Saint Petersburg State University, Institute of Earth Sciences

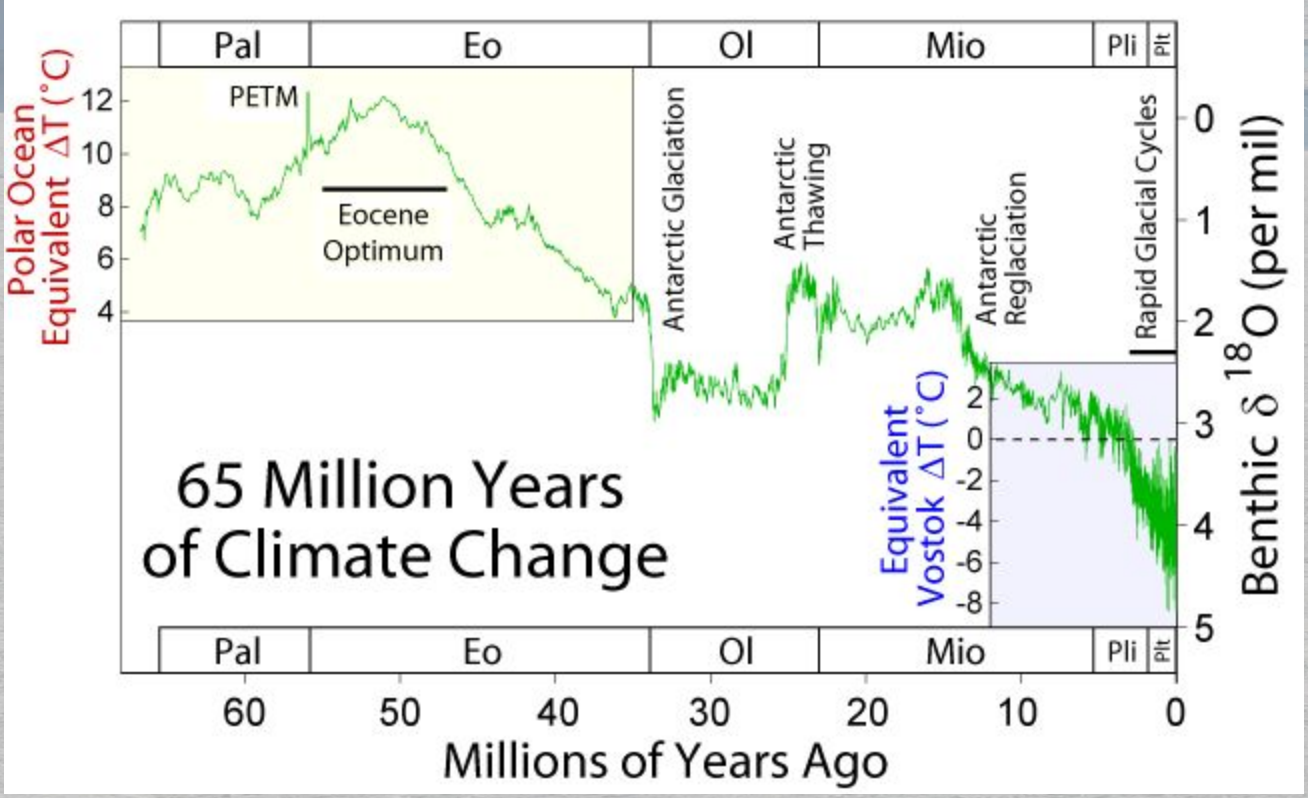
Stable Water Isotopes in Glaciology and Paleogeography

Alexey Ekaykin

Arctic and Antarctic Research Institute

ekaykin@aari.ru

Stable isotopes – main source of paleoclimatic information



Application of stable isotopes:

Science: (but not only in science)

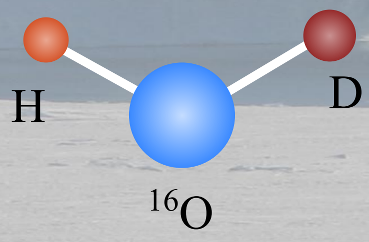
Paleoclimatology
- ice cores
- marine sediments
- corals
- speleothems (cave deposits)
- dendrochronology
- …

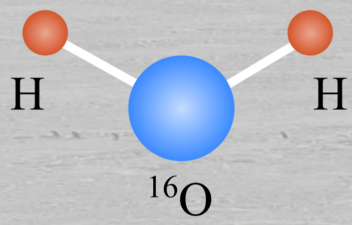
Hydrology
Glaciology
etc.

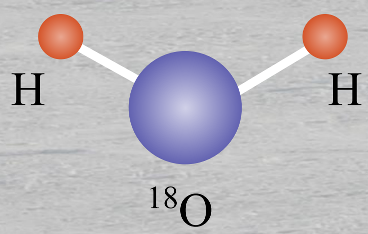
Isotopes (ισος — “equal”, “same” and τόπος — “place”) – elements that occupy the same cell in the Periodic table of elements

Frederick Soddy

Isotopes of hydrogen and oxygen







$$\delta = \frac{R_{SA} - R_{ST}}{R_{ST}} \times 1000$$

^{1}H: 1p, 0 n; m = 1, z = 1
^{2}H (D): 1p, 1n; m = 2, z = 1

^{16}O: 8 p, 8 n; m = 16, z = 8
^{17}O: 8 p, 9 n; m = 17, z = 8
^{18}O: 8 p, 10 n; m = 18, z = 8

In sea water (SMOW):

R [$^{1}H_2{}^{18}O$] = 2005 ppm
R [$HD^{16}O$] = 312 ppm

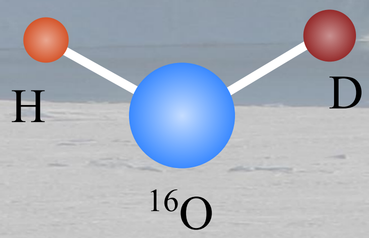
δD: from +10 to -500 ‰

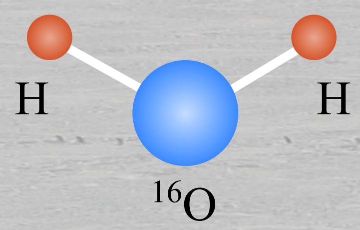
$\delta^{18}O$: from +5 to -60 ‰

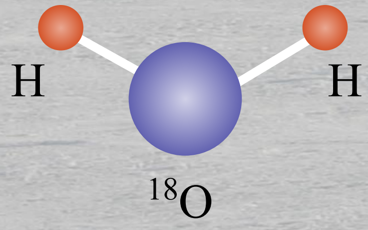
Isotopes of hydrogen and oxygen

Slightly different physical properties:

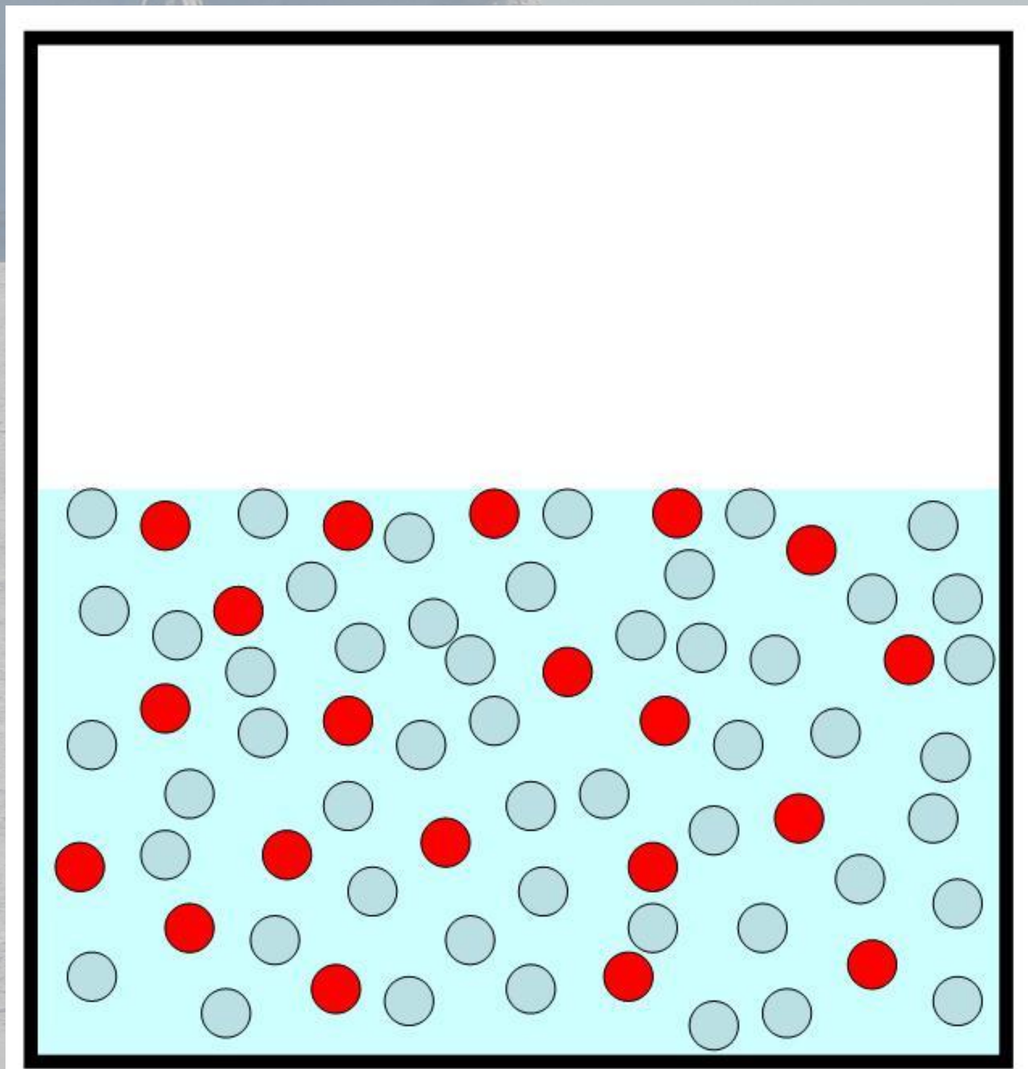
- saturation vapor pressure
- diffusion coefficients



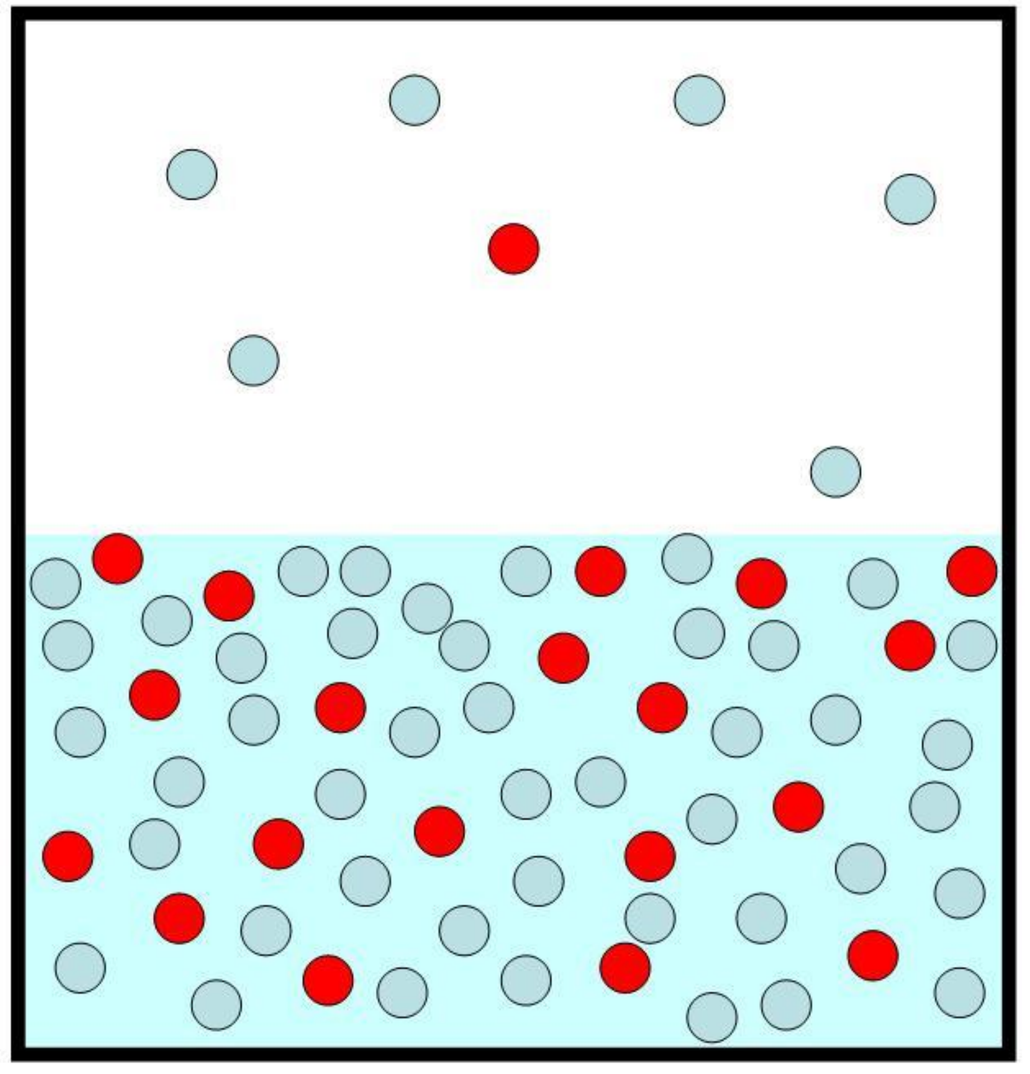




Behaviour of isotopes during evaporation of water

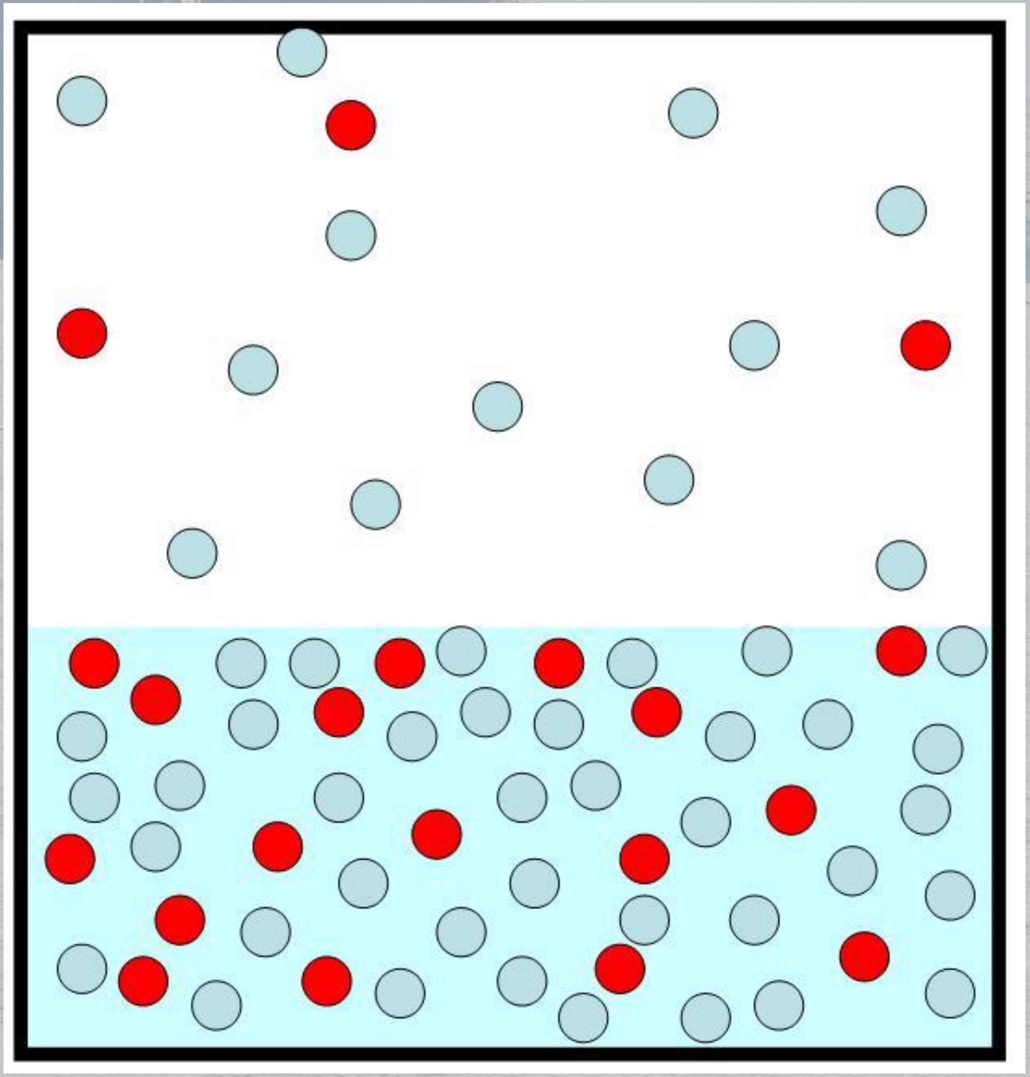


Behaviour of isotopes during evaporation of water



First portion of water vapor is enriched in light isotopes

Behaviour of isotopes during evaporation of water

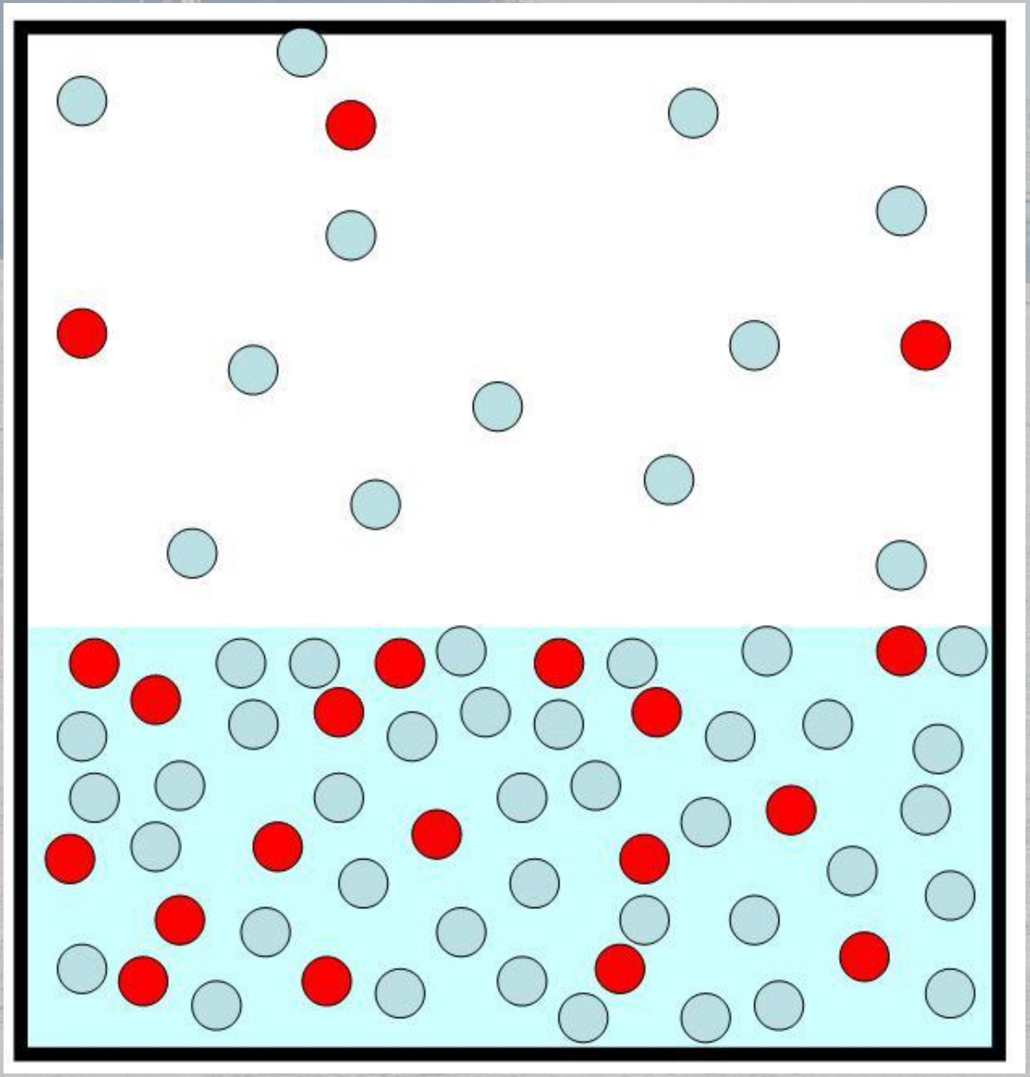


System comes to equilibrium:
water vapor is saturated

Saturation vapor pressure is **less** for heavy molecules than for light molecules

Concentration of heavy isotopes in vapor is less than in water

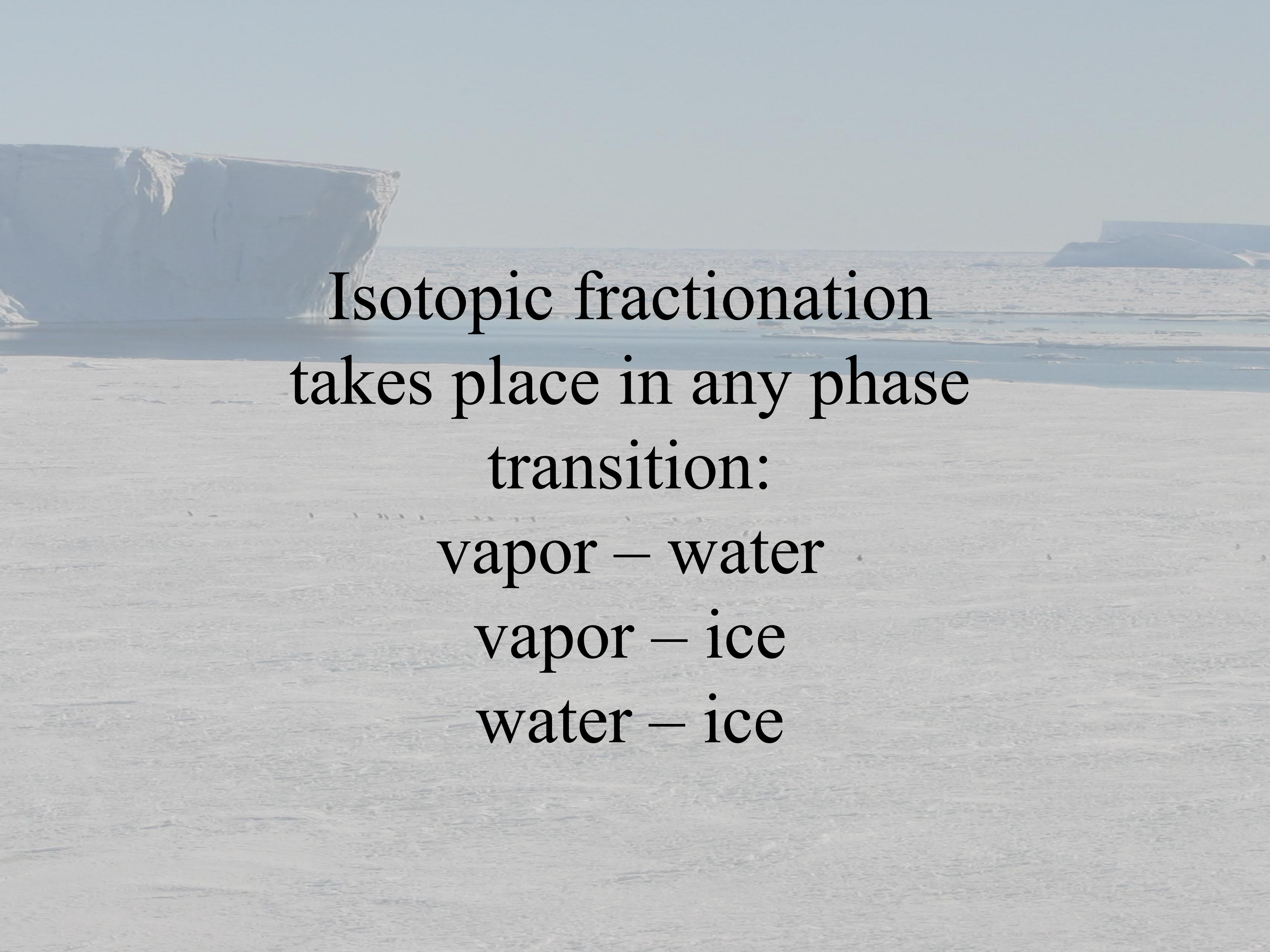
Behaviour of isotopes during evaporation of water



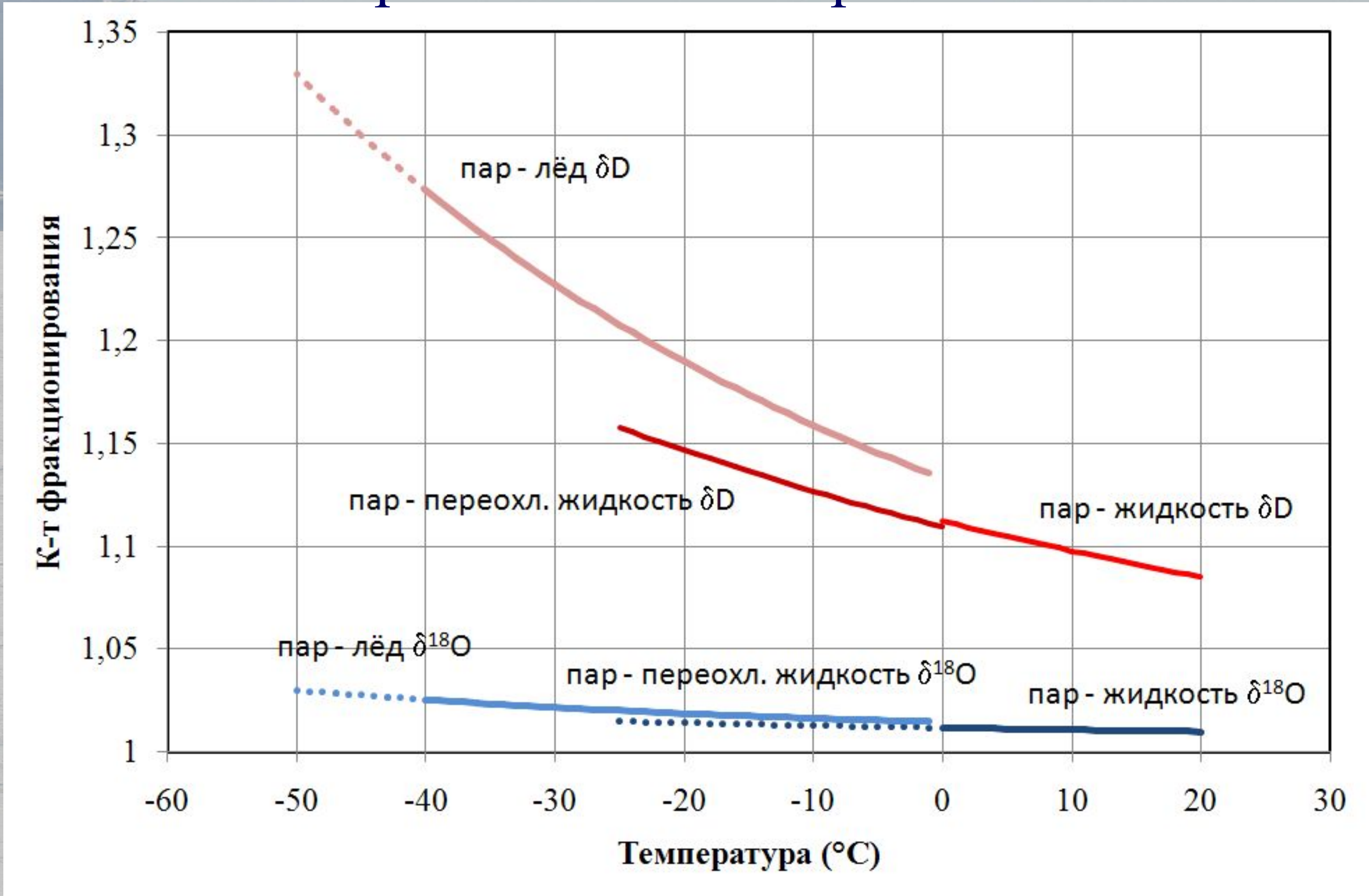
Fractionation coefficient:

