰$$

$\delta^{18}O$ Records from Stalagmite Calcite

$\delta^{18}O_{CaCO3} = \delta^{18}O_{drip\ water}$ (T, precip, ..) + ε_{eq} (T)

or

$\delta^{18}O_{CaCO3} = \delta^{18}O_{drip\ water}$ (T, precip, ..) + ε_{kin}(T, precip, ..)



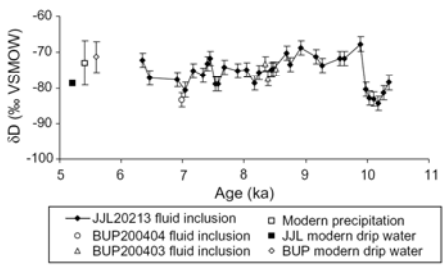
Wang et al., 2008. Nature 451:1090-1093

Drip Water Isotopes from Fluid Inclusions

$\delta^{18}O_{dripwater}$ may be altered by exchange with calcite, but not δ^2H

$\delta^{18}O_{dripater}$ can be calculated from δ^2H using GMWL or LMWL

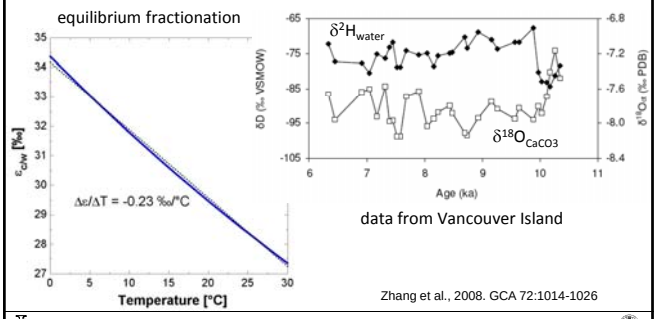
Drip water isotopes contain T information of precipitation



Zhang et al., 2008. Geochim. Cosmochim. Acta 72:1014-1026

Drip Water & Carbonate Isotopes as Thermometer

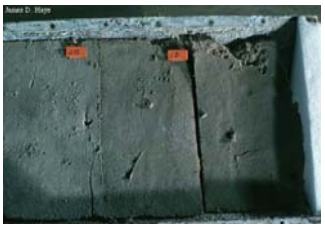
If $\delta^{18}O_{water}$ and $\delta^{18}O_{CaCO3}$ known, and equilibrium fractionation:
Calculate T from ε_{eq} (T) = $\delta^{18}O_{CaCO3}$ - $\delta^{18}O_{water}$

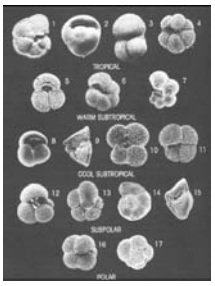


Zhang et al., 2008. GCA 72:1014-1026

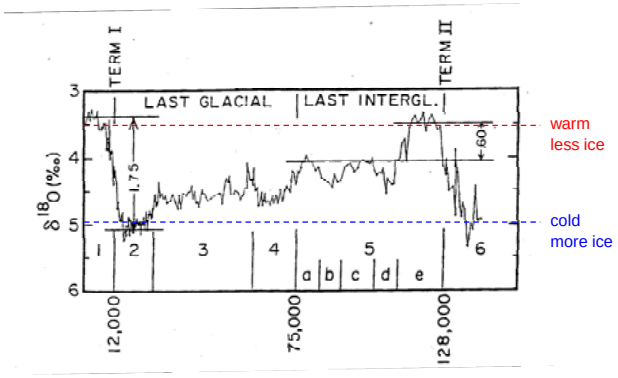
Example 4: The Oceanic $\delta^{18}O$ Record

- Climate Parameter: Ice volume (and temperature)
- Proxy: $\delta^{18}O$ in carbonate ($CaCO_3$) shells of foraminifera
- Archive: Forams in ocean sediments
- Dating: ^{14}C, indicators, orbital tuning





The Oceanic $\delta^{18}O$ Record: Marine Isotope Stages

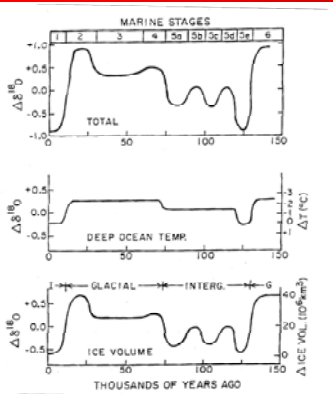


from Broecker, 1995: The Glacial World According to Wally

Stable Isotopes in Ice, Ocean and Foraminifera

- Present day:
  - Ocean: 97 % of water on Earth, $\delta^{18}O$ = 0 ‰ (standard)
  - Mean depth of the ocean: 3800 m
  - Ice: 2 % of water on Earth, $\delta^{18}O \approx$ -35 ‰
- Last glacial maximum (LGM):
  - Sea level ~ 120 m lower: 120/3800 ≈ 3 % less water
  - Ice: 5 % of water on Earth, $\delta^{18}O \approx$ -40 ‰
  - Ocean: ~ 94 % of water, $\delta^{18}O$ enriched to ~ 0.03·40 = 1.2 ‰
- Benthic (bottom dwelling) foraminifera
  - $CaCO_3$ shells in isotopic equilibrium with deep sea water
  - ⇒ mainly record deep water $\delta^{18}O$ ⇔ ice volume
  - Complication: T-dependence of eq. isotope fractionation

Stable Isotopes in Ocean Sediments



$\delta^{18}O$ record from carbonate shells of benthic foraminifera

Temperature effect: T-dependence of carbonate/water fractionation

Ice volume effect: Glacial ocean enriched in heavy isotopes

from Broecker, 1995: The Glacial World According to Wally

Summary

- Water isotopes in the hydrological cycle
  - δ^2H and $\delta^{18}O$ correlated along Global Meteoric Water Line
  - Temperature effect due to progressive rainout with cooling
- Other factors influencing stable isotopes in precipitation
  - Latitude, seasonal, continental, altitude effects (from T)
  - Amount effect (precipitation, tropics)
  - Ice volume effect (glacial – interglacial time scale)
- Applications of stable isotopes
  - Markers: Decompose mixtures, e.g. hydrograph separation
  - Process studies: Evaporation, water exchange & flow, WRI, …
  - Paleotemperature reconstruction from many archives
  - Paleo ice volume reconstruction from ocean sediments