$\alpha = R_{water} / R_{vapor}$

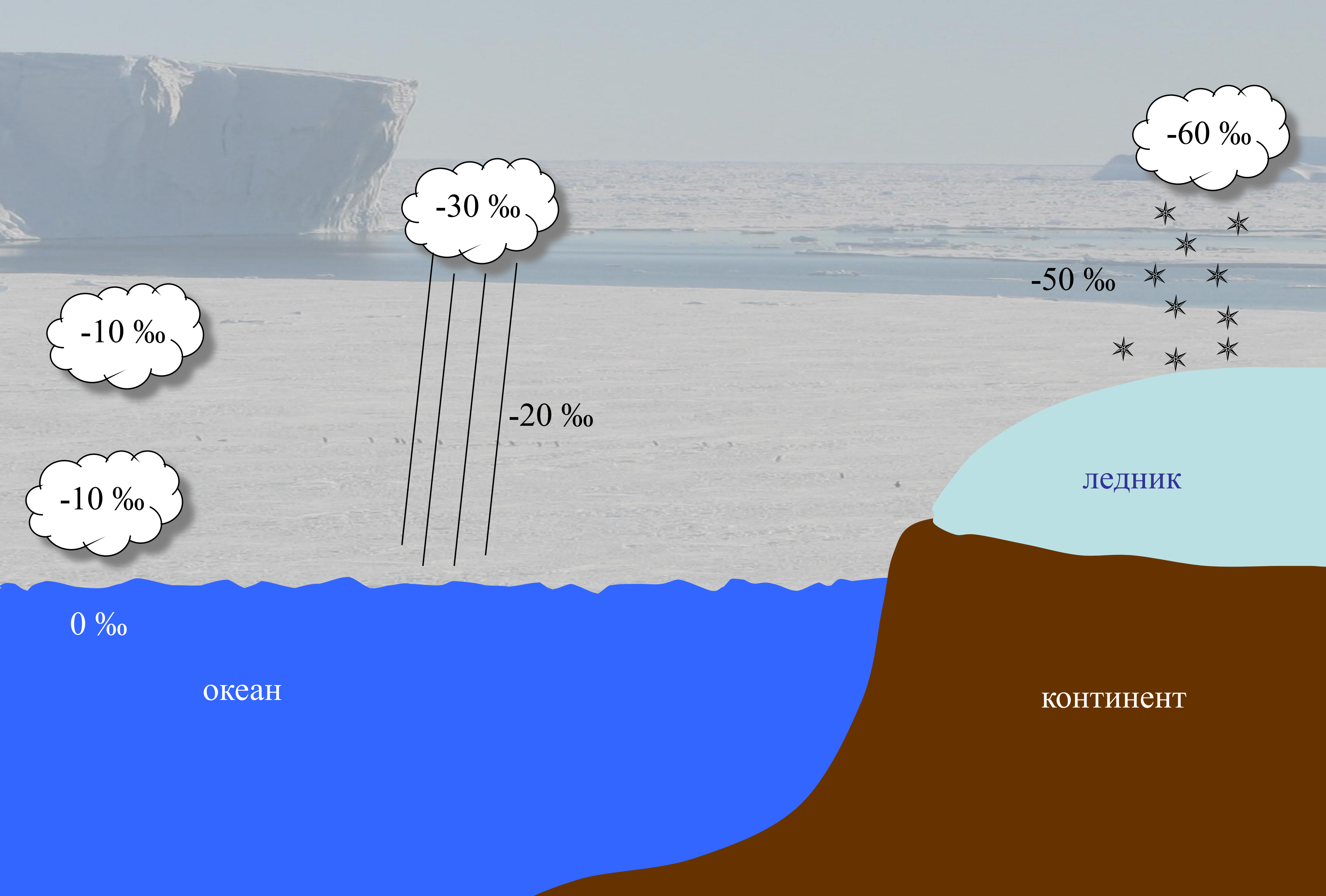
α = 1,1 … 1,3 for δD
α = 1,01 … 1,03 for $\delta^{18}O$


Isotopic fractionation
takes place in any phase
transition:
vapor – water
vapor – ice
water – ice

Equilibrium fractionation coefficients for vapour-water and vapour-ice



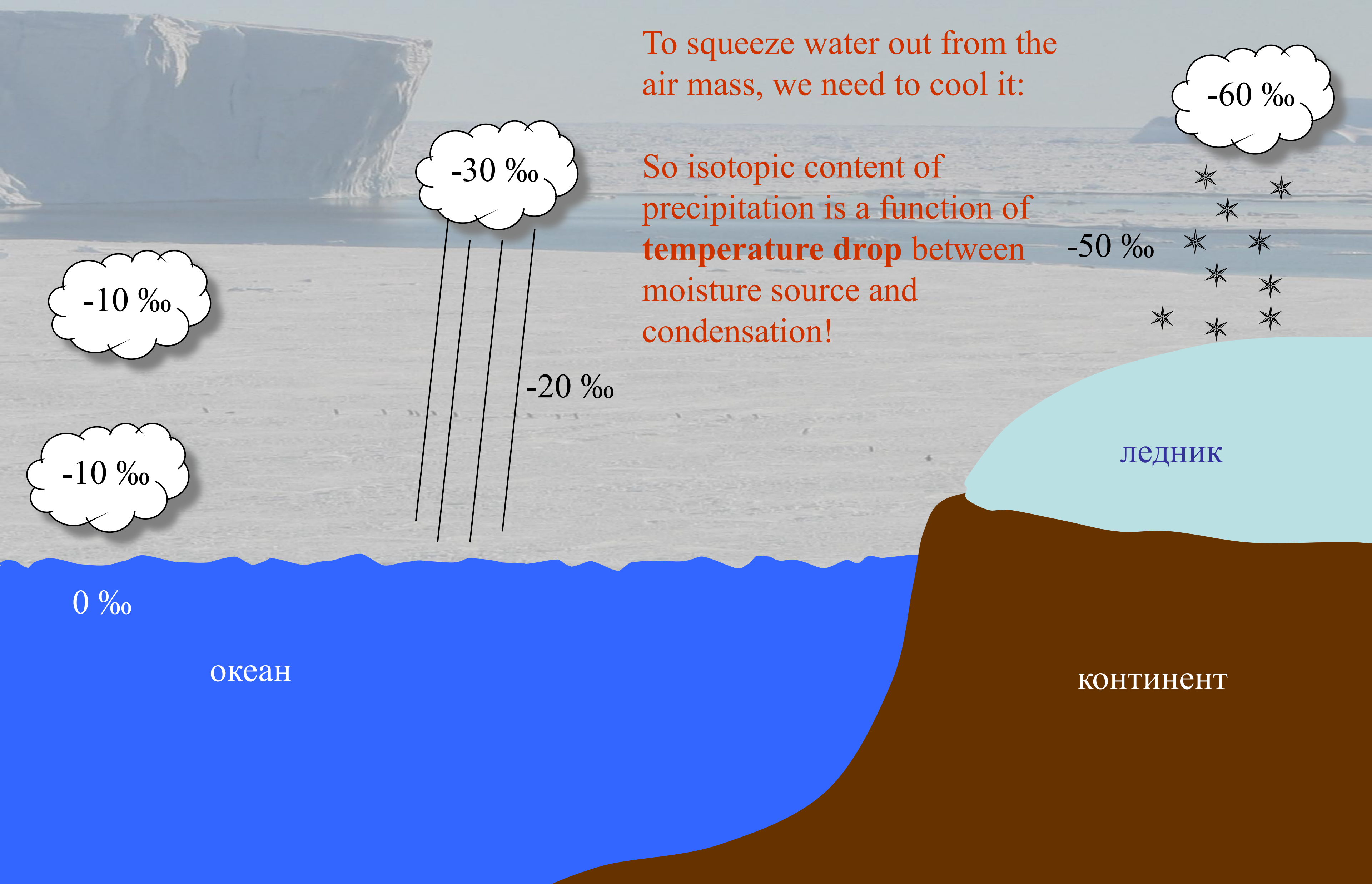
Distillation of heavy isotopes from air mass



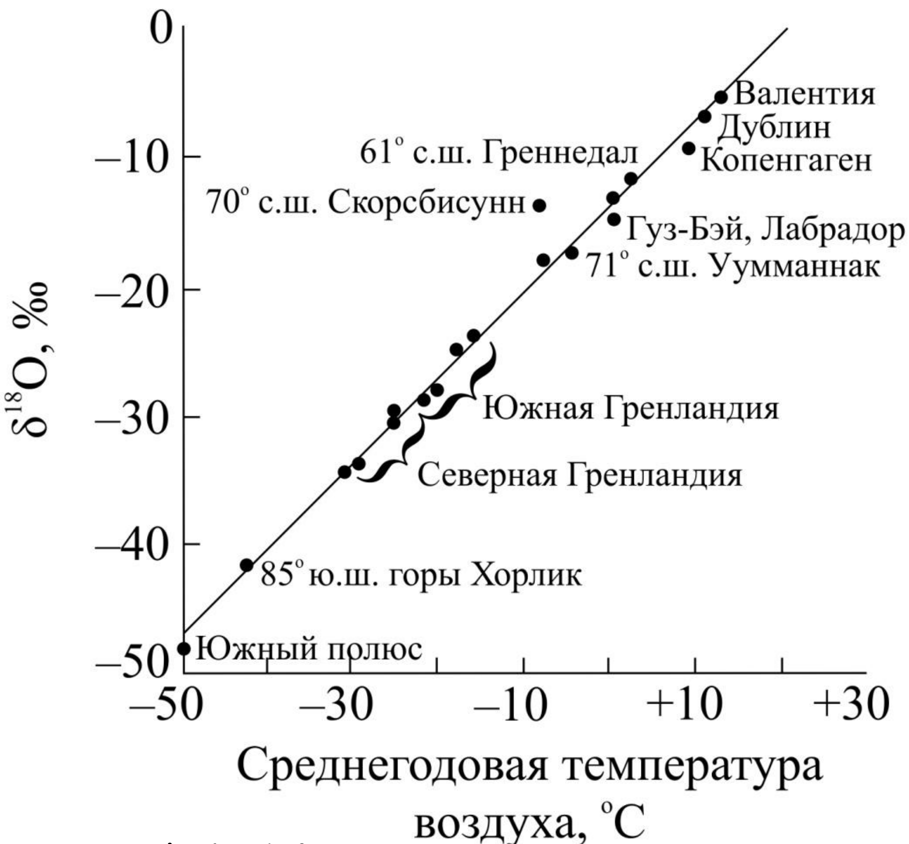
Distillation of heavy isotopes from air mass

To squeeze water out from the air mass, we need to cool it:

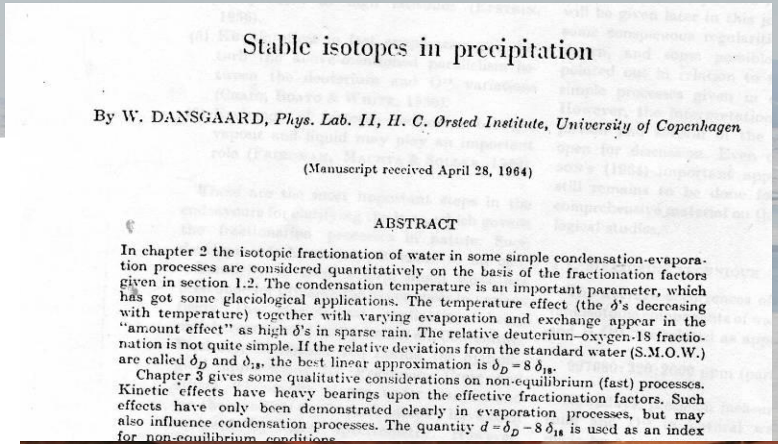
So isotopic content of precipitation is a function of **temperature drop** between moisture source and condensation!



Isotopic content of precipitation is a function of temperature!



Dansgaard, 1964



Stable isotopes in precipitation

By W. DANSGAARD, *Phys. Lab. II, H. C. Ørsted Institute, University of Copenhagen*

(Manuscript received April 28, 1964)

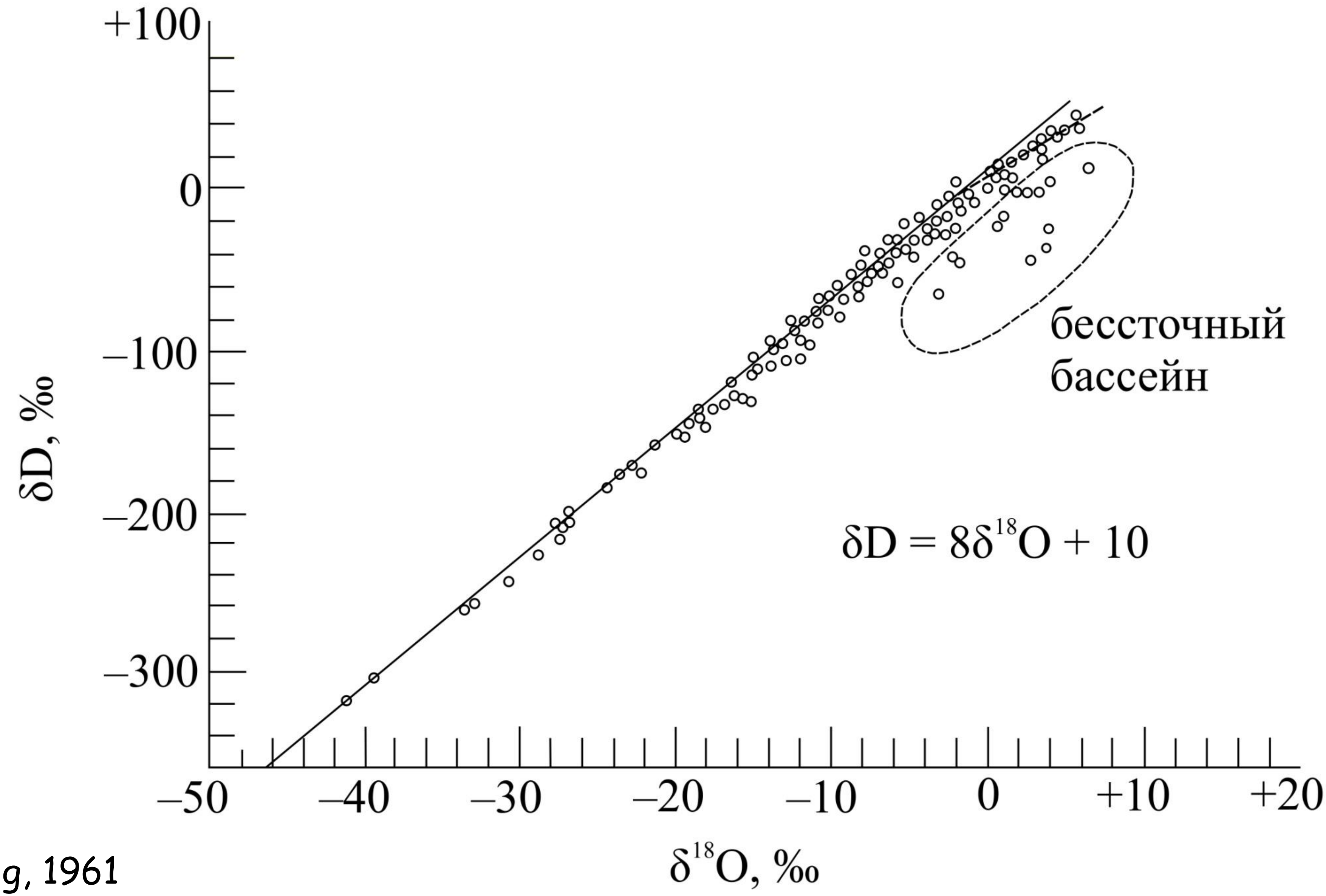
ABSTRACT

In chapter 2 the isotopic fractionation of water in some simple condensation-evaporation processes are considered quantitatively on the basis of the fractionation factors given in section 1.2. The condensation temperature is an important parameter, which has got some glaciological applications. The temperature effect (the δ's decreasing with temperature) together with varying evaporation and exchange appear in the "amount effect" as high δ's in sparse rain. The relative deuterium-oxygen-18 fractionation is not quite simple. If the relative deviations from the standard water (S.M.O.W.) are called δ_D and δ_{18}, the best linear approximation is $\delta_D = 8\,\delta_{18}$.
Chapter 3 gives some qualitative considerations on non-equilibrium (fast) processes. Kinetic effects have heavy bearings upon the effective fractionation factors. Such effects have only been demonstrated clearly in evaporation processes, but may also influence condensation processes. The quantity $d = \delta_D - 8\,\delta_{18}$ is used as an index for non-equilibrium conditions.

Isotopic content of precipitation is a function of temperature!

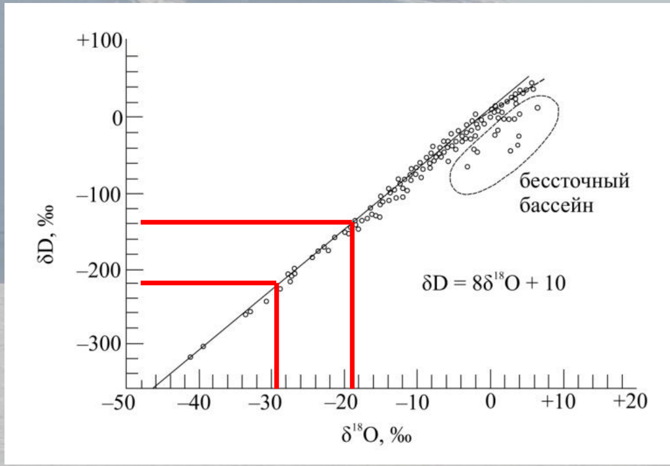
Latitudinal effect
Altitudinal effect
Seasonal effect

δD versus $\delta^{18}O$: Global Meteoric Water Line



Craig, 1961

δD versus $\delta^{18}O$: Global Meteoric Water Line



Why the slope between deuterium and oxygen-18 is 8?

Ratio between isotopic composition of vapor and water:

$R_{water} = \alpha R_{vapor}$

Let's write it in "δ" notation:

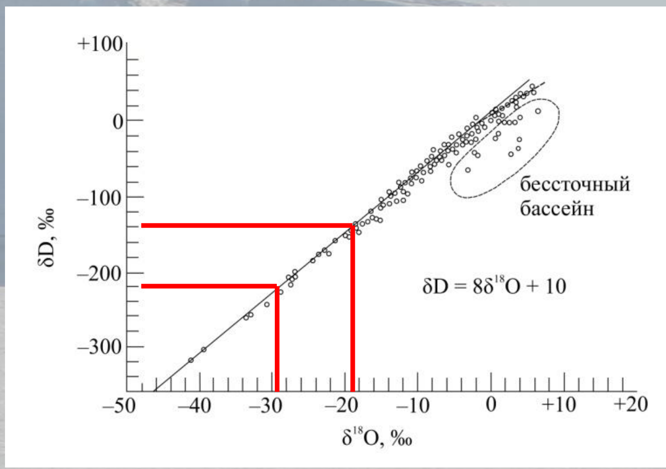
$$\frac{\delta_{water}}{1000} + 1 = \alpha \left(\frac{\delta_{vapor}}{1000} + 1 \right)$$

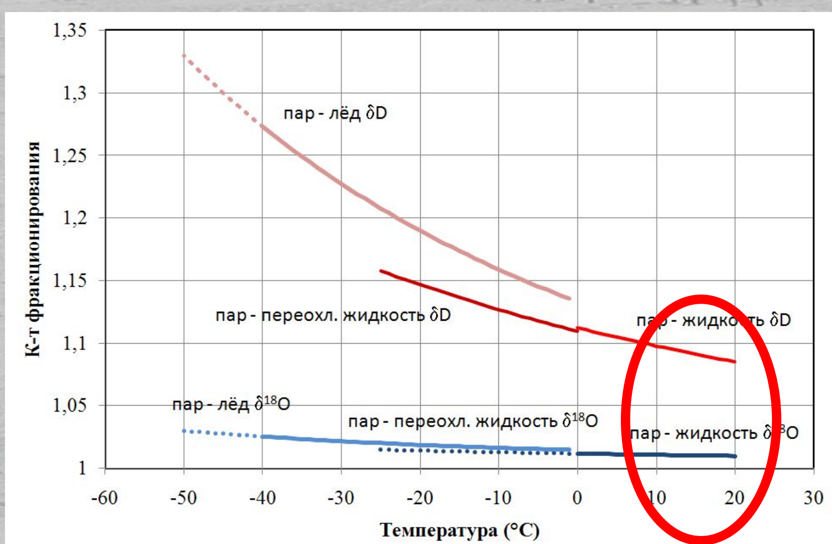
The slope between δD and $\delta^{18}O$ is:

$$slope = \frac{\delta D_{water} - \delta D_{vapor}}{\delta^{18}O_{water} - \delta^{18}O_{vapor}}$$

$$slope = \frac{\dfrac{\delta D_{water}}{1000} + 1}{\dfrac{\delta^{18}O_{water}}{1000} + 1} \frac{\alpha_D - 1}{\alpha_{18} - 1}$$

δD versus δ^{18}O: Global Meteoric Water Line





For high temperatures:

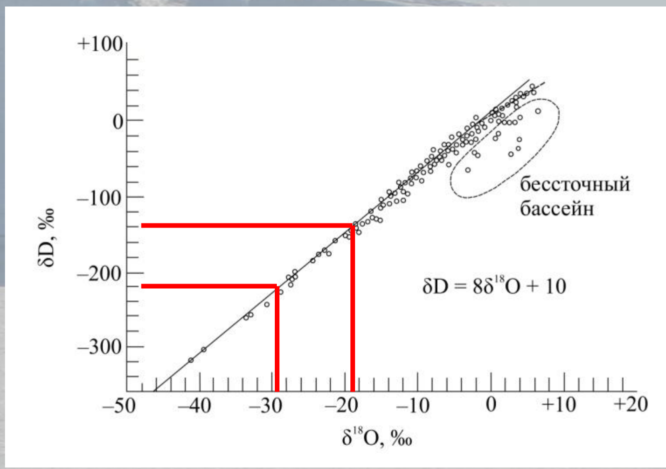
$$slope = \frac{\dfrac{\delta D_{water}}{1000}+1}{\dfrac{\delta^{18}O_{vapor}}{1000}+1} \cdot \frac{\alpha_{waterD}-1}{\alpha_{vapor18}-1}$$

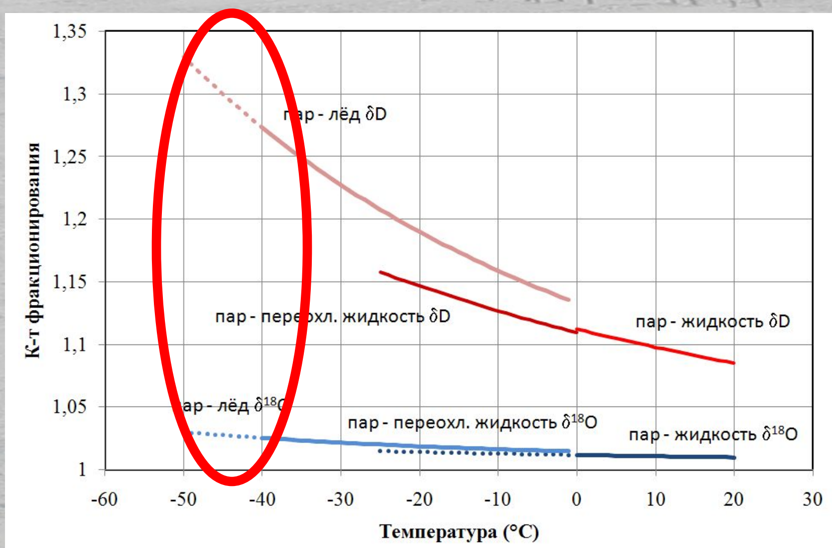
$\approx 0{,}9$

≈ 9

Slope is 8

δD versus δ^{18}O: Global Meteoric Water Line





For low temperatures:

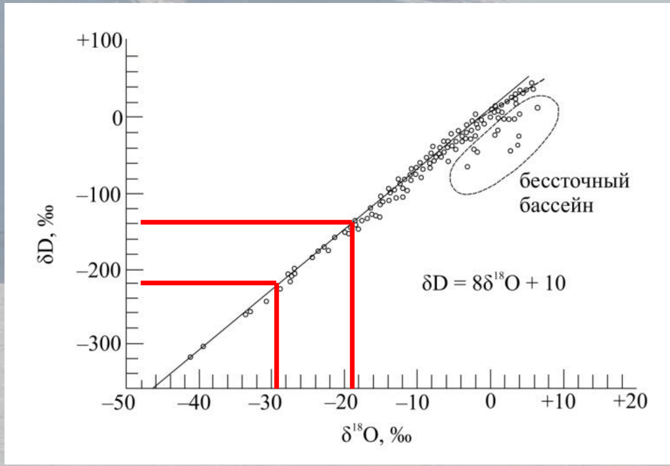
$$slope = \frac{\frac{\delta D_{water}}{1000}+1}{\frac{\delta^{18}O_{vapor}}{1000}+1} \cdot \frac{\alpha_{waterD}-1}{\alpha_{vapor18}-1}$$

≈ 0,6 ≈ 13

Slope is 8

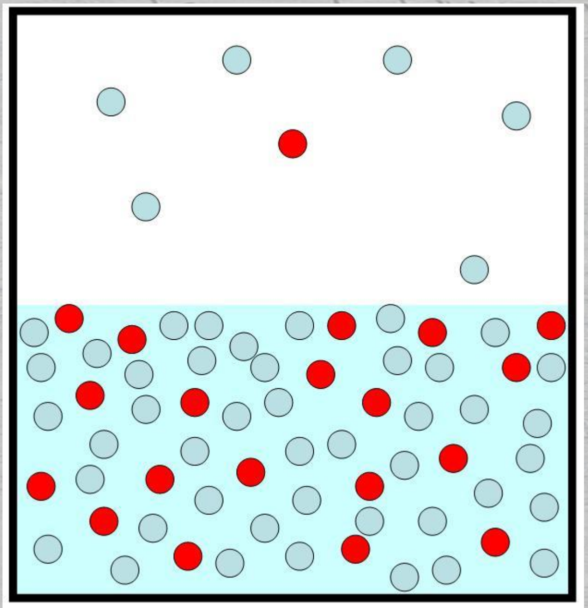
The meteoric water line is actually not perfectly linear

Deuterium excess



Why free member of the GMWL is not zero?!

Well, because of kinetic fractionation during the evaporation from sea water



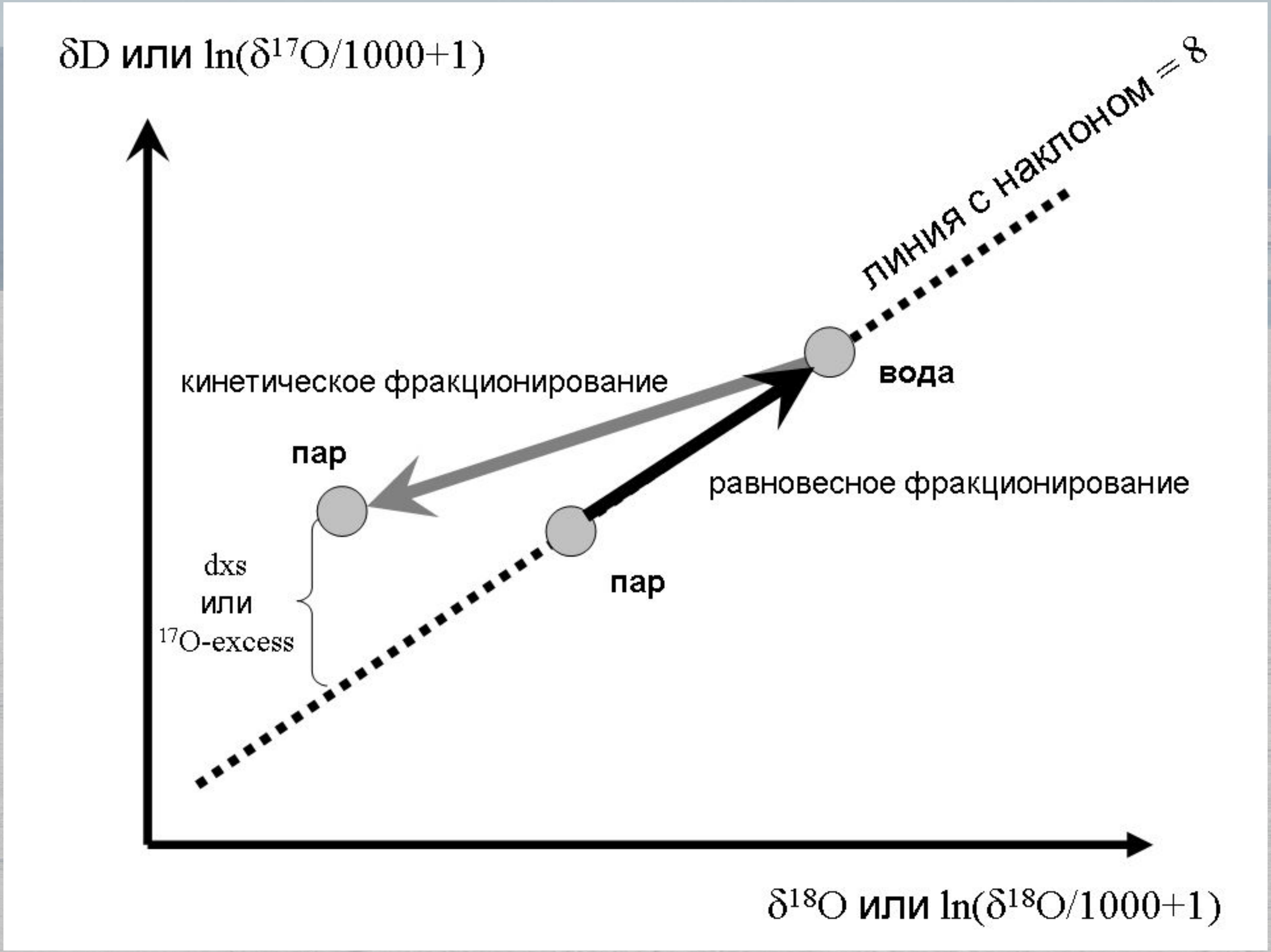
Let's introduce "deuterium excess":

$dxs = \delta D - 8\ \delta^{18}O$

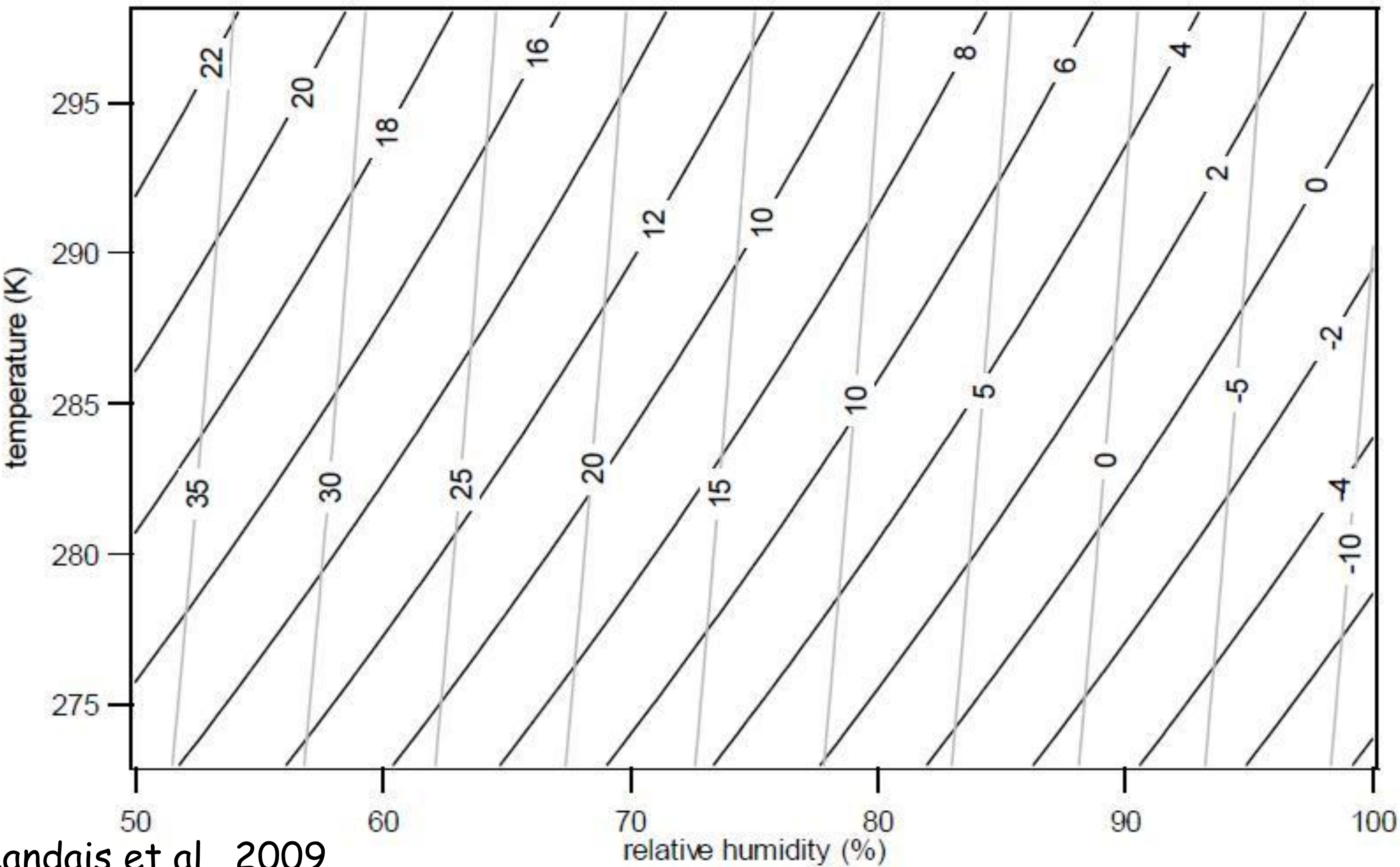
dxs is changing during kinetic fractionation (evaporation)

and is "constant" during equilibrium fractionation (condensation)

Deuterium excess

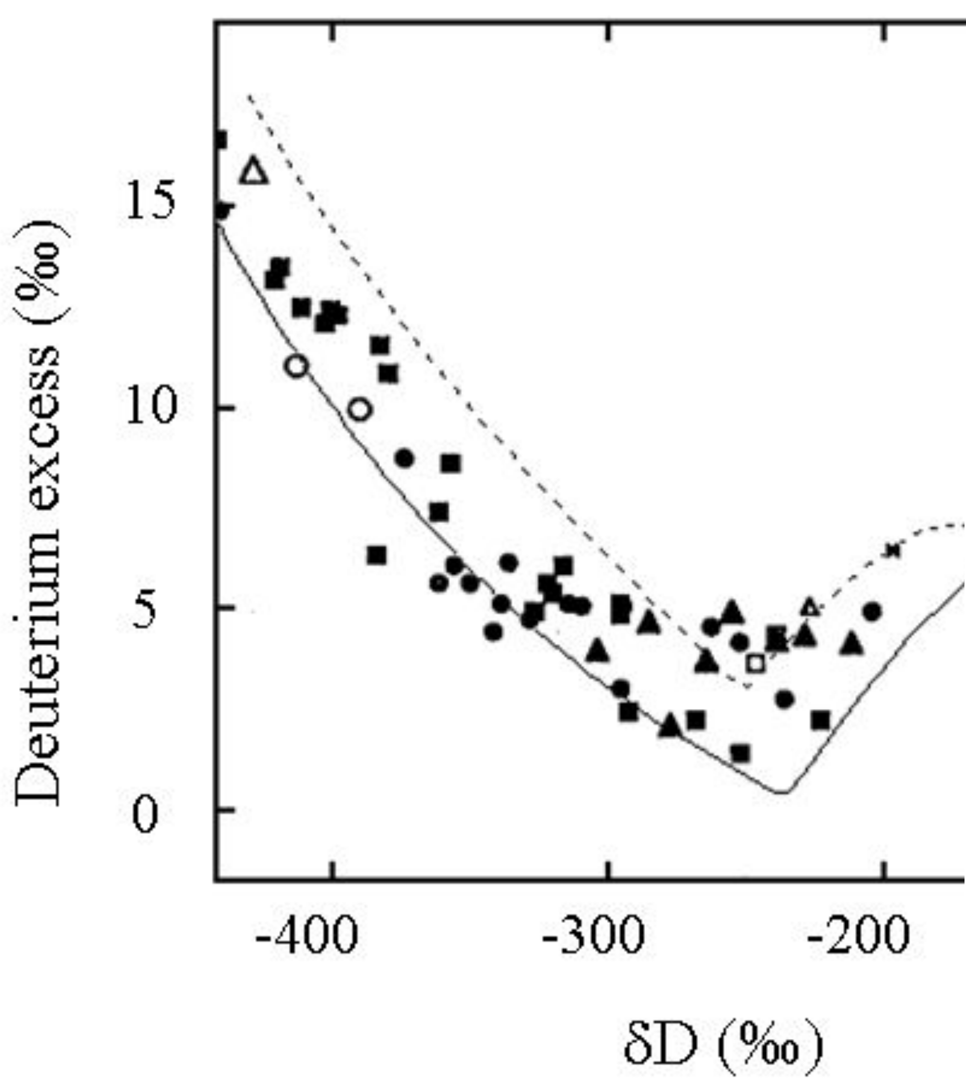


Deuterium excess as a characteristic of moisture source conditions

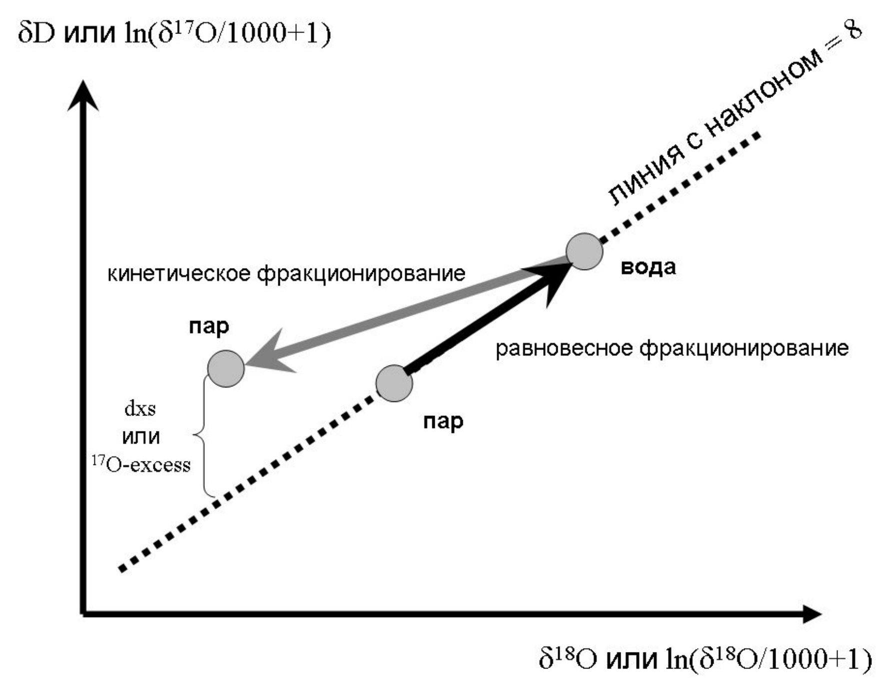


Landais et al., 2009

…well, it’s not that simple actually

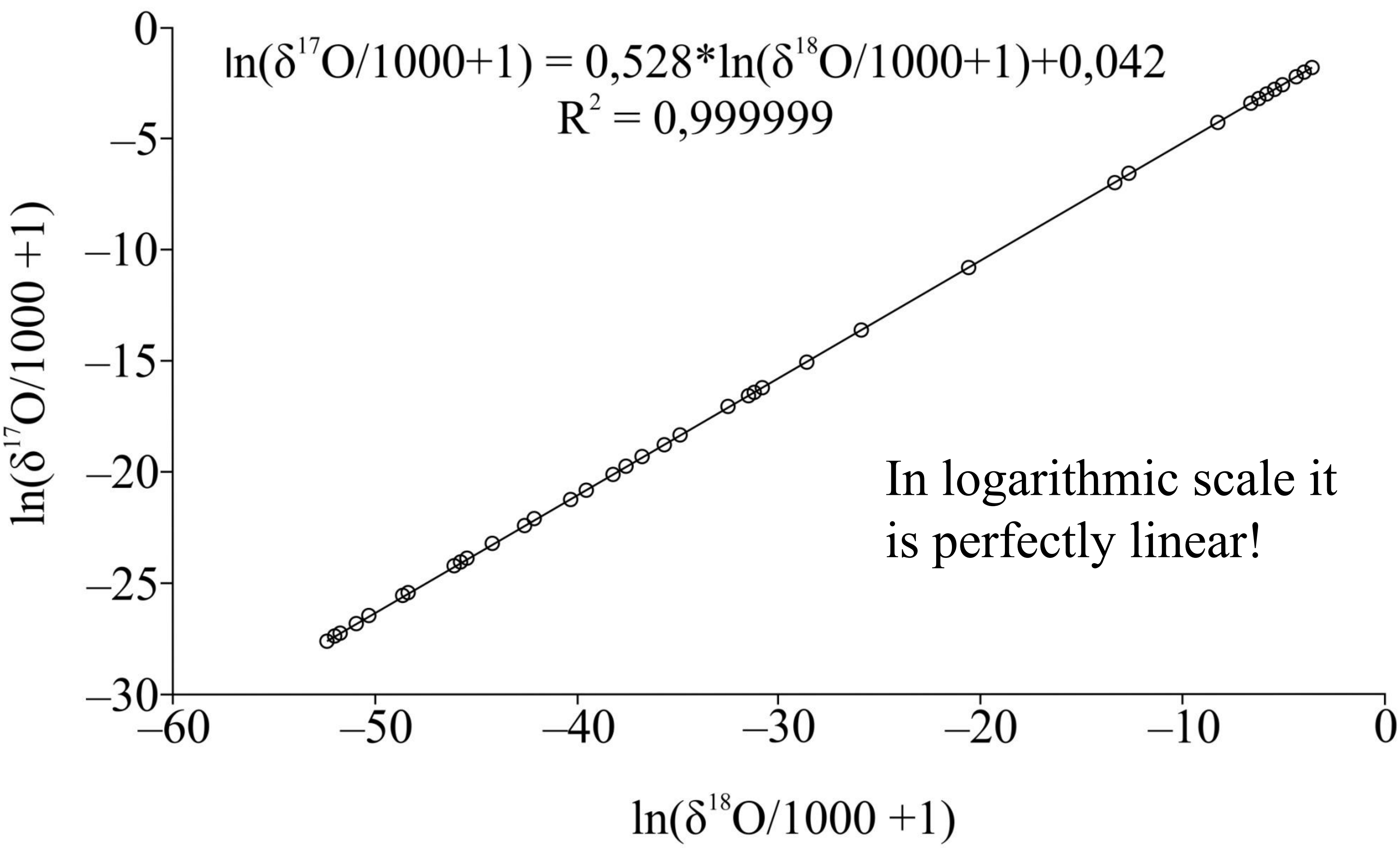


In the region of low temperatures the $\delta D/\delta^{18}O$ slope is < 8 ⇒ dxs is increasing



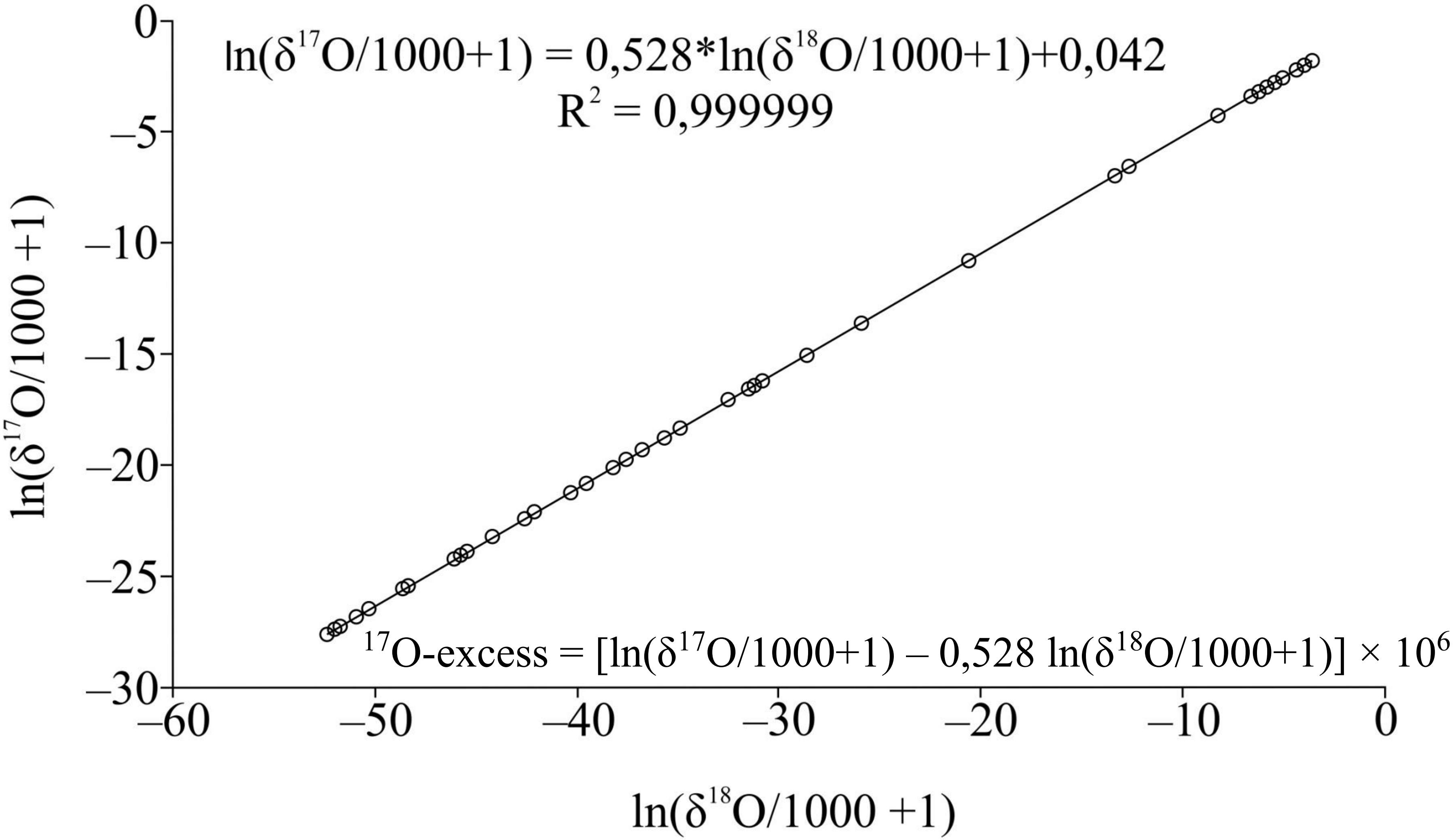
Salamatin et al., 2004

Oxygen-17 versus oxygen-18



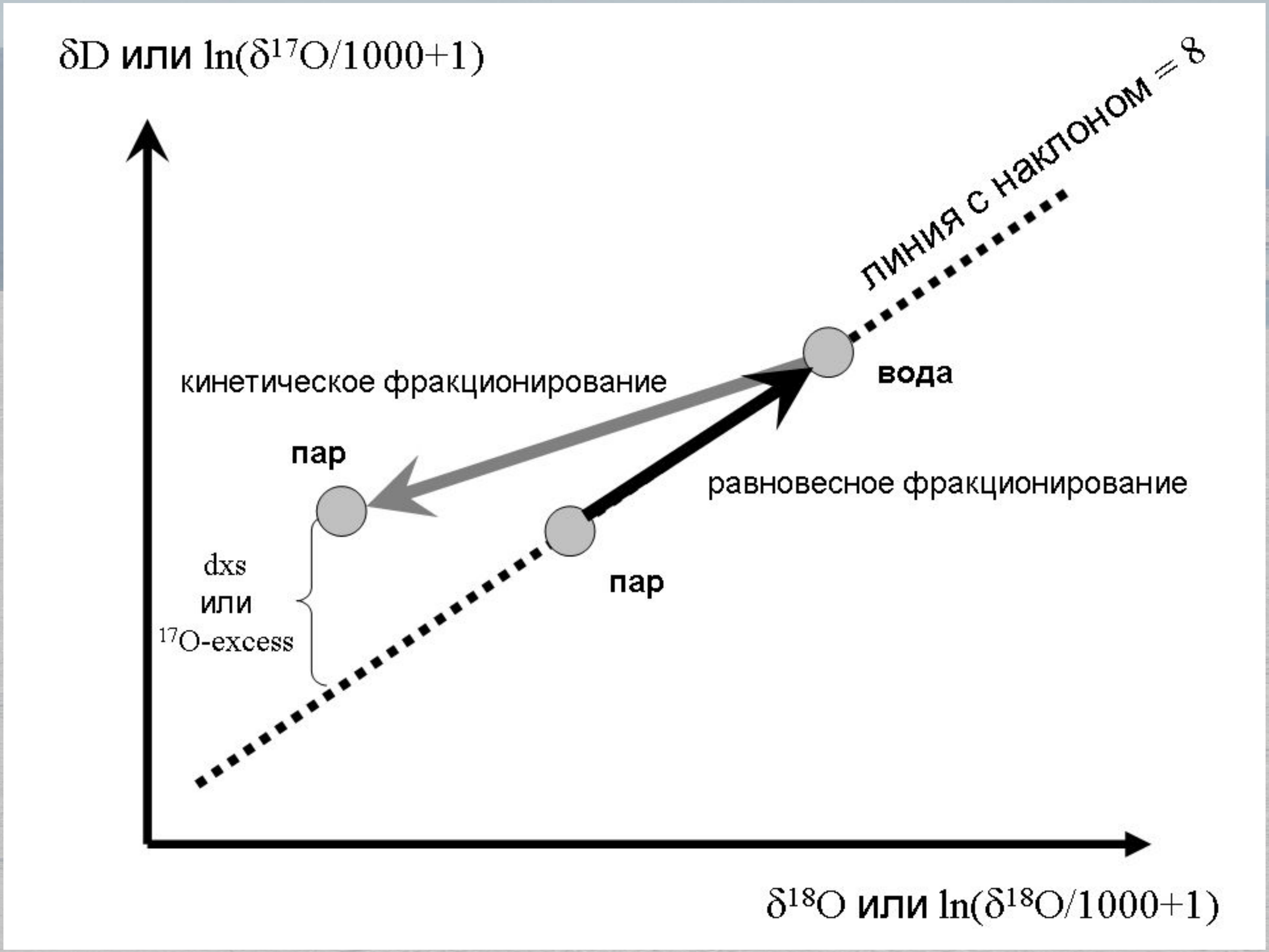
Landais et al., 2009

Oxygen-17 versus oxygen-18



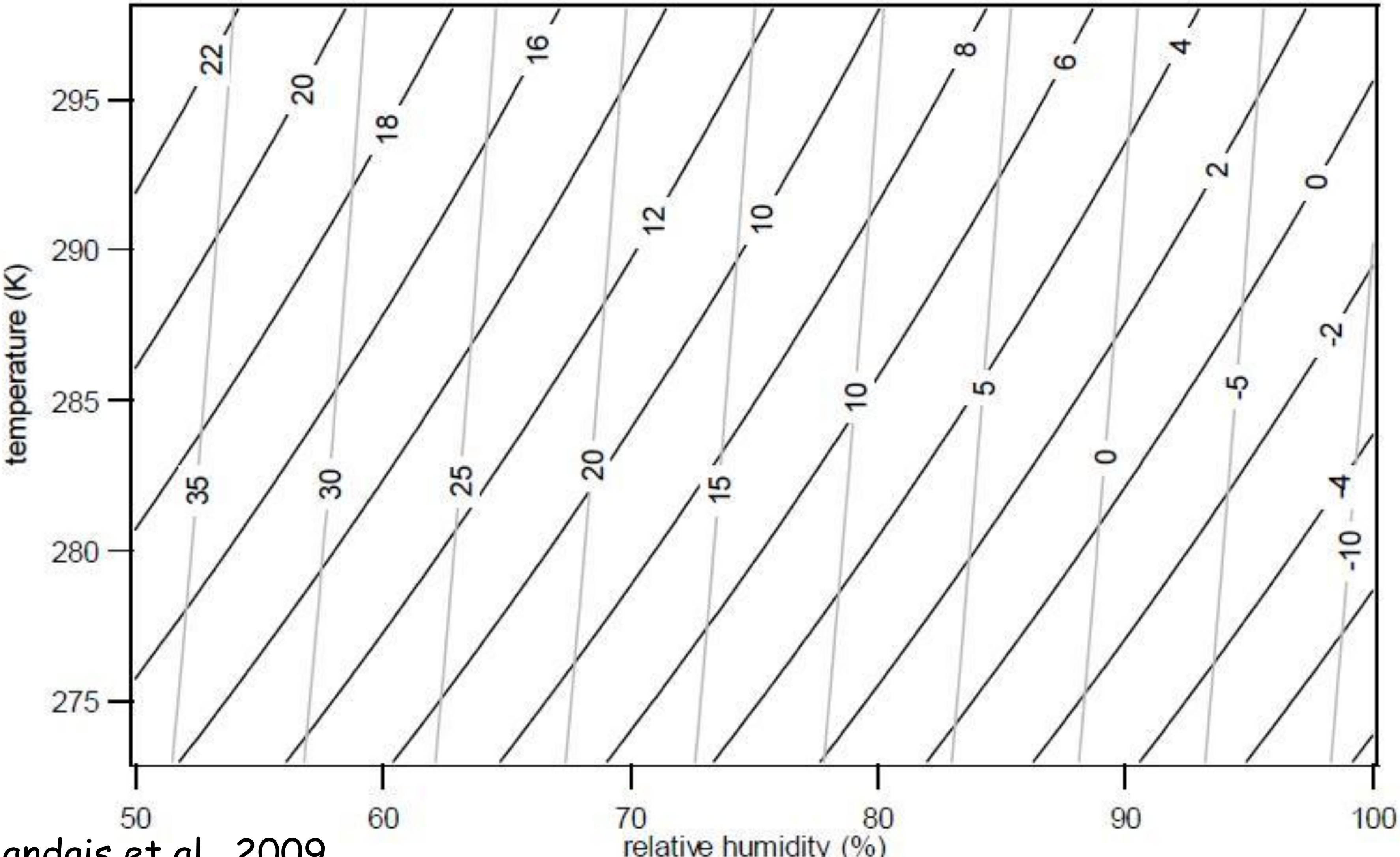
Landais et al., 2009

^{17}O-excess



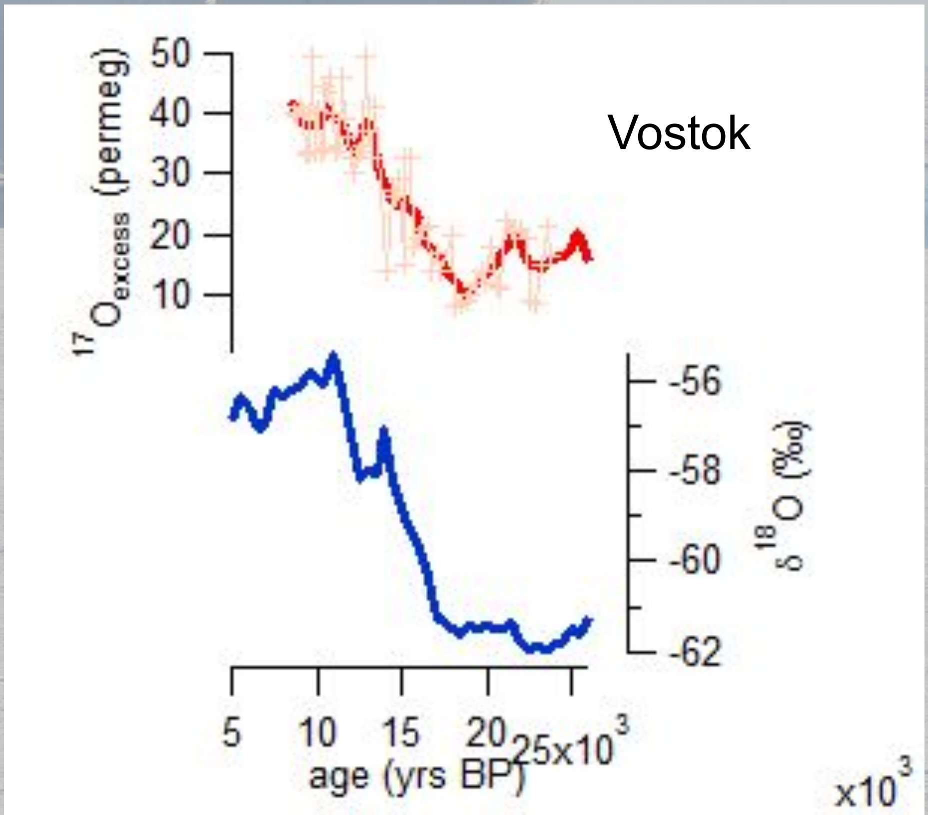
δD или ln(δ17O/1000+1)
линия с наклоном = 8
кинетическое фракционирование
вода
пар
равновесное фракционирование
dxs
или
17O-excess
пар
δ18O или ln(δ18O/1000+1)

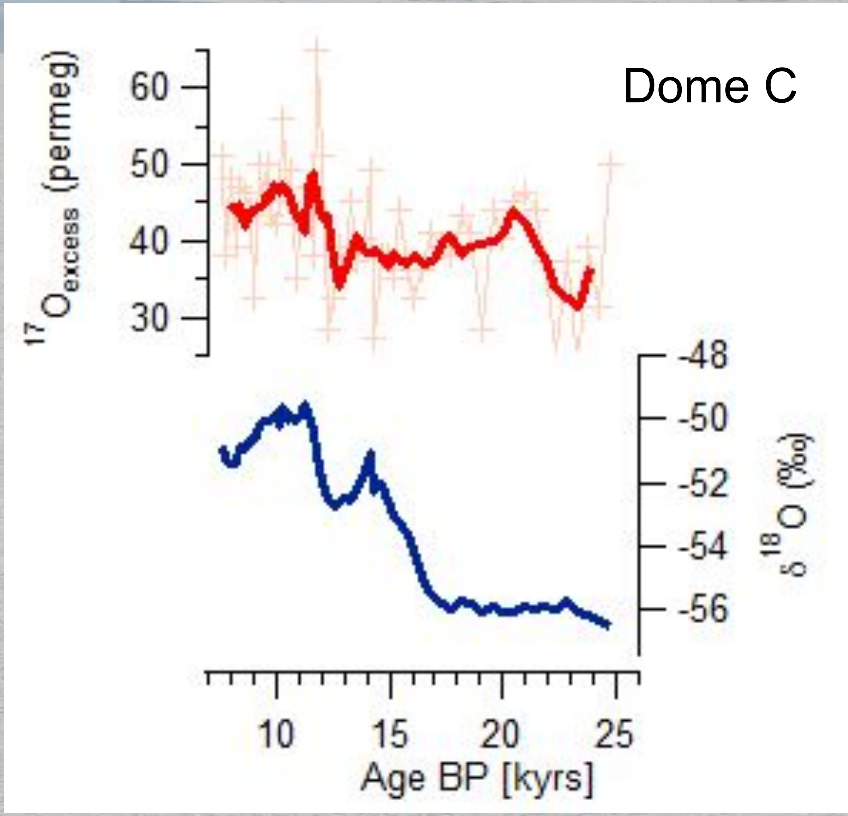
^{17}O-excess does not depend on moisture source temperature!



Landais et al., 2009

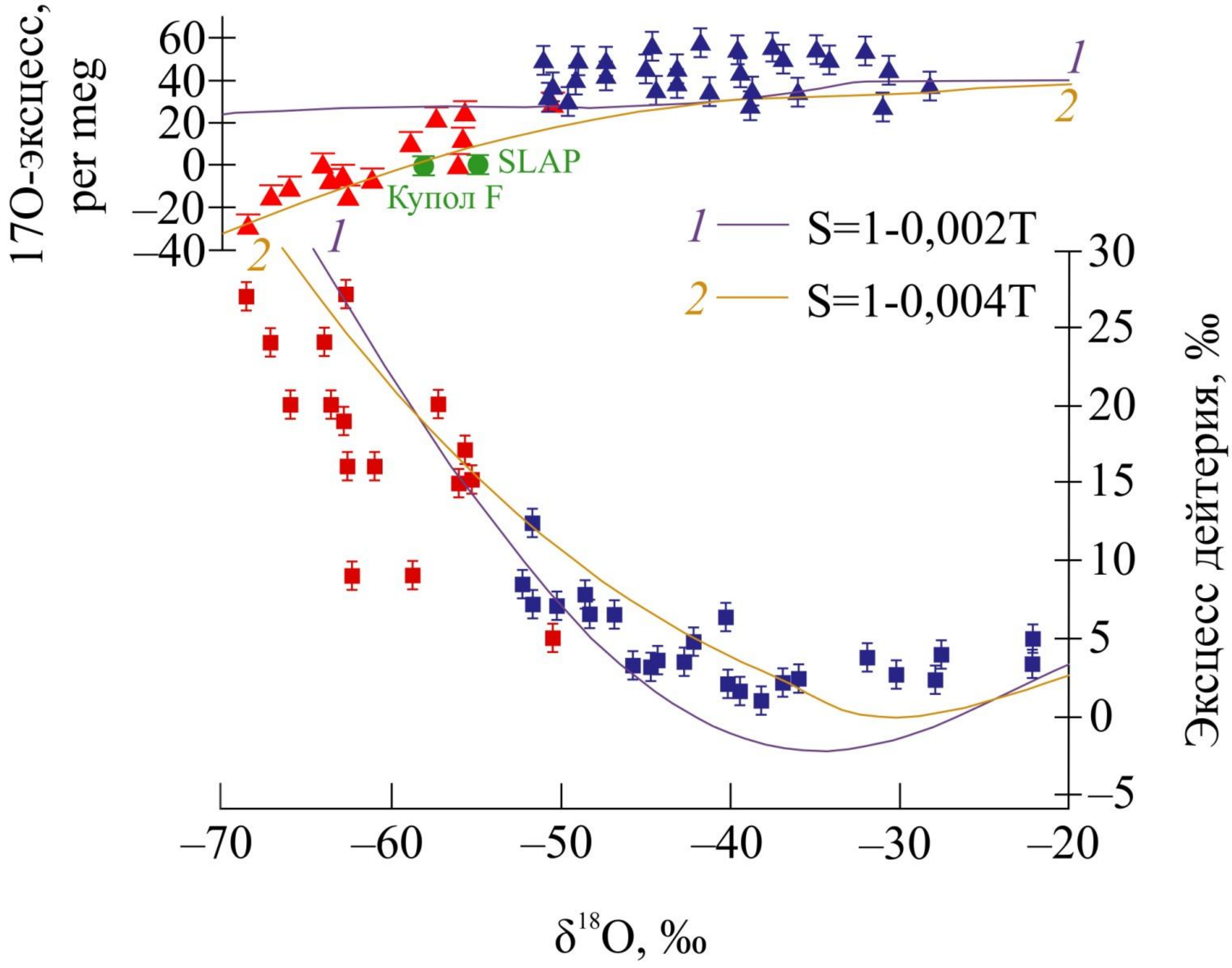
^{17}O-excess is a proxy of air humidity over ocean (?)





Landais et al., 2008

^{17}O-excess is changing during kinetic fractionation in ice clouds

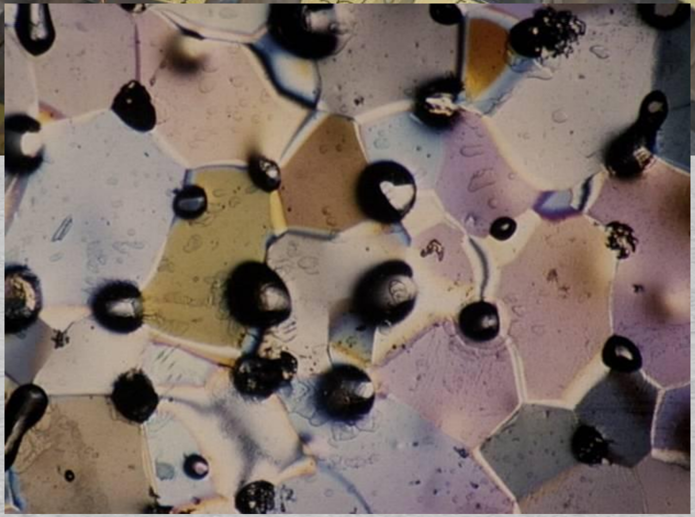


Landais et al., 2012

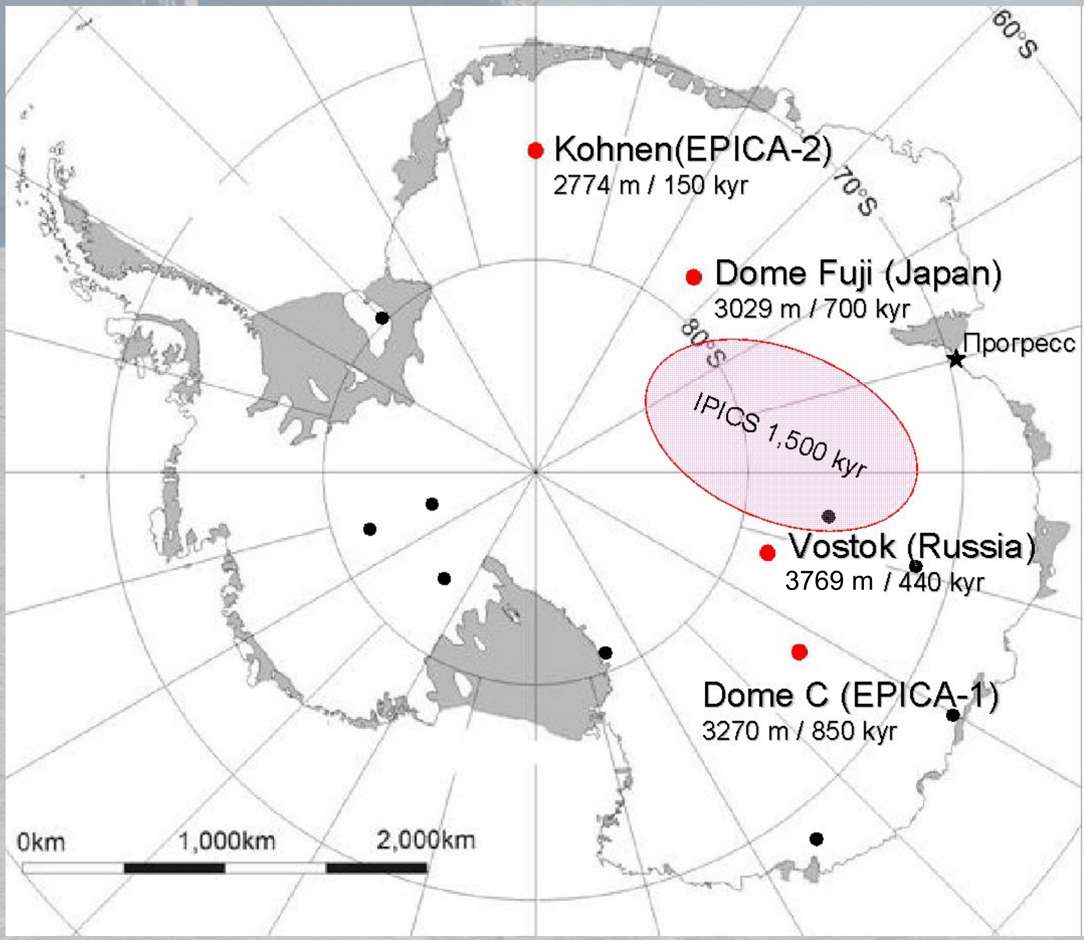
Factors controlling dxs and ^{17}O-excess

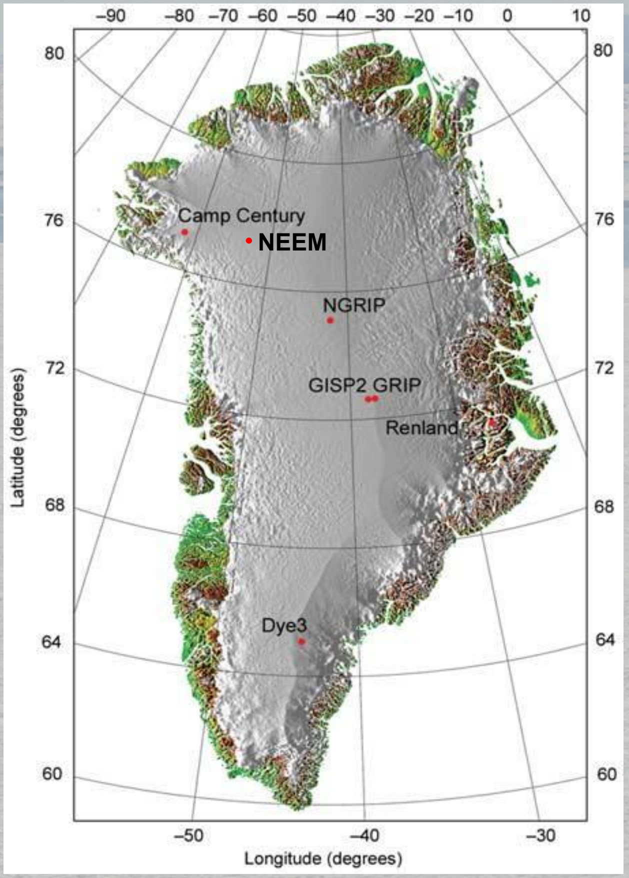
Factor:	dxs	^{17}O-excess
Sea surface temperature	yes	no
Air humidity during evaporation	yes	yes
Equilibrium fractionation during liquid precipitation	no ⇒ yes	no
Kinetic fractionation in ice clouds	yes	yes

Use of stable water isotopes in Paleoclimatology

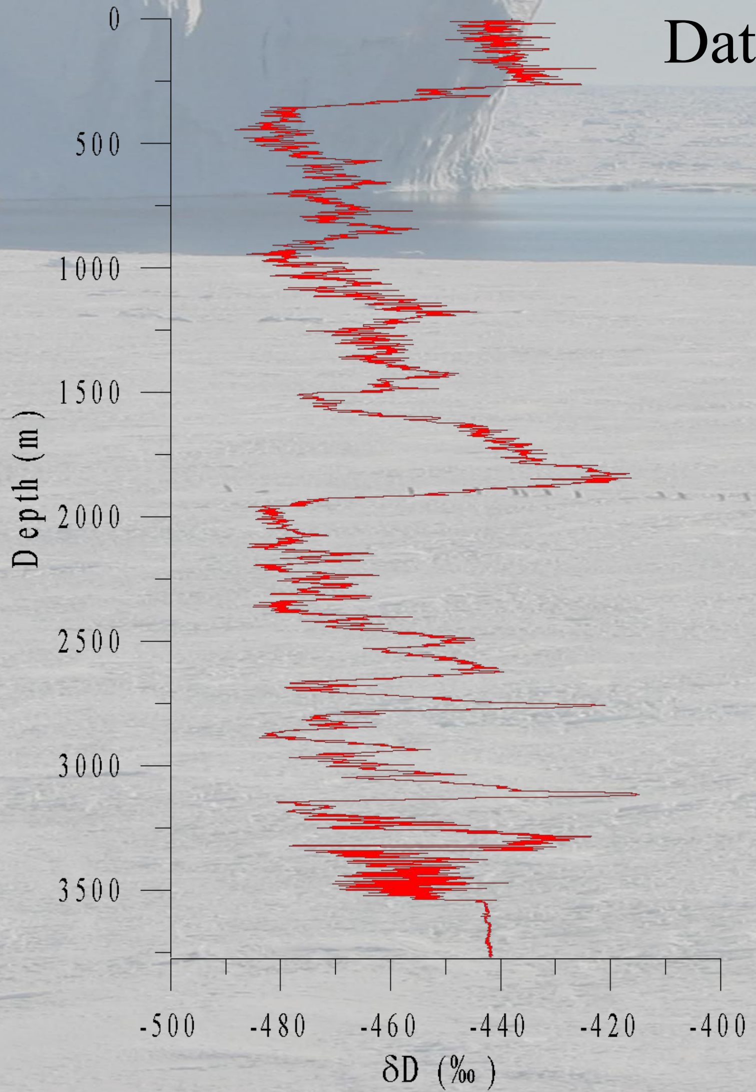


Deep ice drilling projects in Antarctica and Greenland

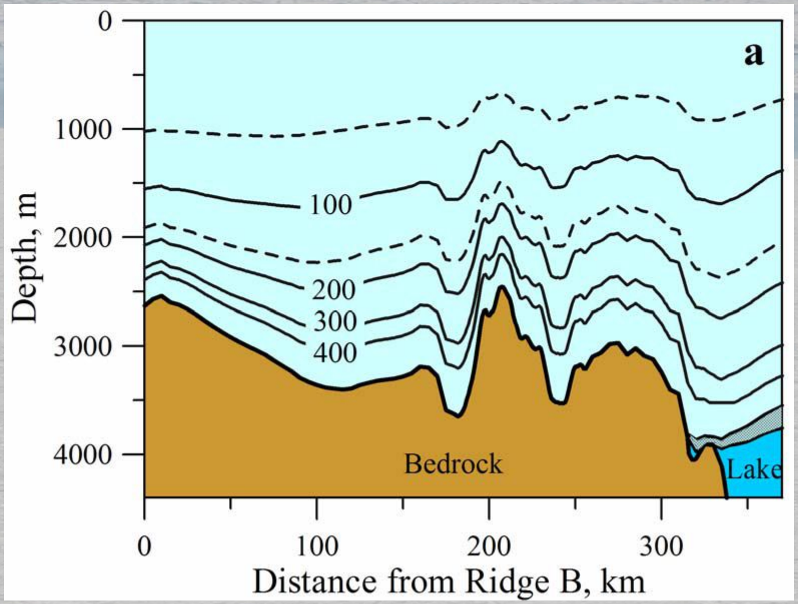




Transforming vertical profile of ice core isotopic composition into time-series of air temperature



Dating (depth ⇒ time)

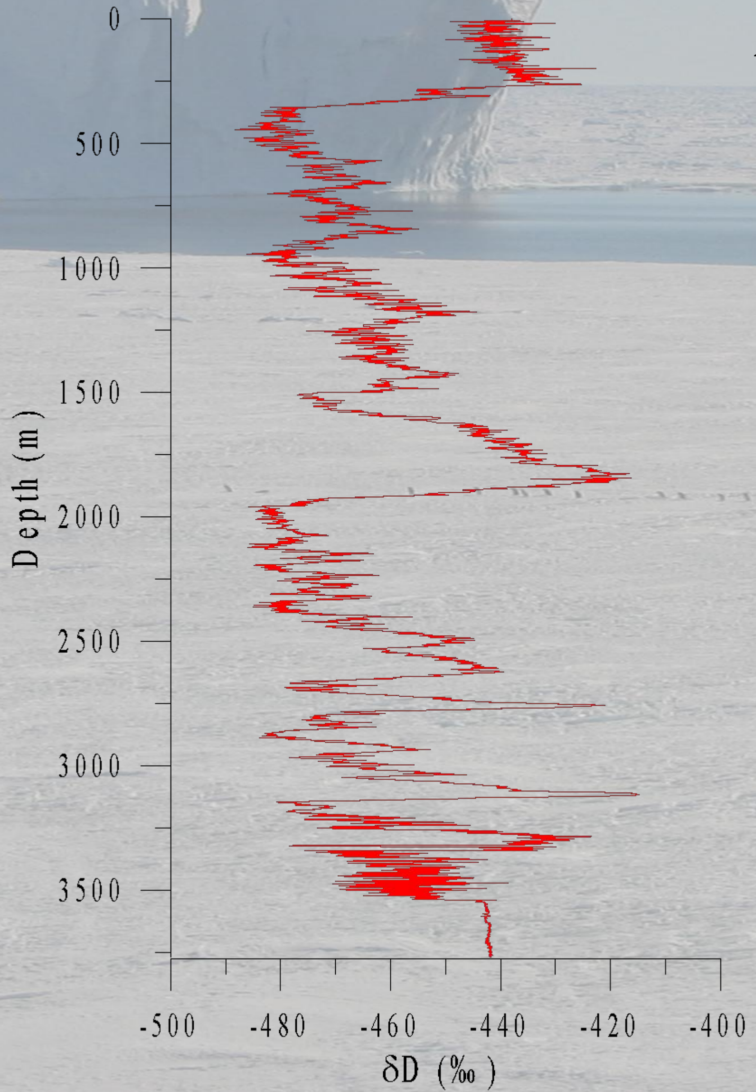


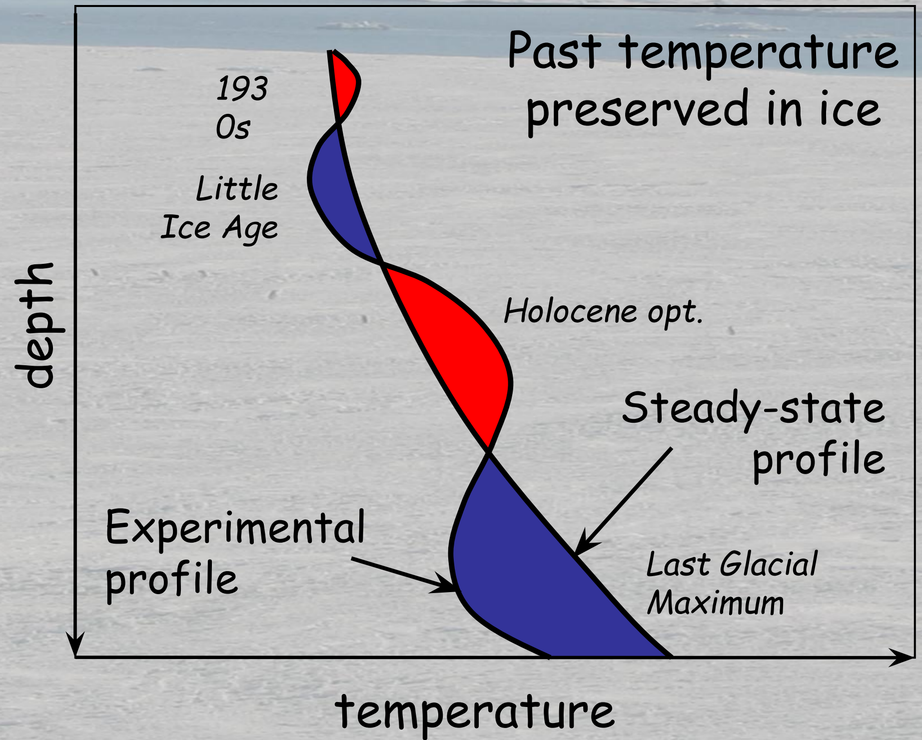
Salamatin et al., 2009

Isotope-temperature calibration

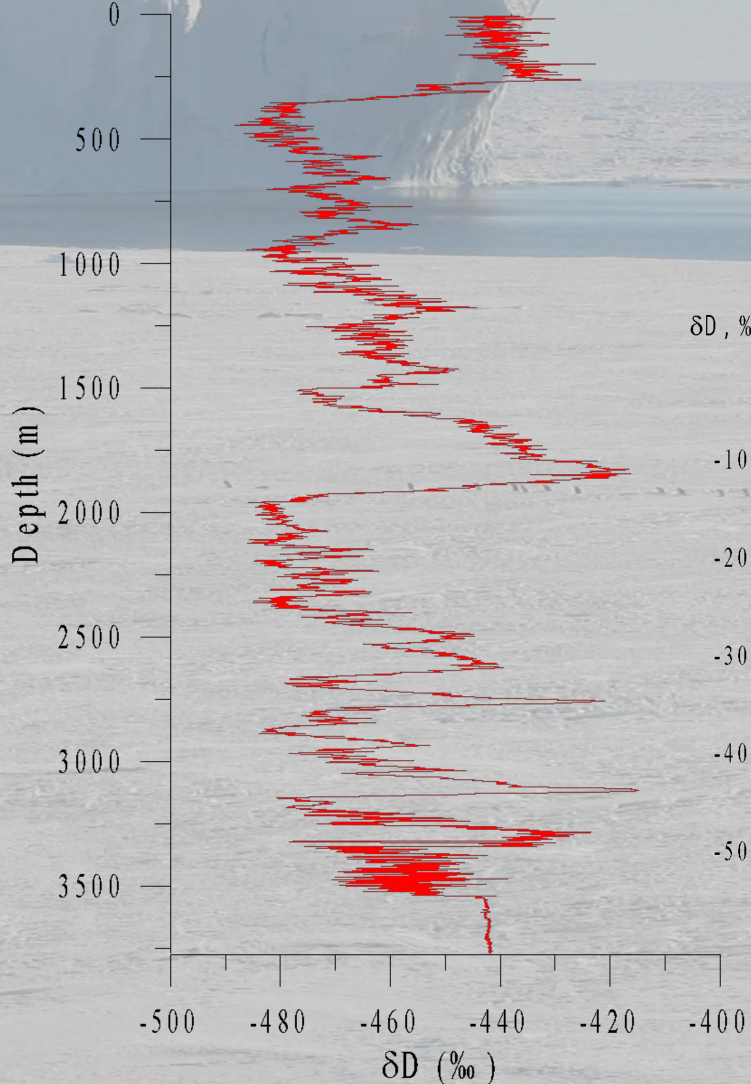
Isotope-temperature calibration

1. Independent data on the temperature in the past (e.g., borehole thermometry)

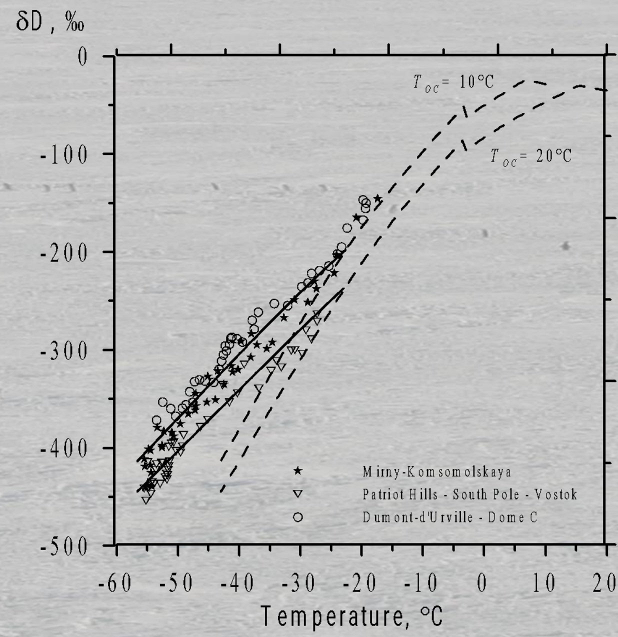




Isotope-temperature calibration

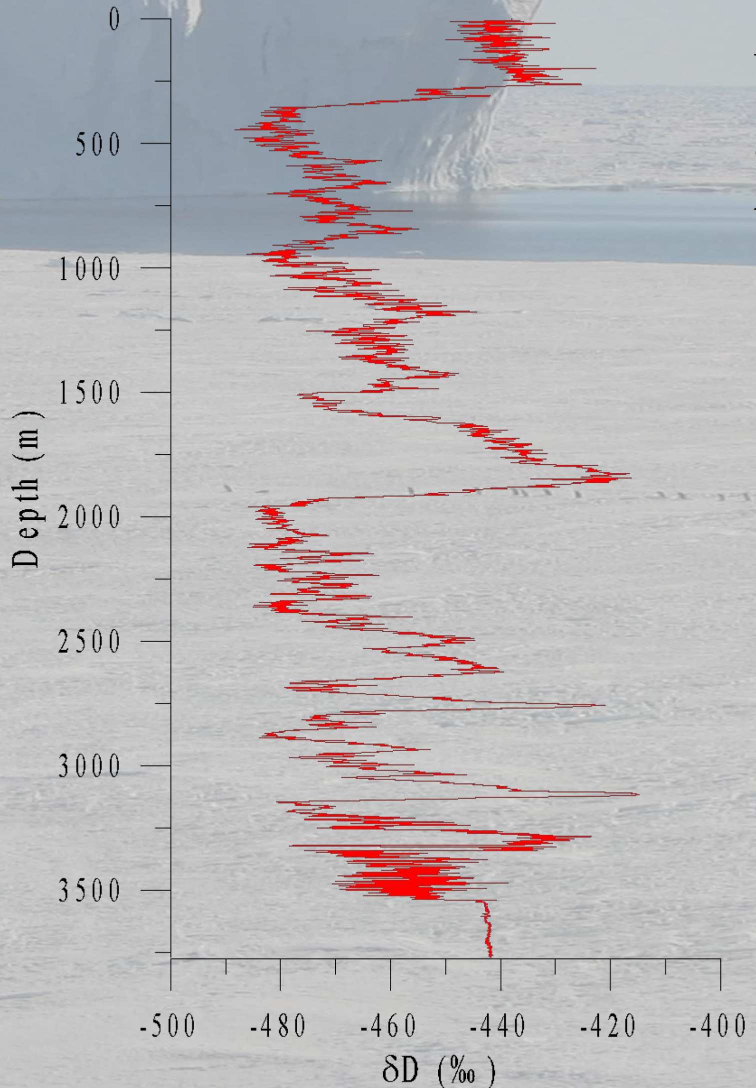


2. Present-day geographical relationship between stable isotopic composition of snow and mean annual air temperature

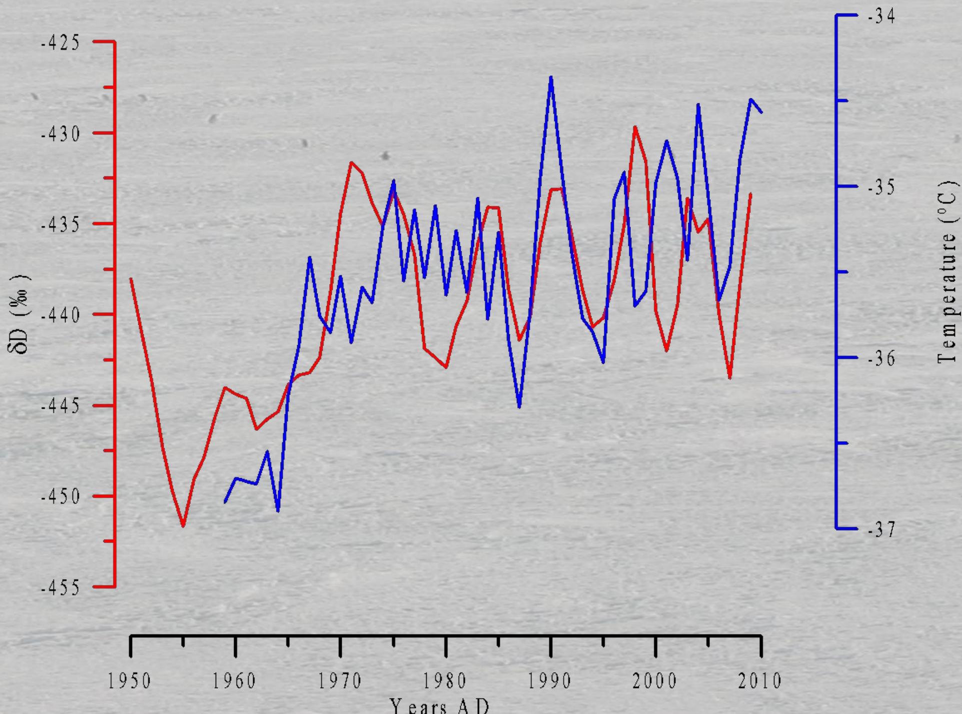


$$\Delta T_i = \frac{\Delta\delta D_{ice} - C_m \Delta\delta^{18}O_m}{C_i}$$

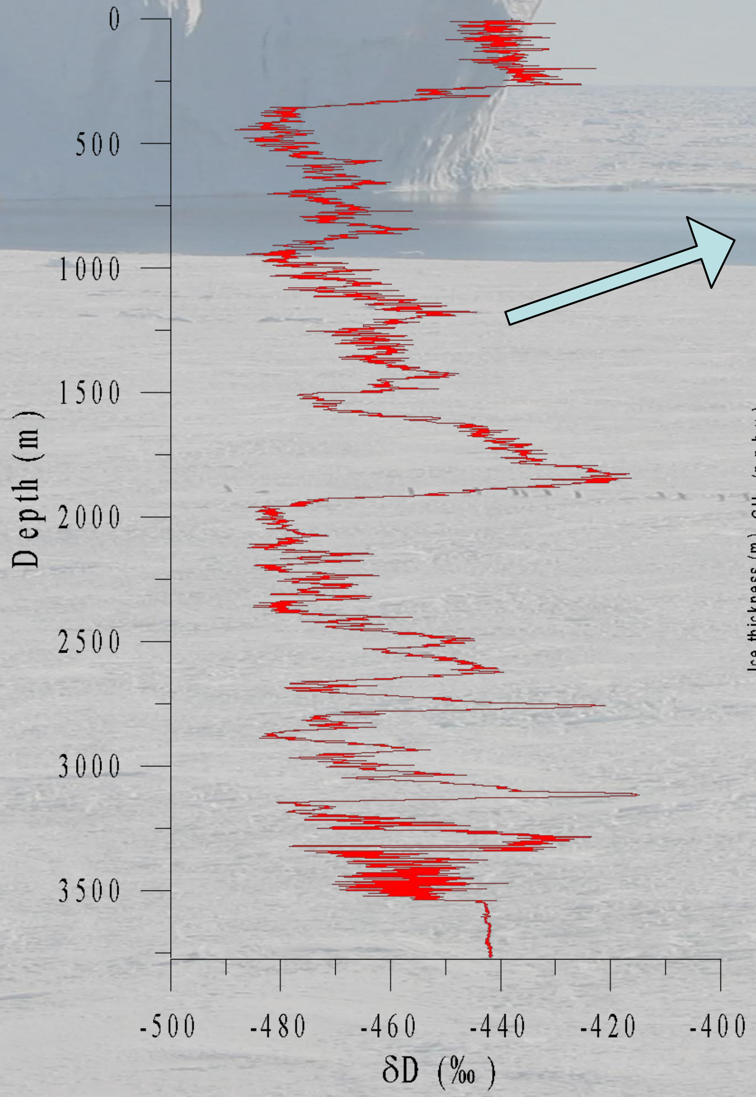
Isotope-temperature calibration

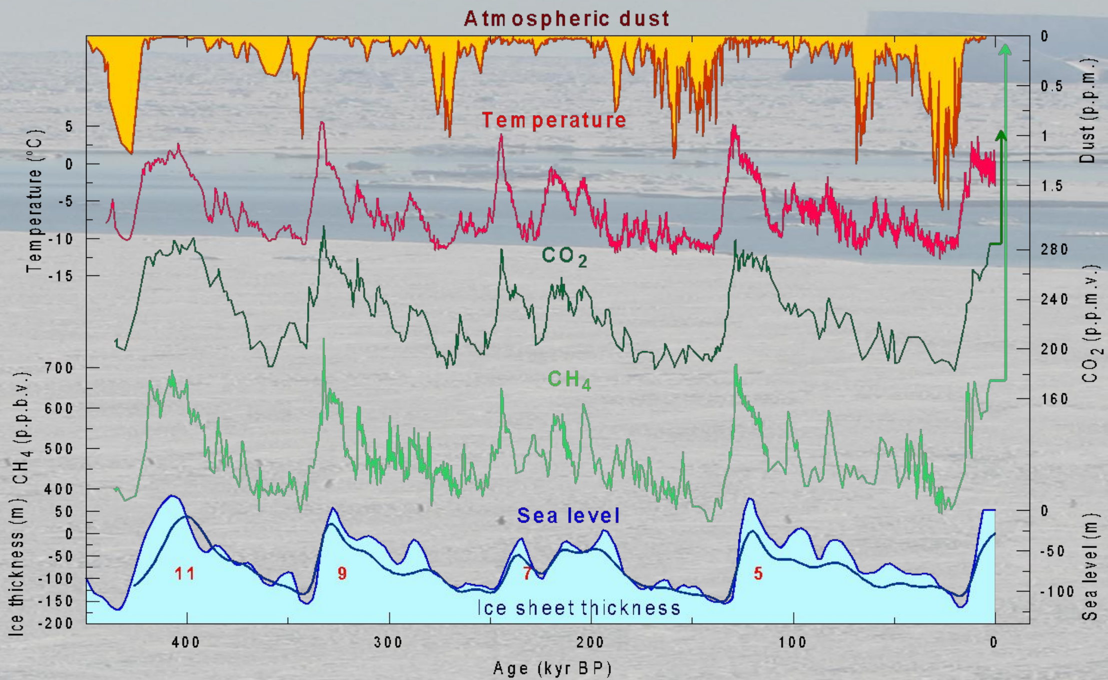


3. Regression between temporal variability of snow isotopic composition and instrumentally obtained air temperature
(only for the past few thousand years)



Isotope-temperature calibration

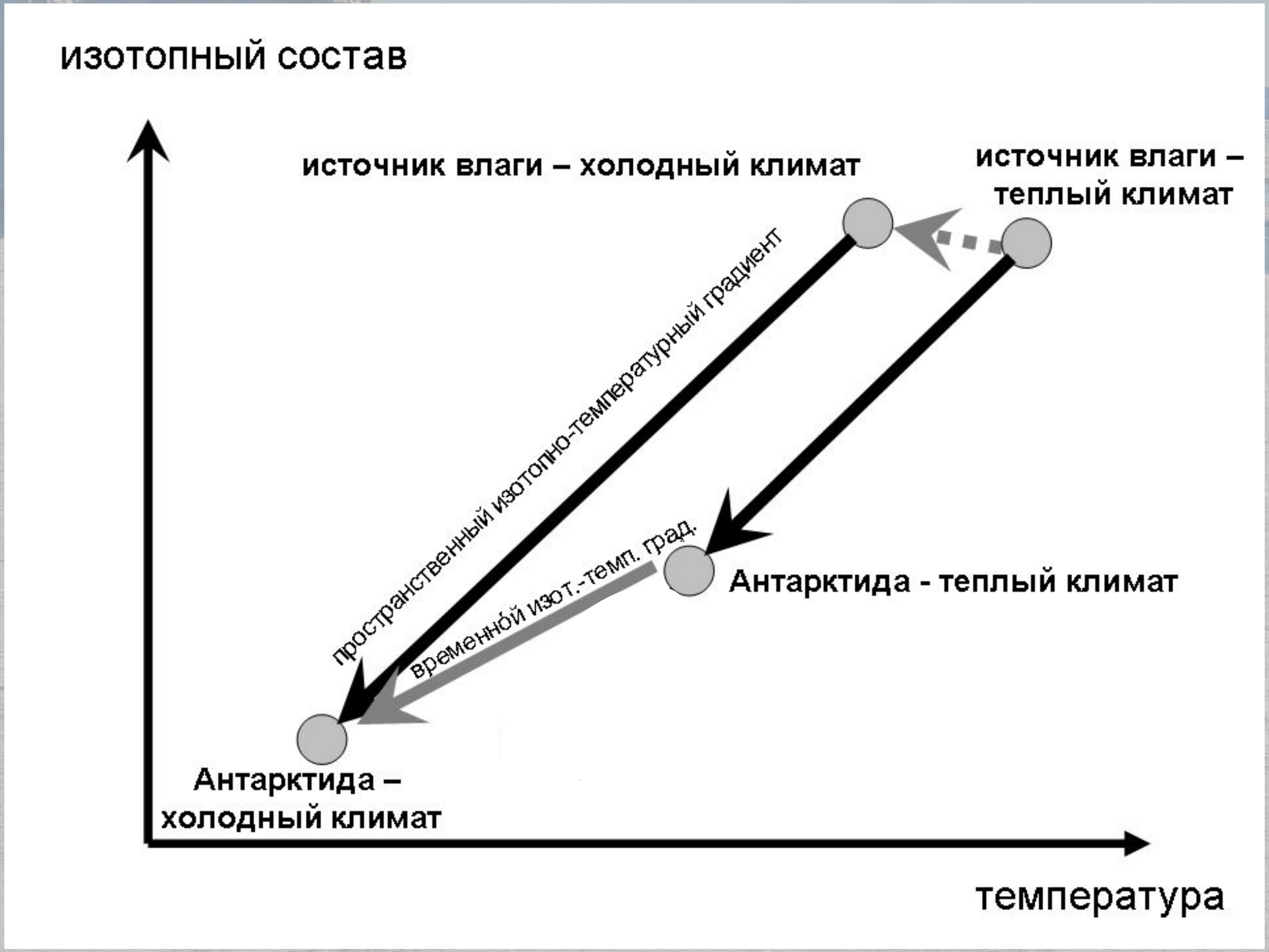




Petit et al., 1999

Sources of uncertainties in the isotope-temperature method:

Sources of uncertainties in the isotope-temperature method:
Temperature changes in the moisture source



Sources of uncertainties in the isotope-temperature method:

Precipitation intermittency and seasonality

Snow and ice deposits only record the isotopic composition of the days when precipitation occurred!

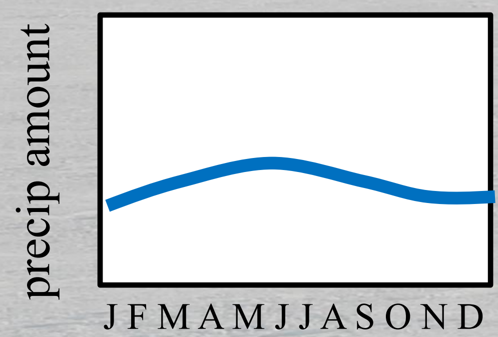
This may cause biases
(Days with precipitations are usually warmer than days without)

Sources of uncertainties in the isotope-temperature method:
Precipitation intermittency and seasonality

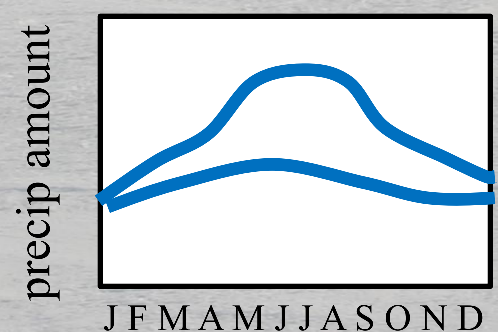
Seasonality:
Mean annual isotopic composition is biased towards wetter season

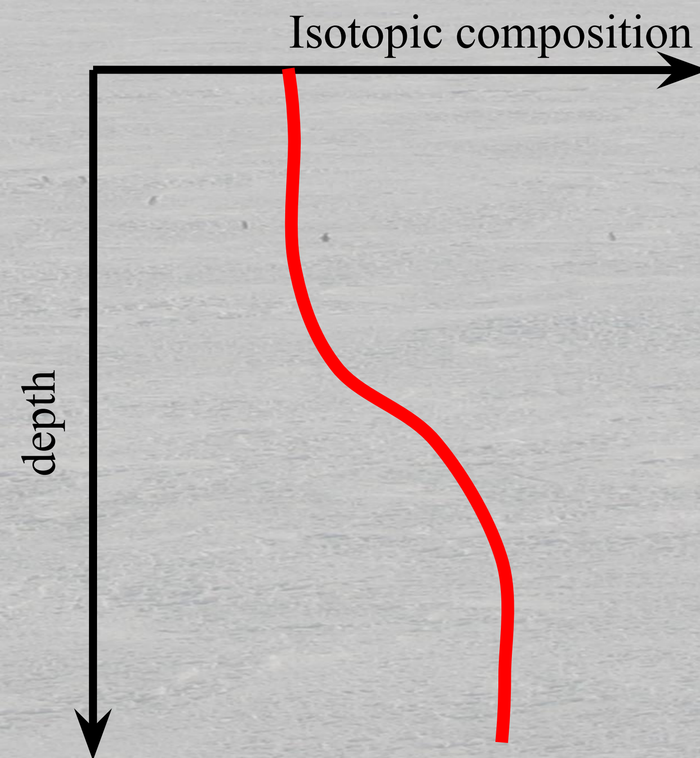
Changing seasonality of precipitation may cause to wrong interpretation of ice cores data

Now:



Past:

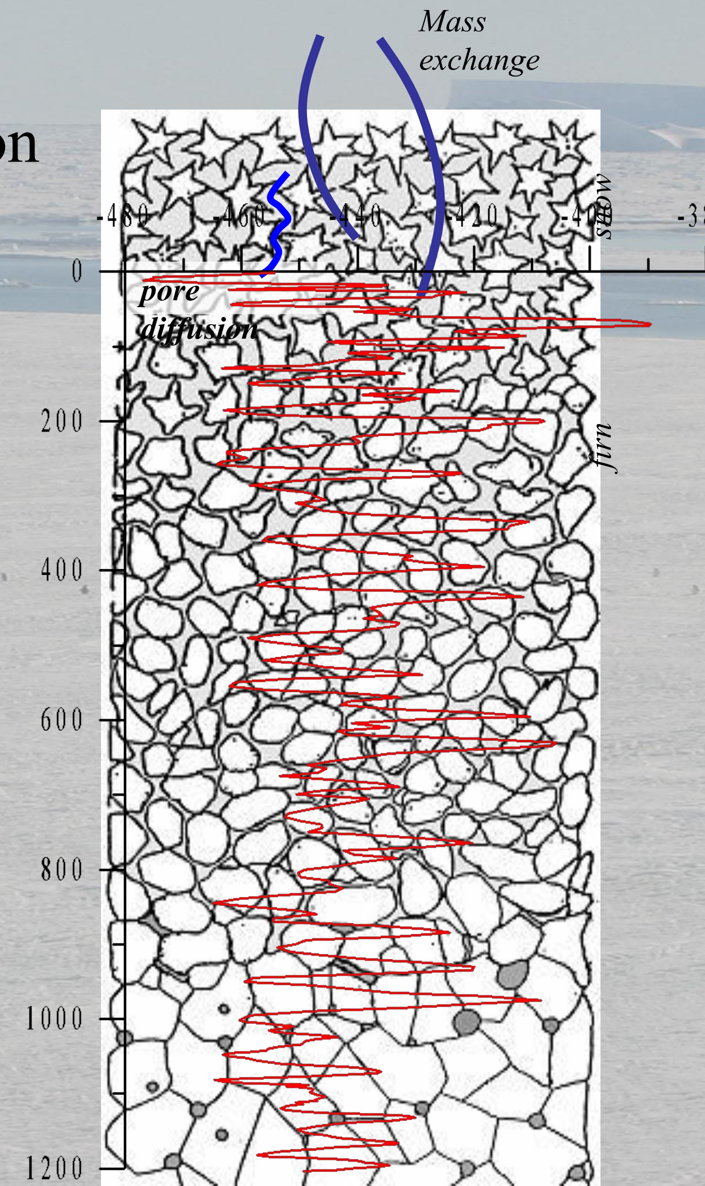




Sources of uncertainties in the isotope-temperature method: Post-depositional processes

Isotopic composition of precipitation may change in the snow thickness after deposition due to mass- and isotopic exchange with atmosphere

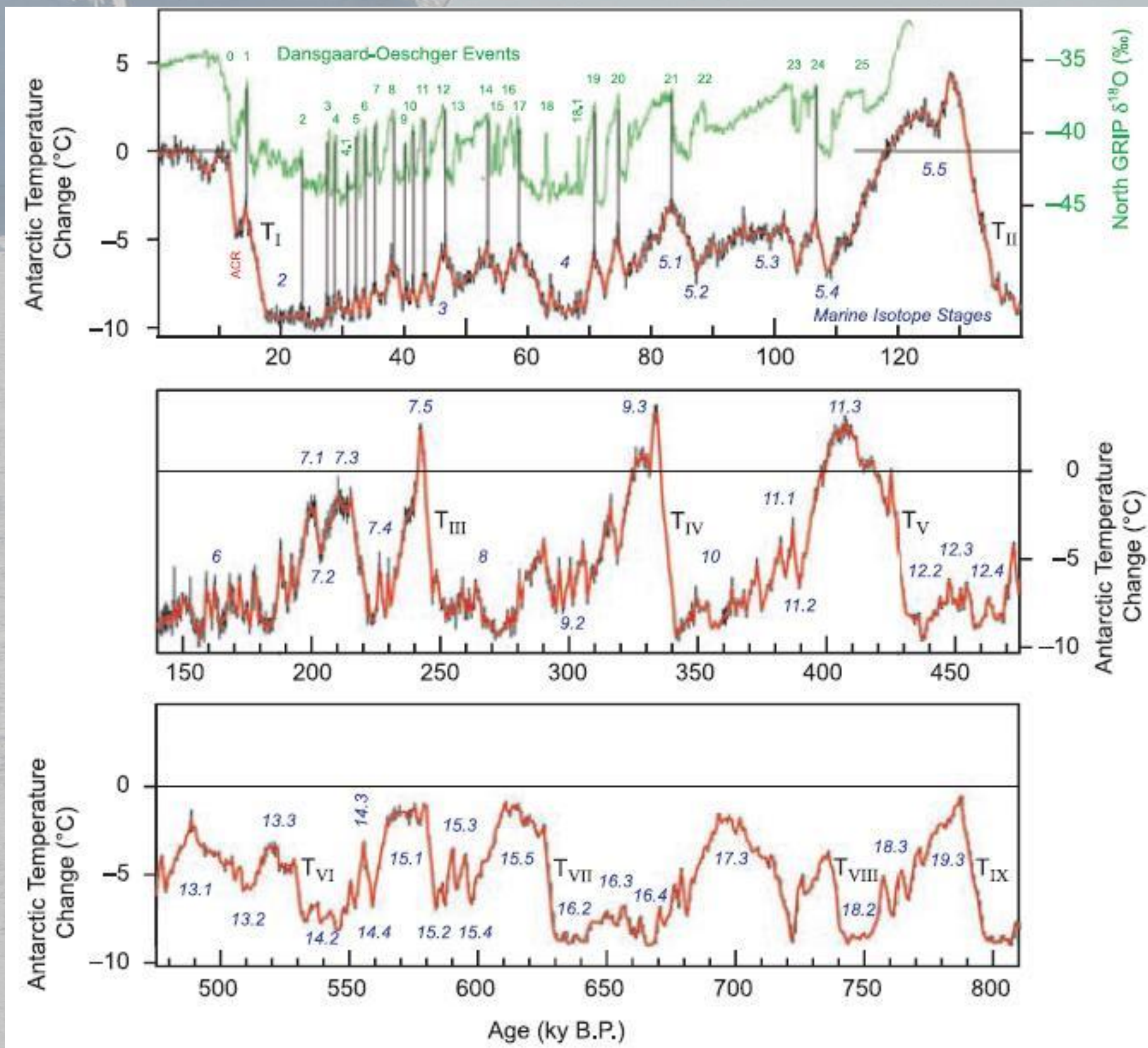
As a result, the snow isotopic content shifts towards heavier values
and the amplitude of the isotopic variability decreases



Sources of uncertainties in the isotope-temperature method: Other factors

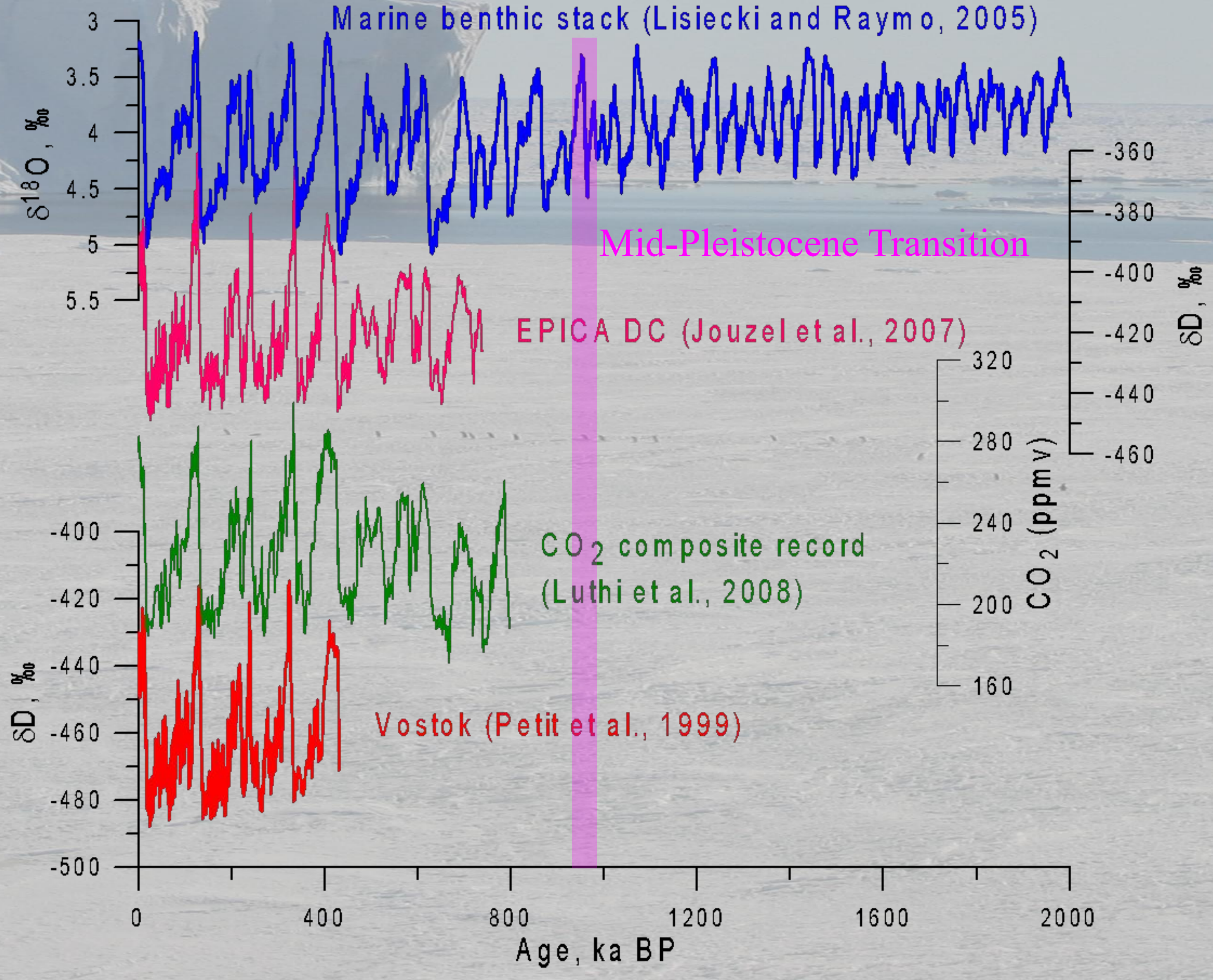
1. Relationship between near-surface air temperature and condensation temperature
2. Non-climatic changes of temperature in the past (altitude of glacier)
3. Snow removal by wind
4. “Stratigraphic noise”

Climate of late Pleistocene based on stable isotopic composition of ice cores

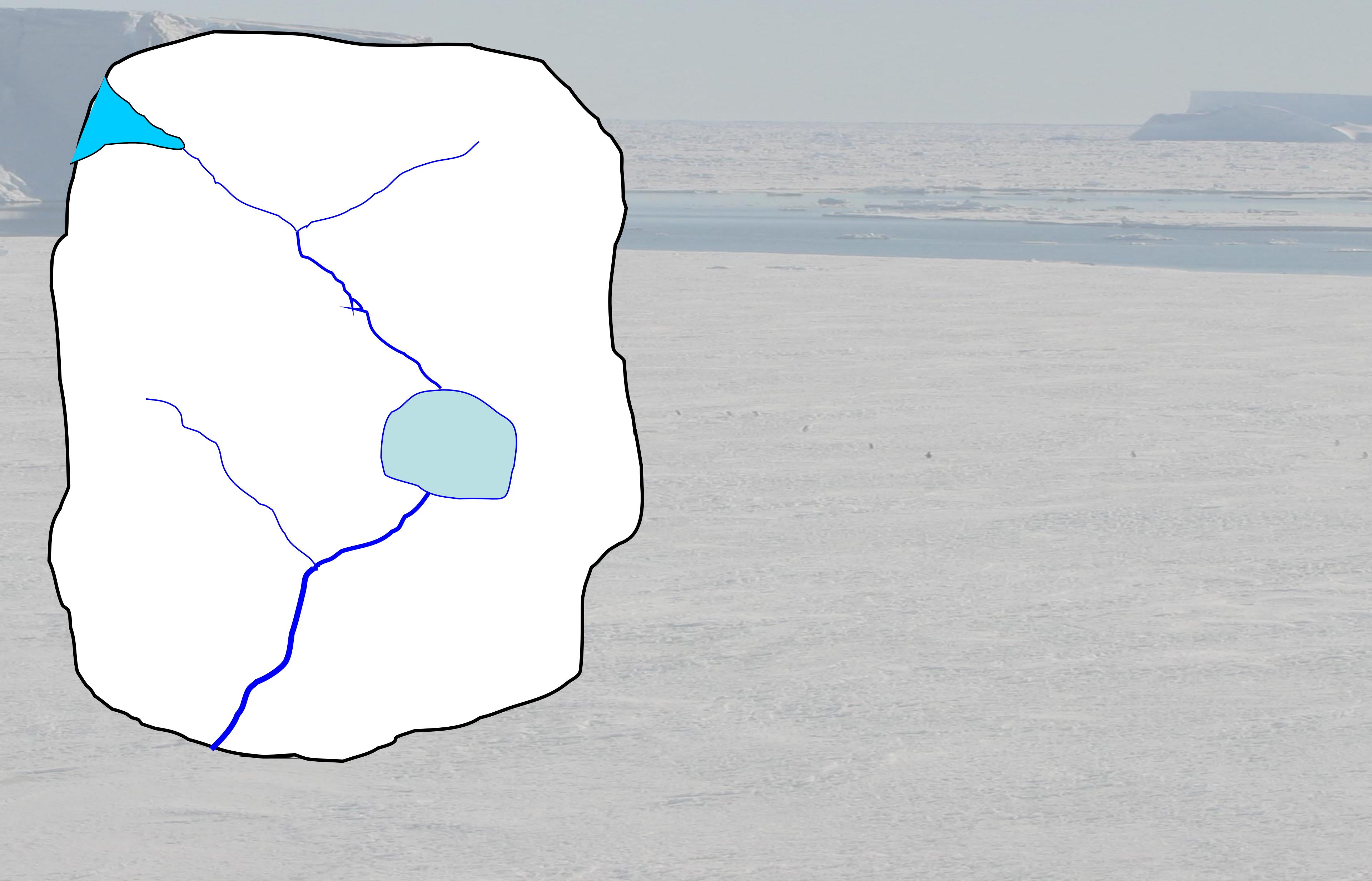


Jouzel et al., 2007

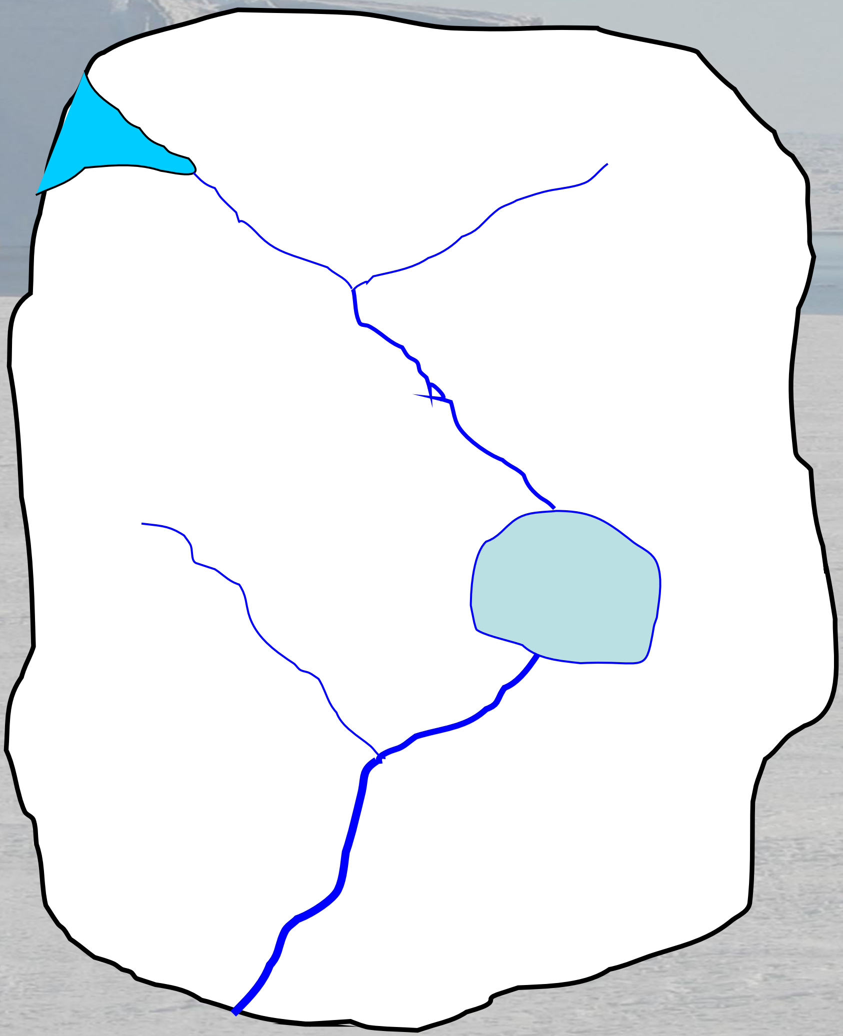
Climate of late Pleistocene based on stable isotopic composition of ice cores and marine sediments

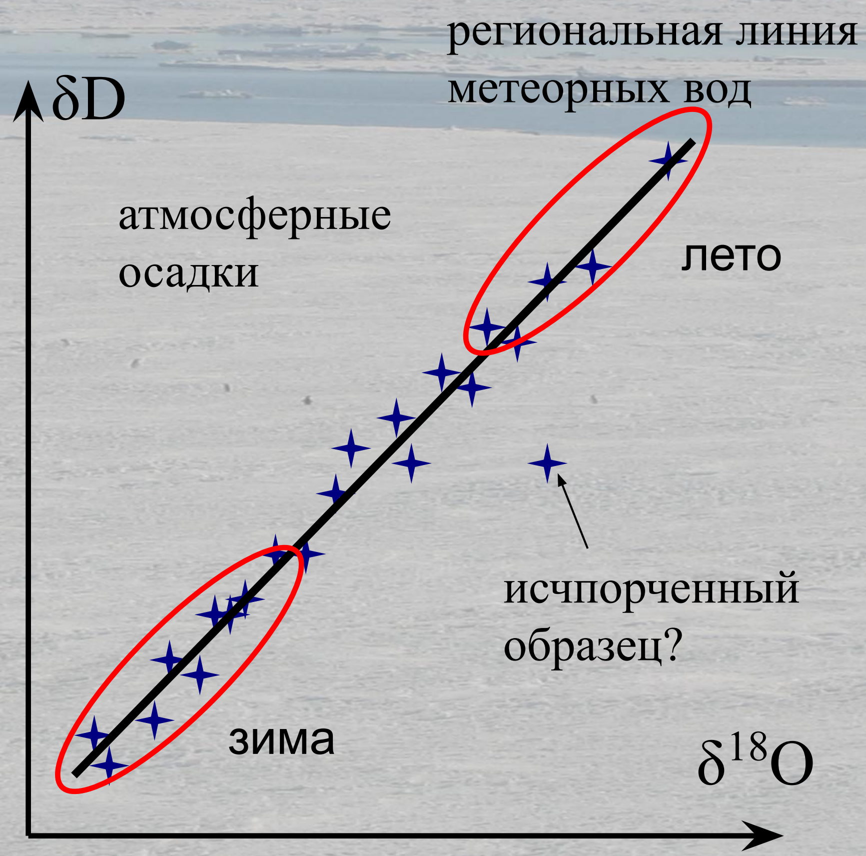


Стабильные изотопы воды в гидрологии



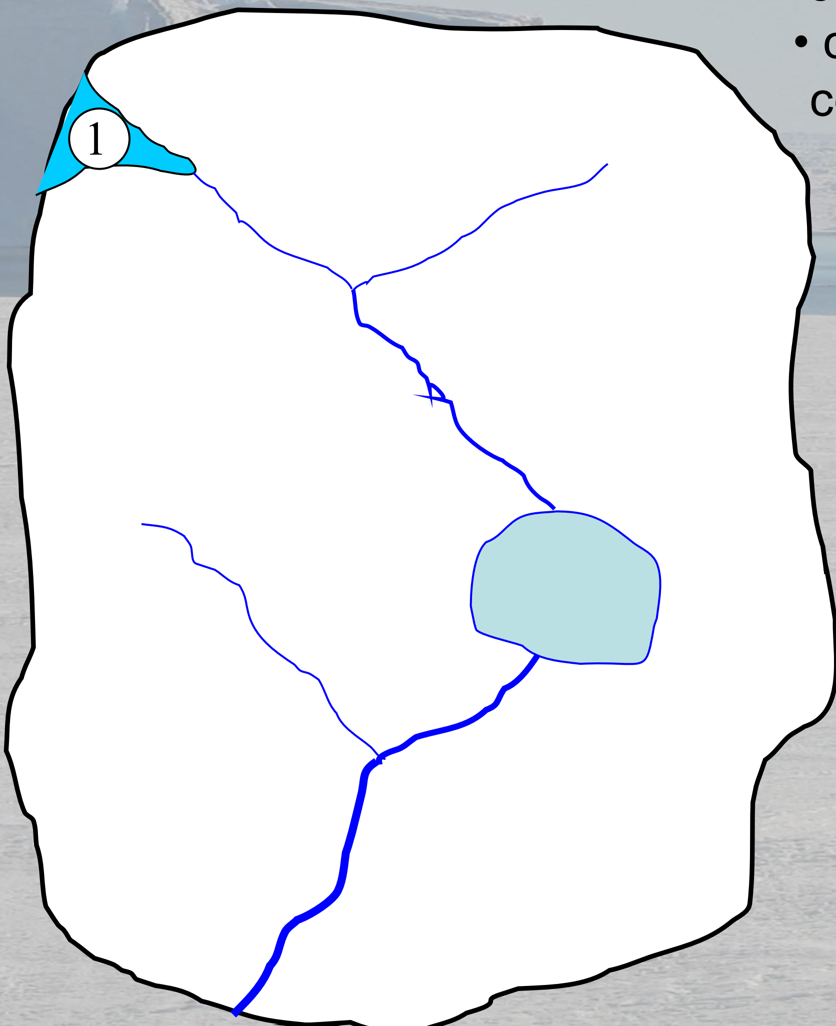
Стабильные изотопы воды в гидрологии

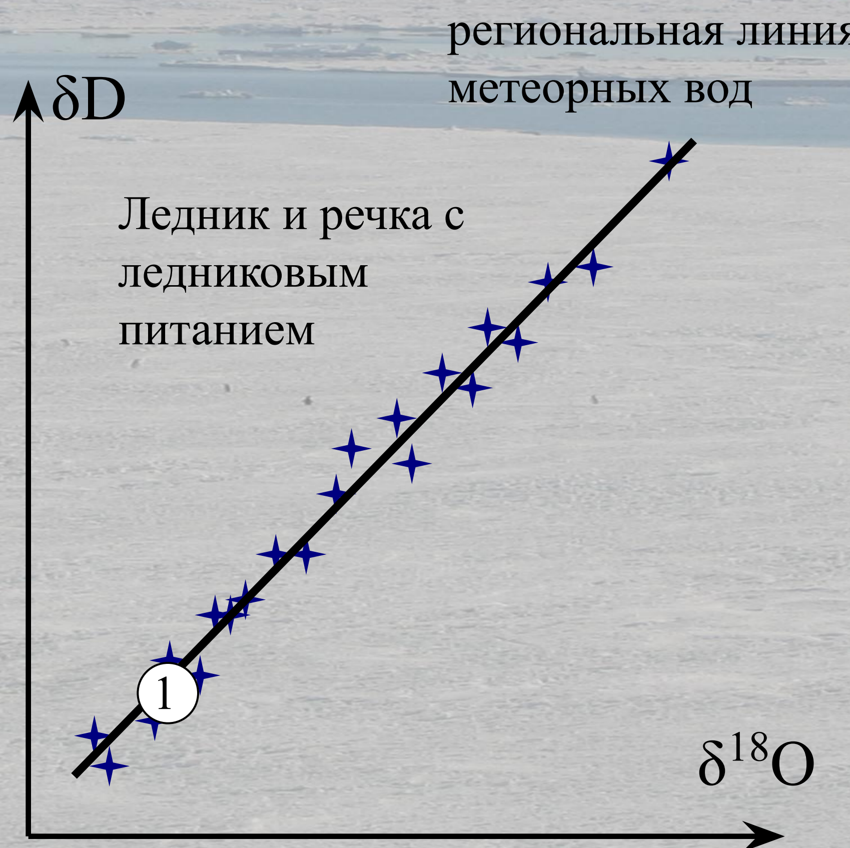




Стабильные изотопы воды в гидрологии

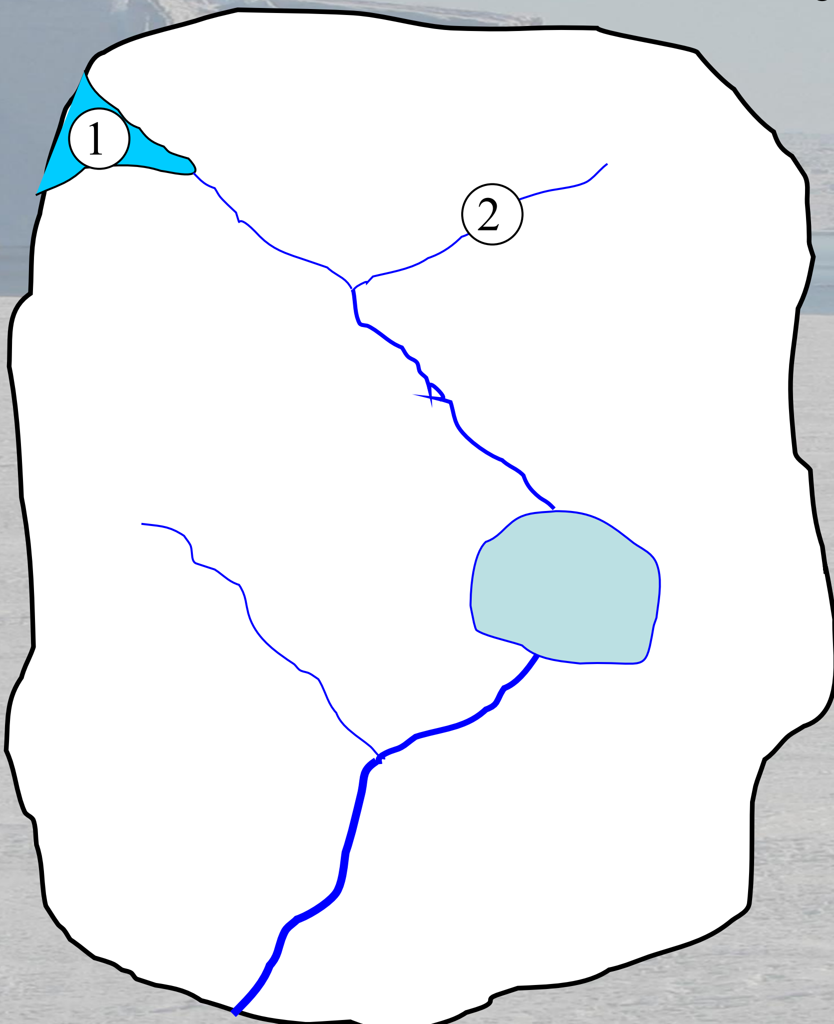
- изотопный состав льда также может зависеть от его возраста
- снег и лёд могут иметь разный изотопный состав

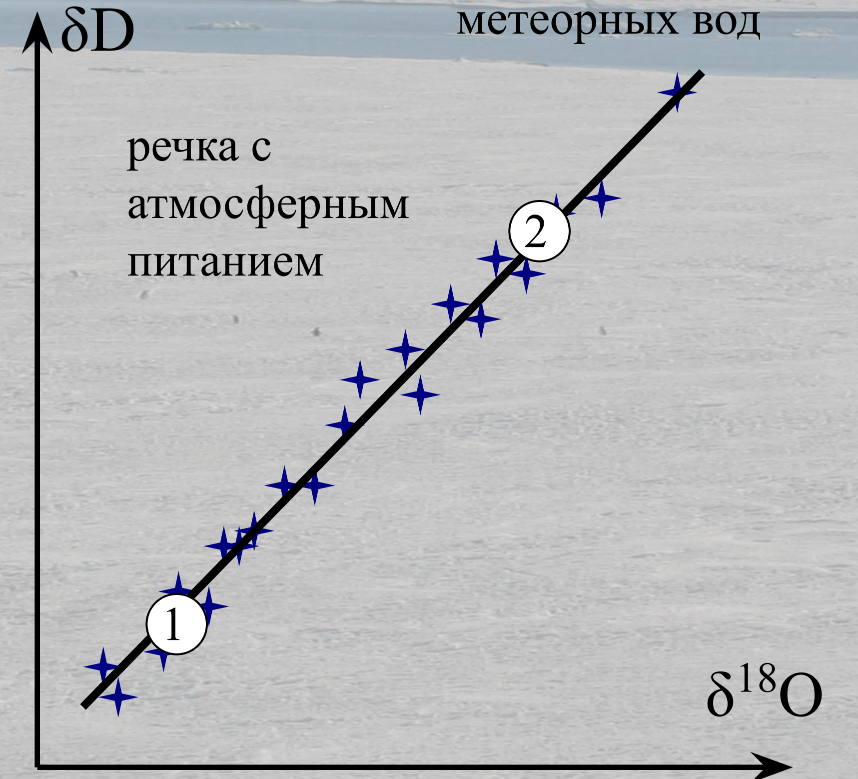




Стабильные изотопы воды в гидрологии

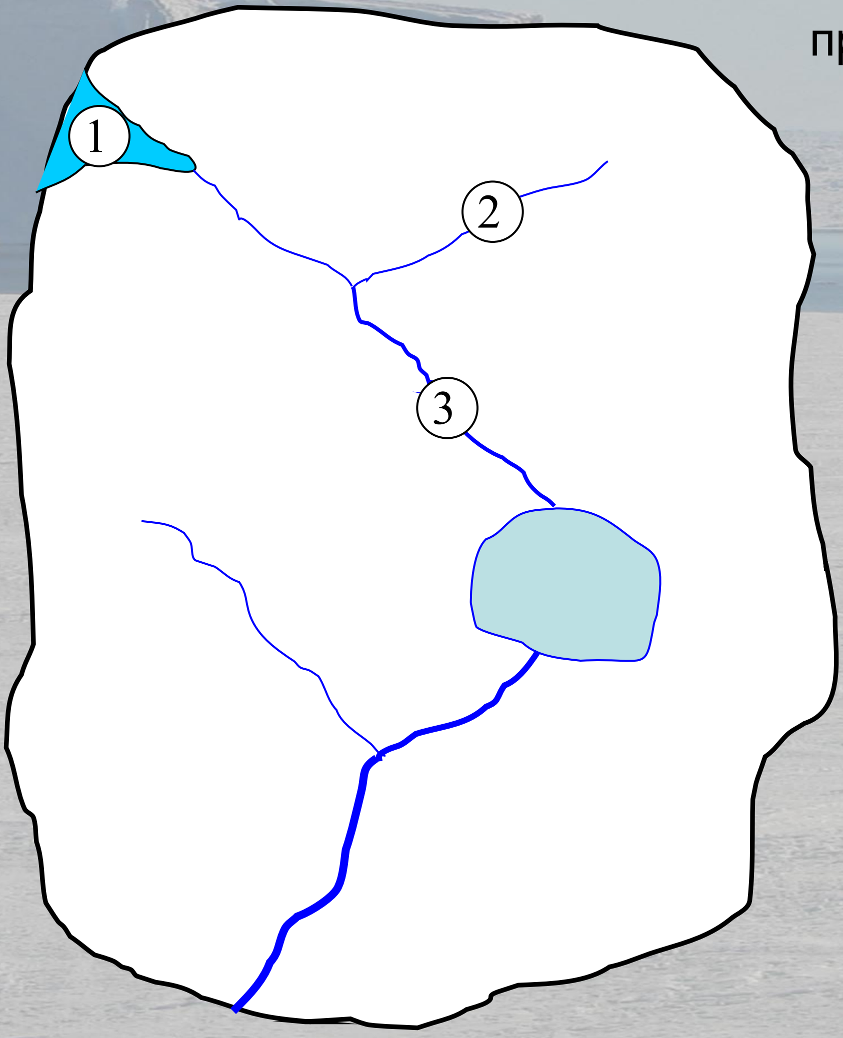
• изотопный состав воды в реке зависит от сезона года и от времени оборота воды

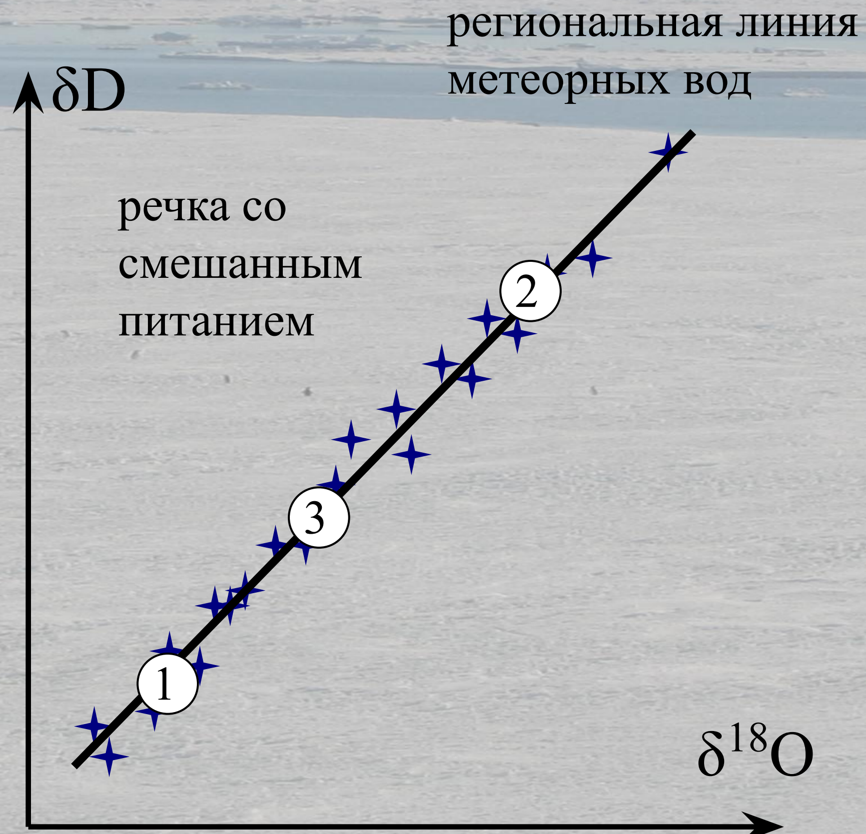




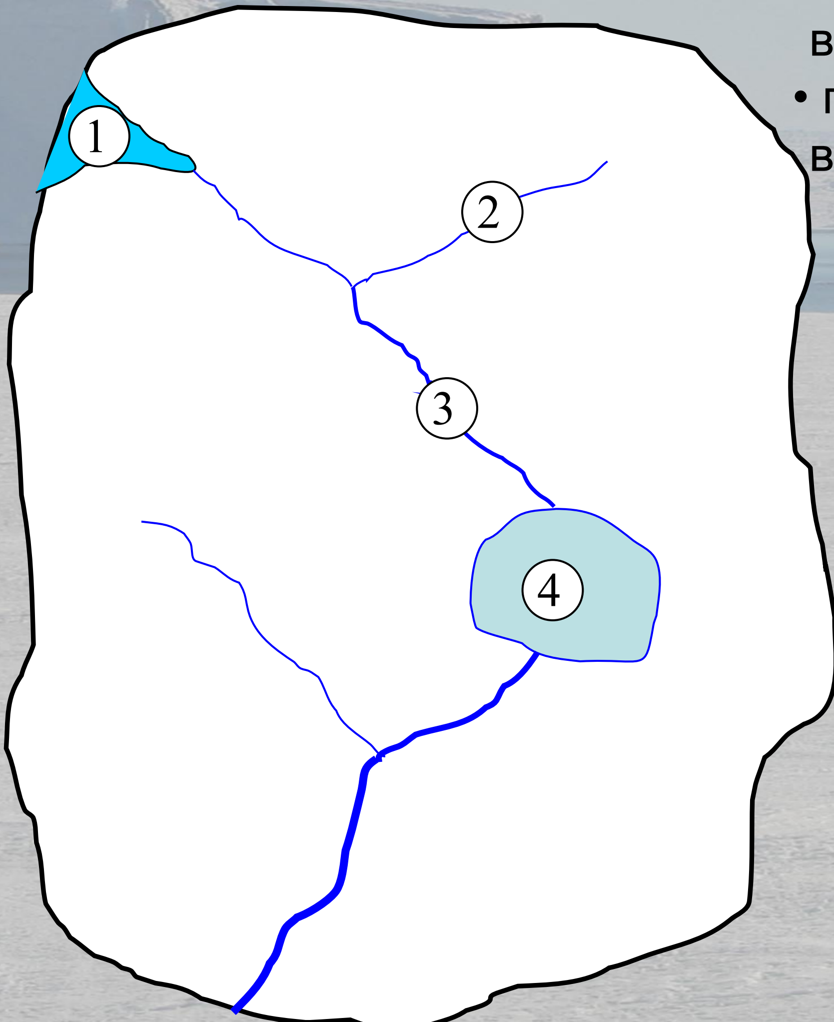
Стабильные изотопы воды в гидрологии

• анализ изотопного состава легко позволяет оценить относительный вклад различных притоков

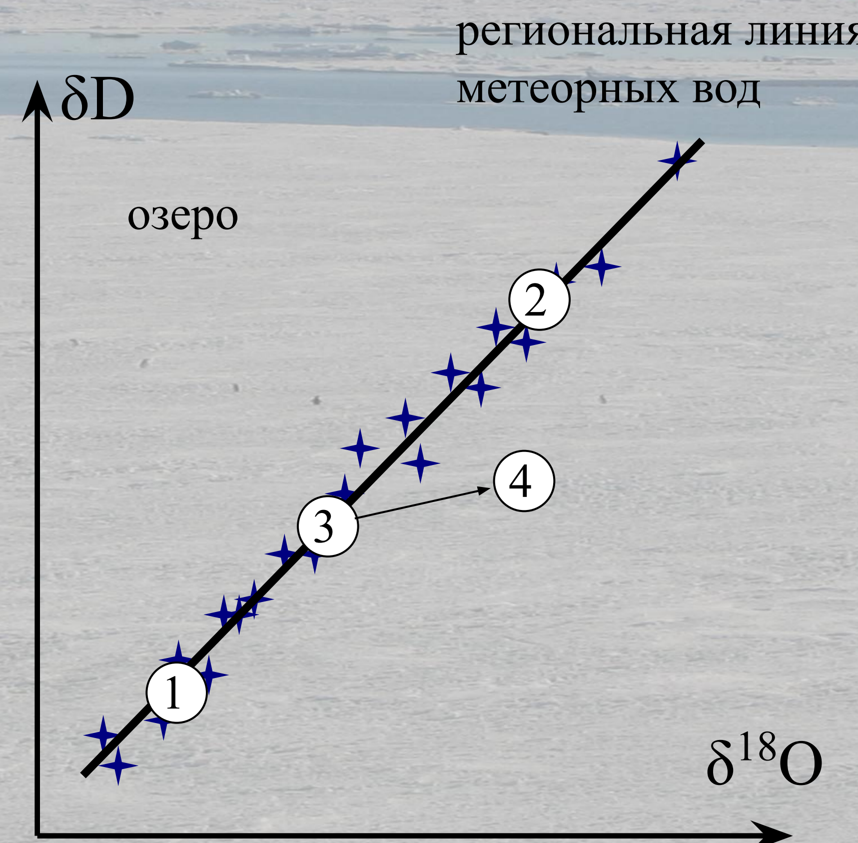




Стабильные изотопы воды в гидрологии

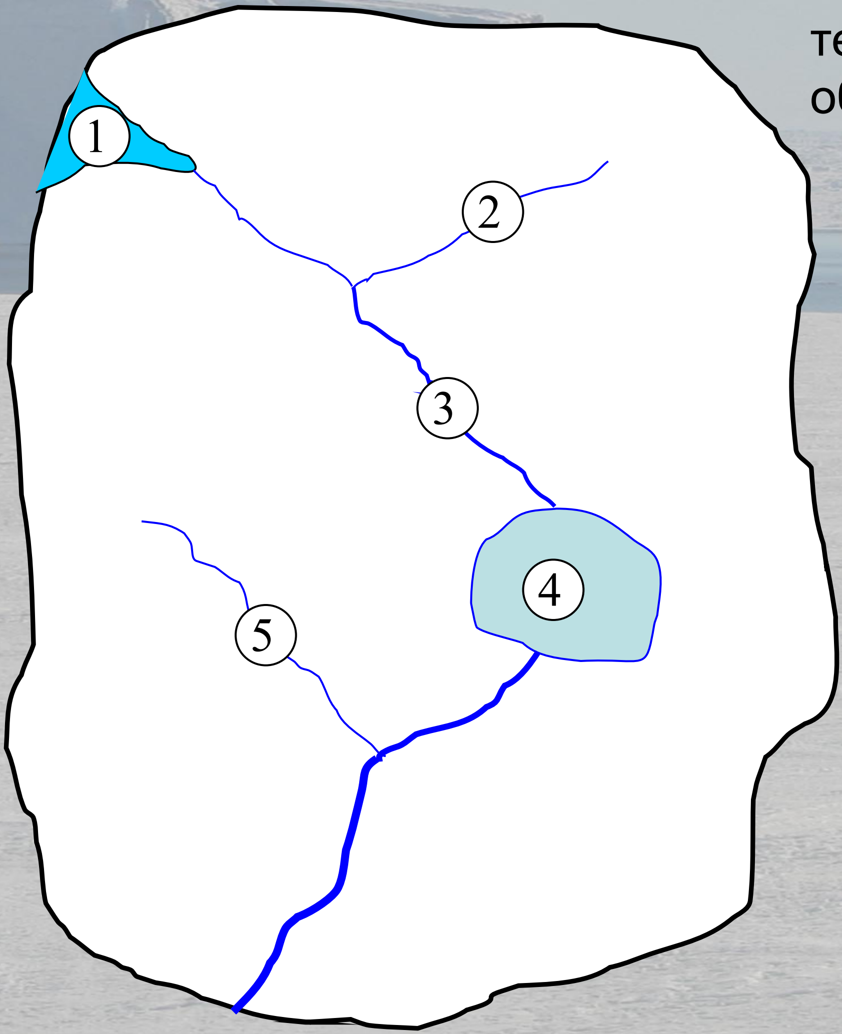


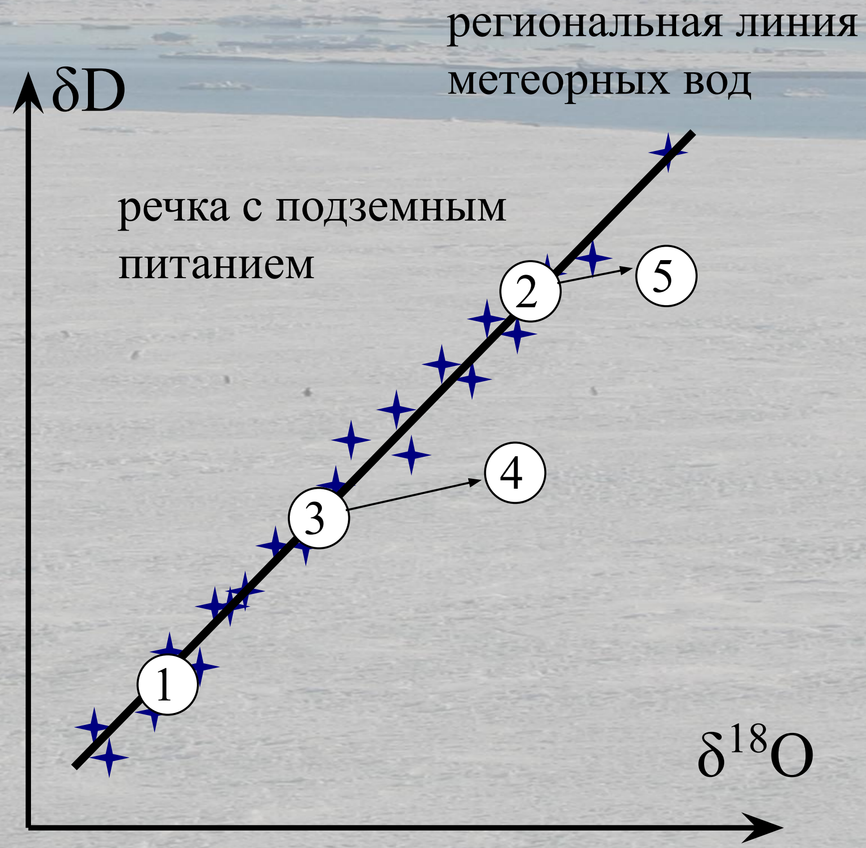
- изотопное смещение будет зависеть от интенсивности испарения (=*f*(tº, R)) и от времени оборота воды в озере
- подобное смещение также м.б. обусловлено влиянием грунтовых вод (см. дальше)



Стабильные изотопы воды в гидрологии

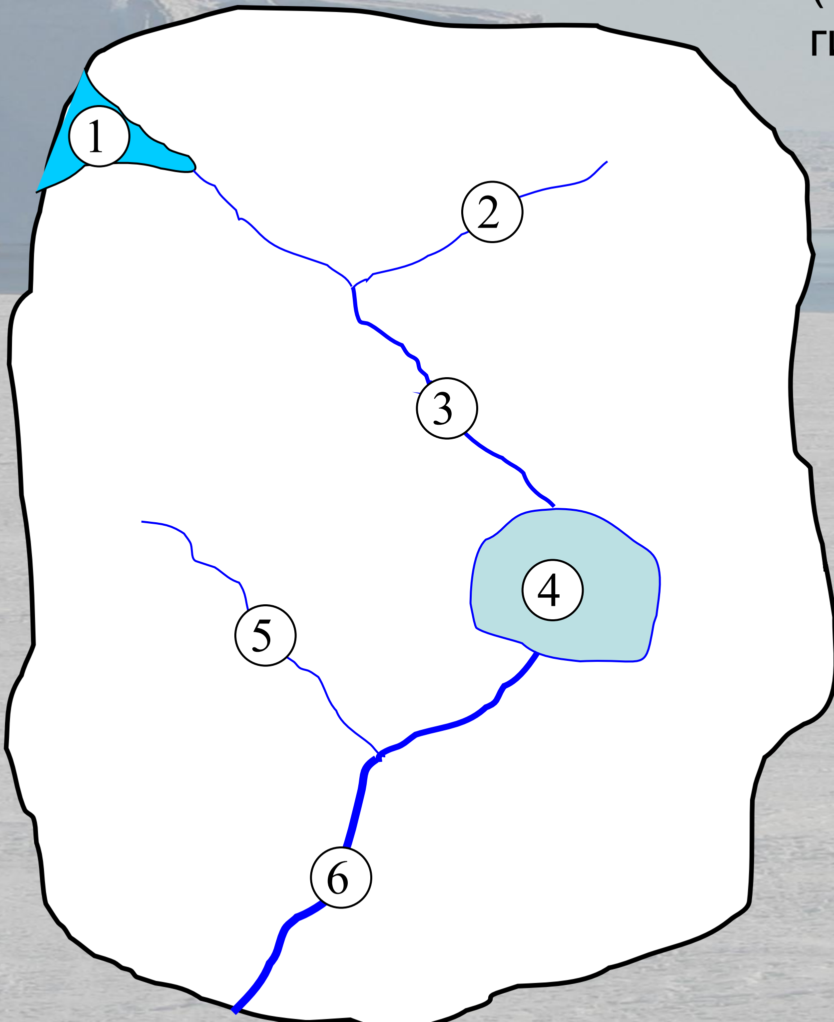
• изотопный состав подземных вод зависит от химического состава пород, от термодинамических условий и от времени оборота воды

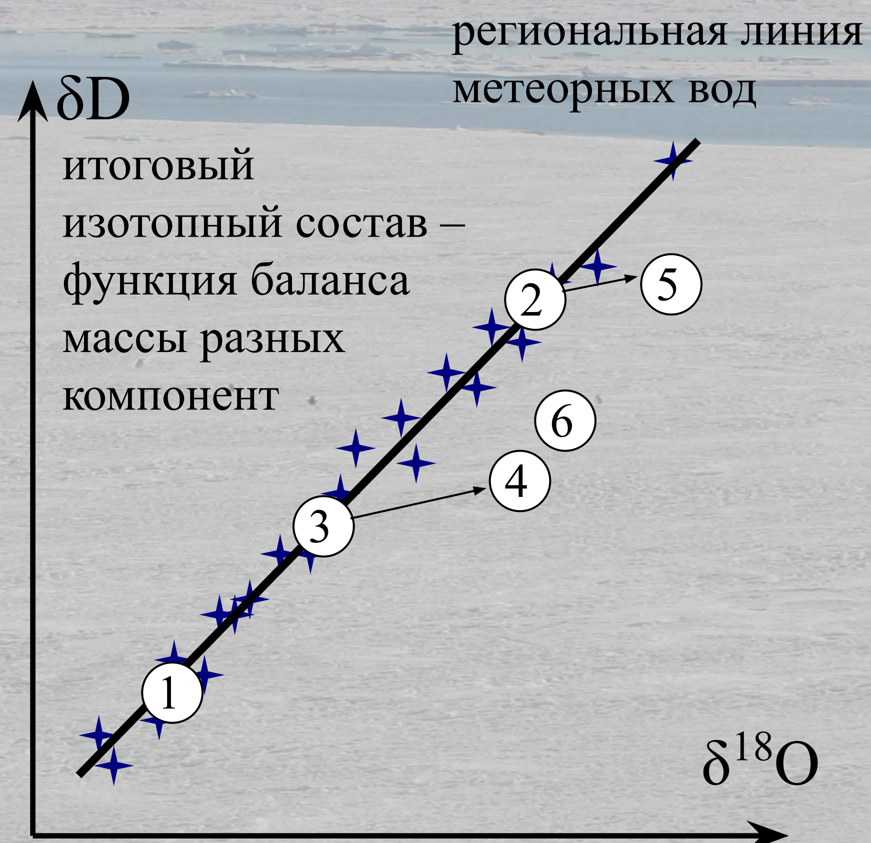




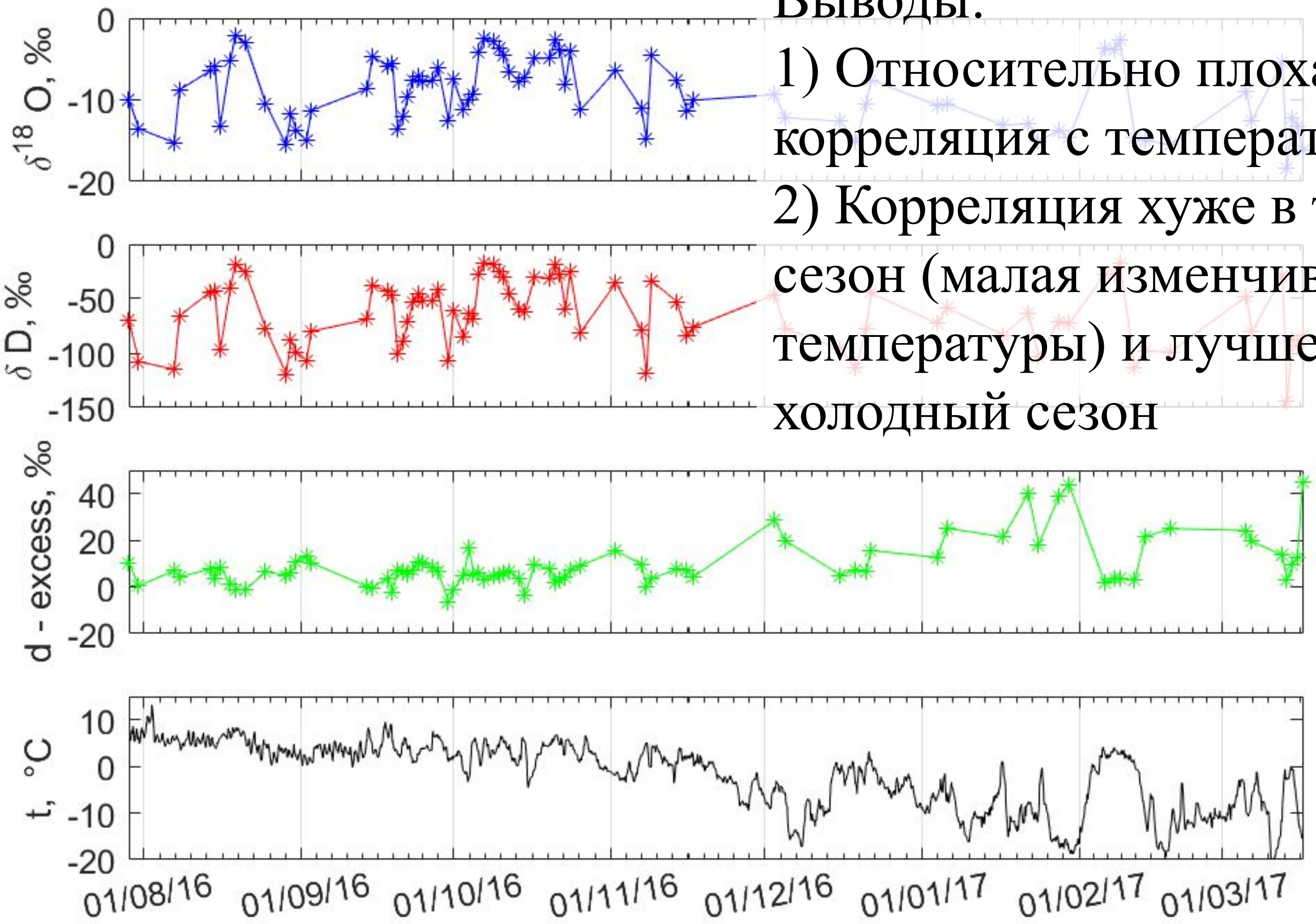
Стабильные изотопы воды в гидрологии

- изотопный метод прекрасно дополняет (иногда – заменяет) другие методы гидрологических исследований





Изучение изотопного состава природных вод в районе Грёнфьорд: Первые результаты

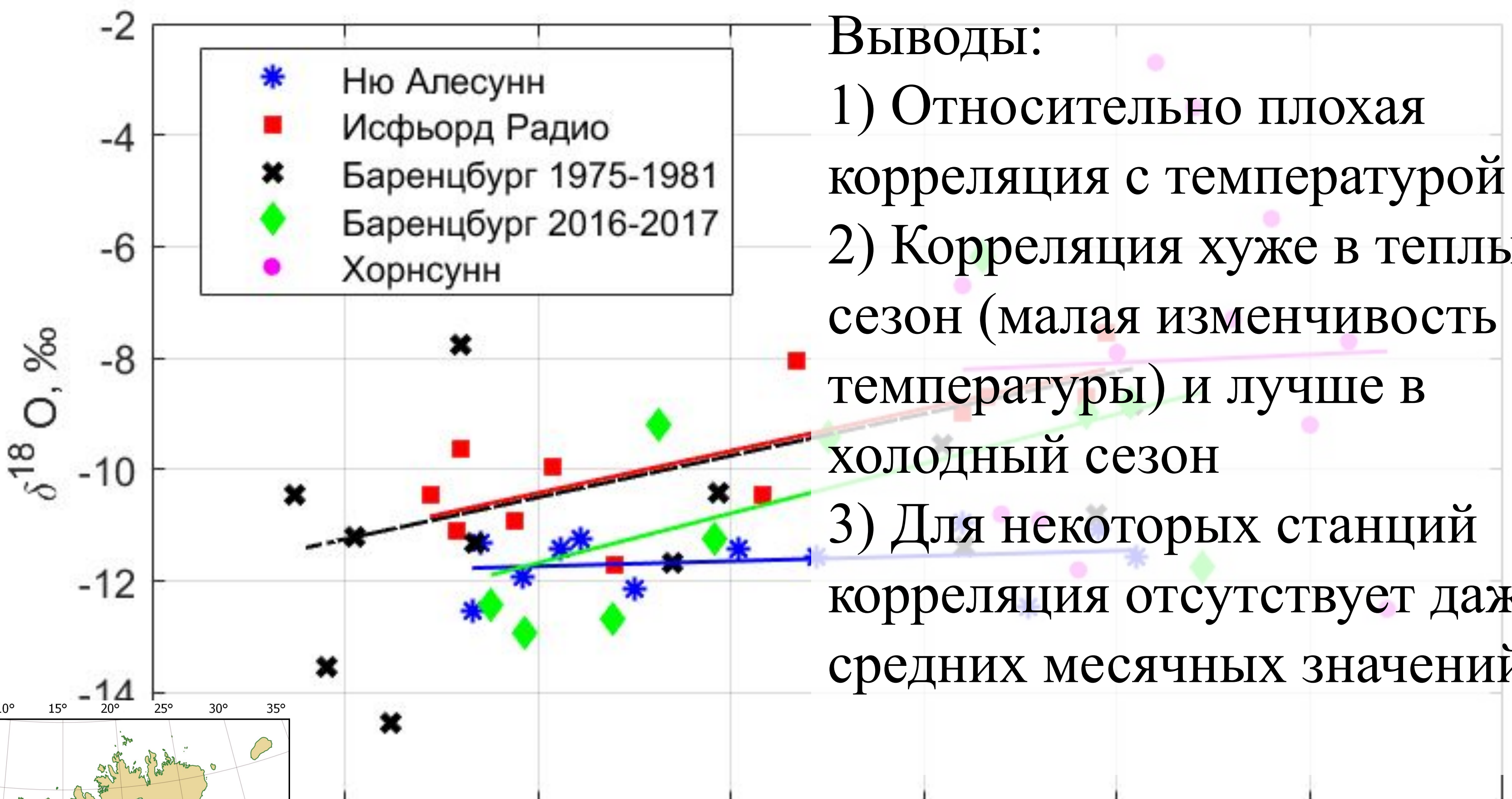


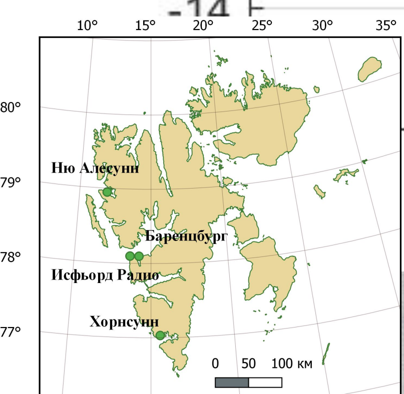
Выводы:

1) Относительно плохая корреляция с температурой!

2) Корреляция хуже в теплый сезон (малая изменчивость температуры) и лучше в холодный сезон

Изучение изотопного состава природных вод в районе Грёнфьорд: Первые результаты





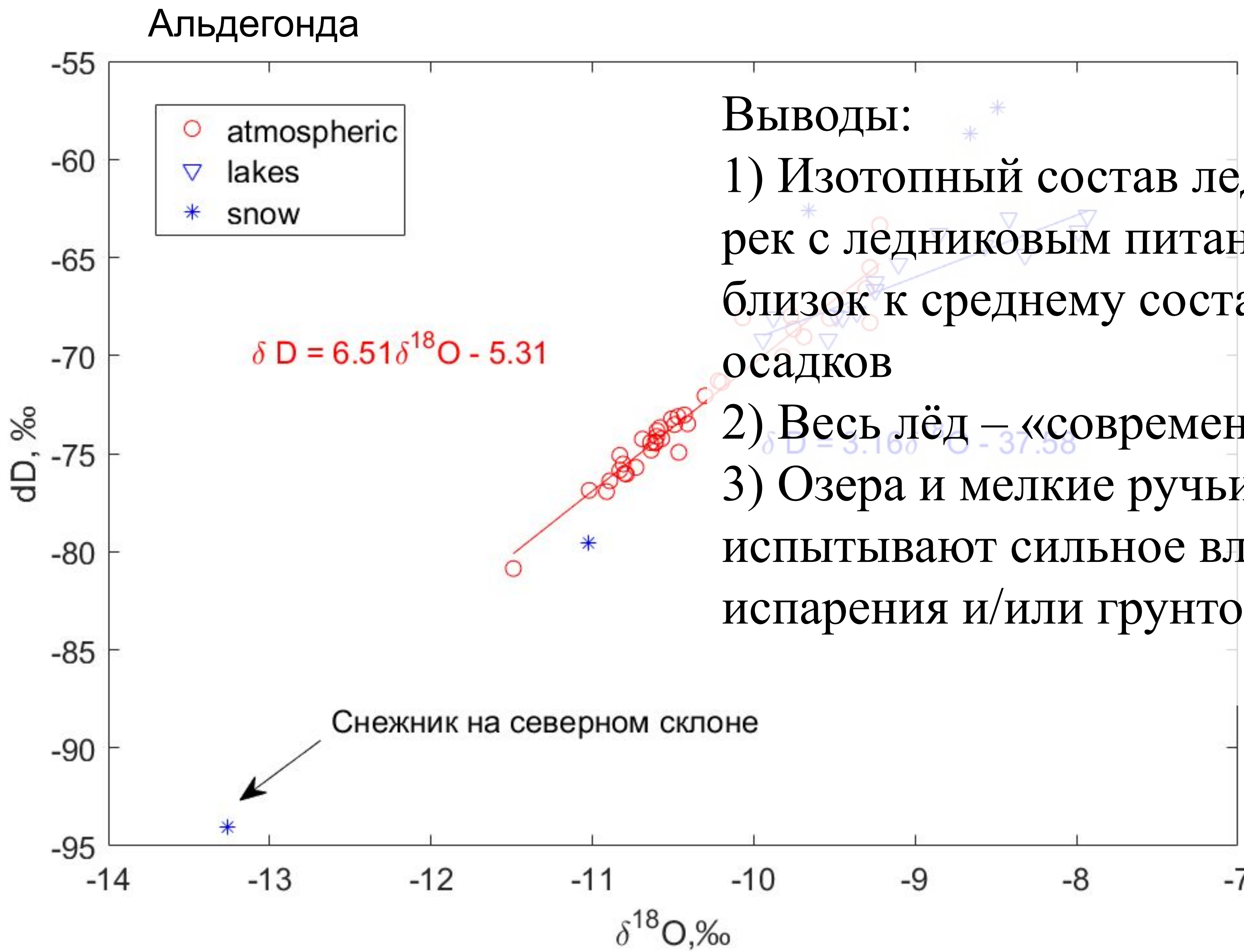
Выводы:

1) Относительно плохая корреляция с температурой!

2) Корреляция хуже в теплый сезон (малая изменчивость температуры) и лучше в холодный сезон

3) Для некоторых станций корреляция отсутствует даже для средних месячных значений

Изучение изотопного состава природных вод в районе Грёнфьорд: Первые результаты



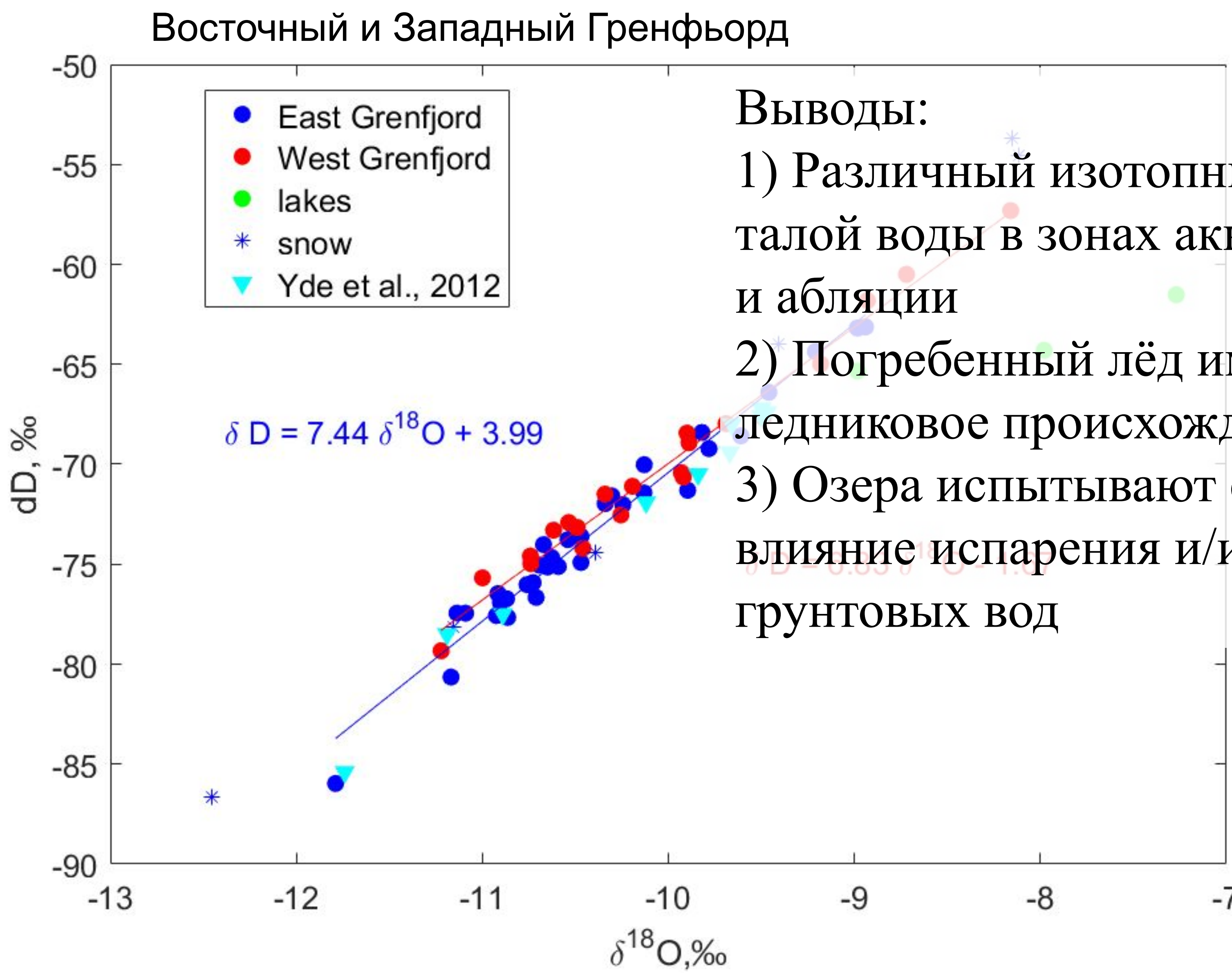
Выводы:

1) Изотопный состав ледников и рек с ледниковым питанием близок к среднему составу осадков

2) Весь лёд – «современный»

3) Озера и мелкие ручьи испытывают сильное влияние испарения и/или грунтовых вод

Изучение изотопного состава природных вод в районе Грёнфьорд: Первые результаты



Выводы:

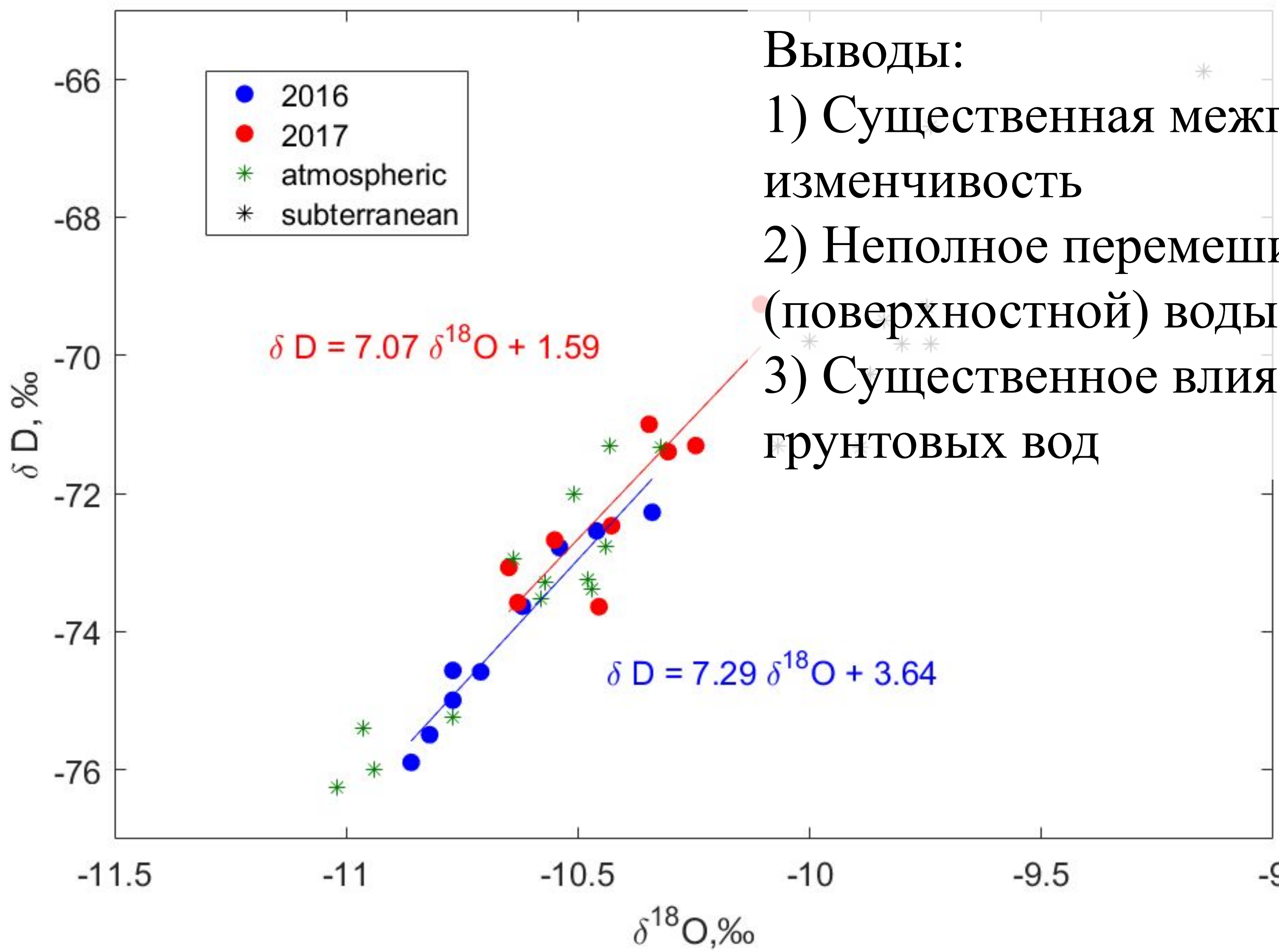
1) Различный изотопный состав талой воды в зонах аккумуляции и абляции

2) Погребенный лёд имеет ледниковое происхождение

3) Озера испытывают сильное влияние испарения и/или грунтовых вод

Изучение изотопного состава природных вод в районе Грёнфьорд: Первые результаты

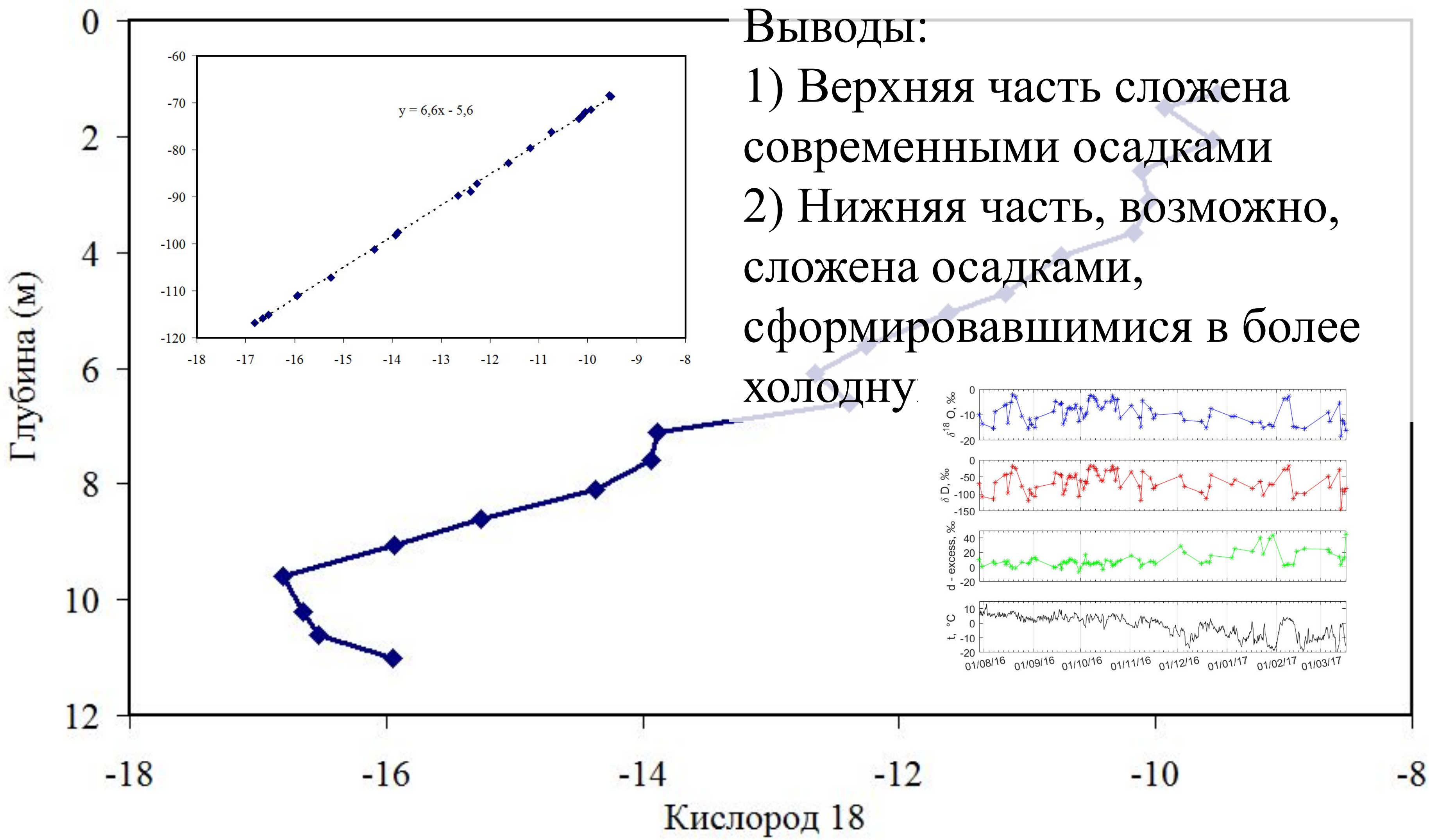
Озеро Конгресс



Выводы:
1) Существенная межгодовая изменчивость
2) Неполное перемешивание (поверхностной) воды
3) Существенное влияние грунтовых вод

Изучение изотопного состава природных вод в районе Грёнфьорд: Первые результаты

булгунях

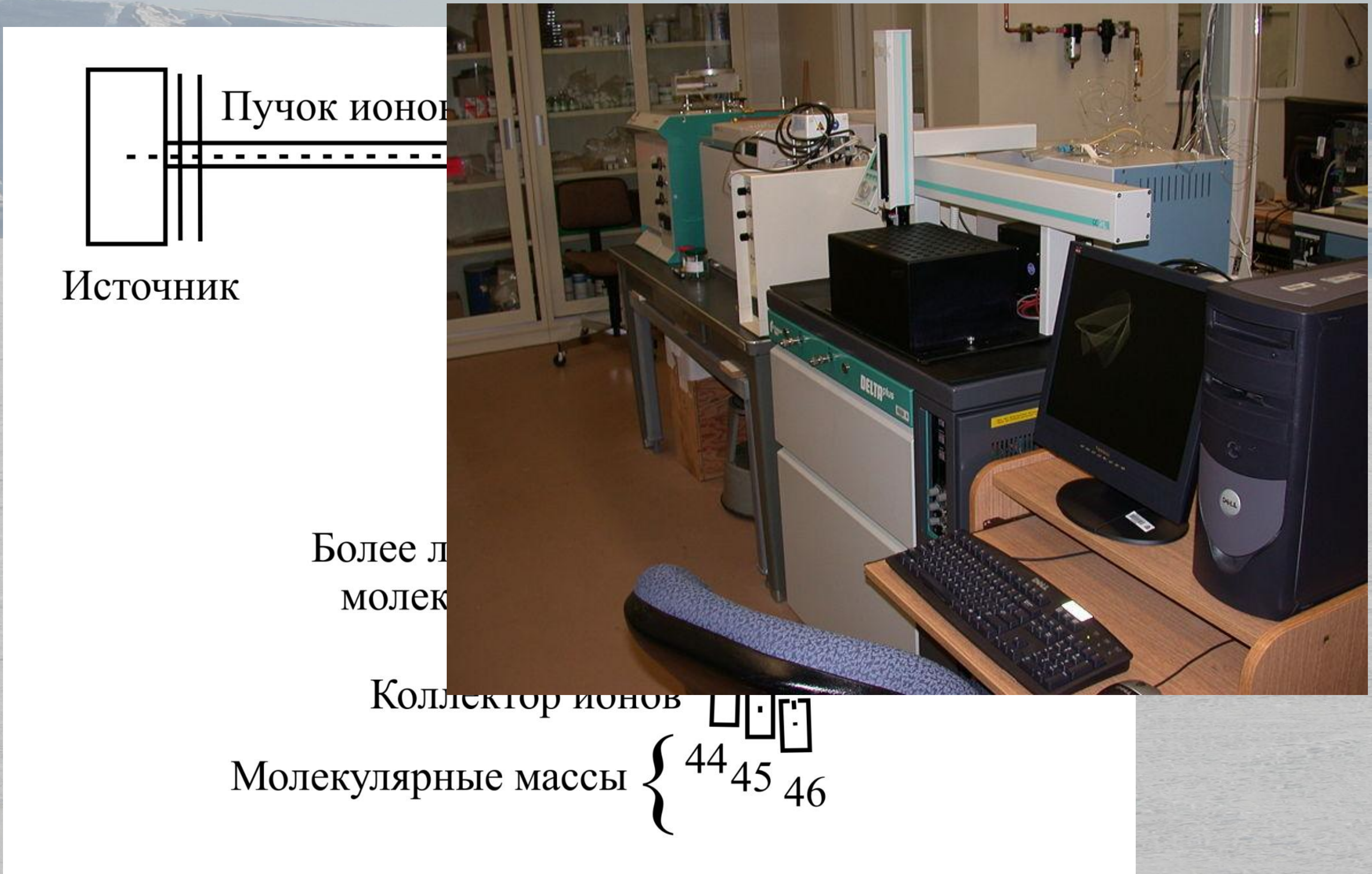


Выводы:

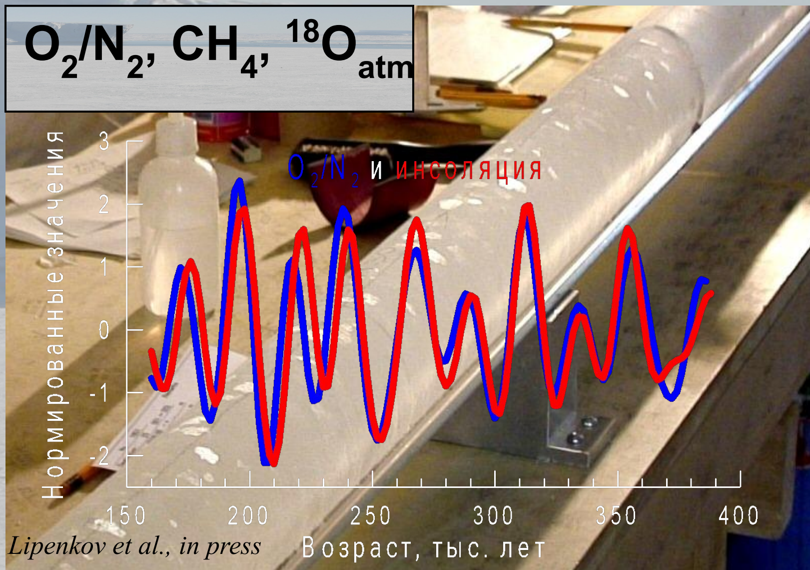
1) Верхняя часть сложена современными осадками

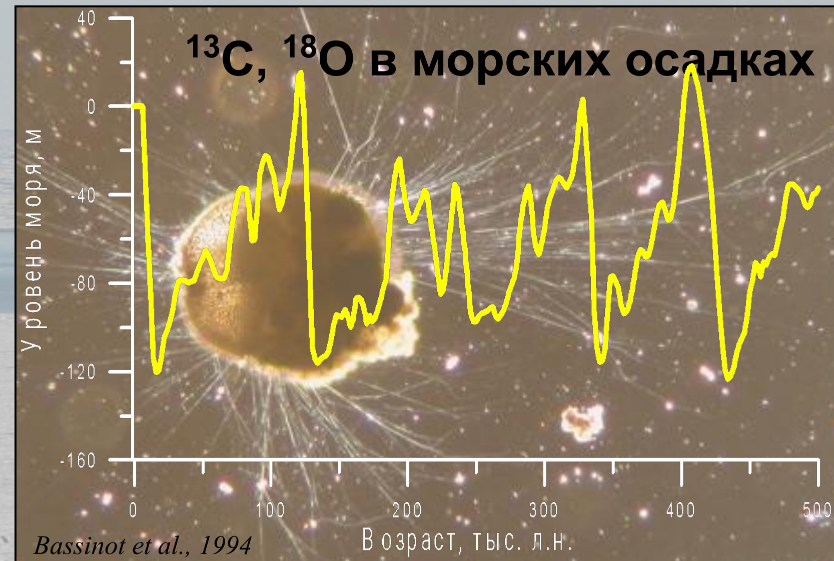
2) Нижняя часть, возможно, сложена осадками, сформировавшимися в более холодну

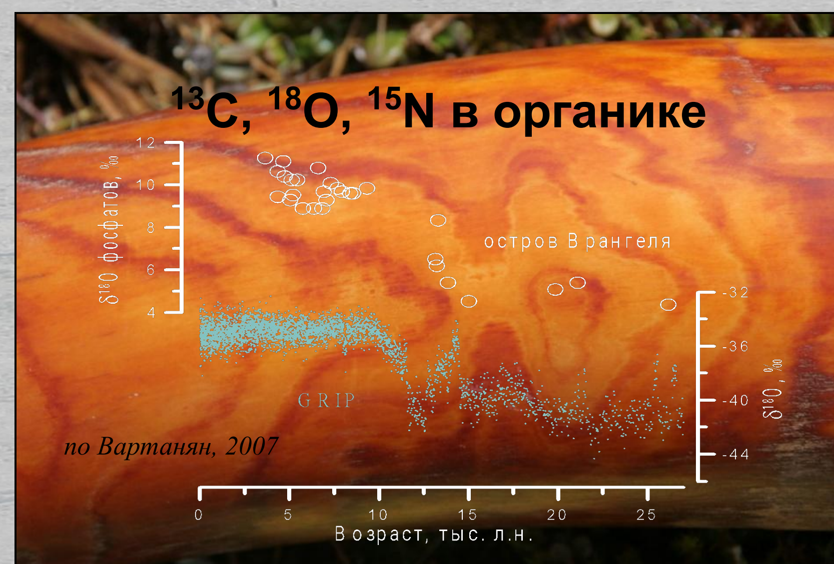
Methods of laboratory analysis of the stable water isotopes: Isotope-Ratio Mass-Spectrometry



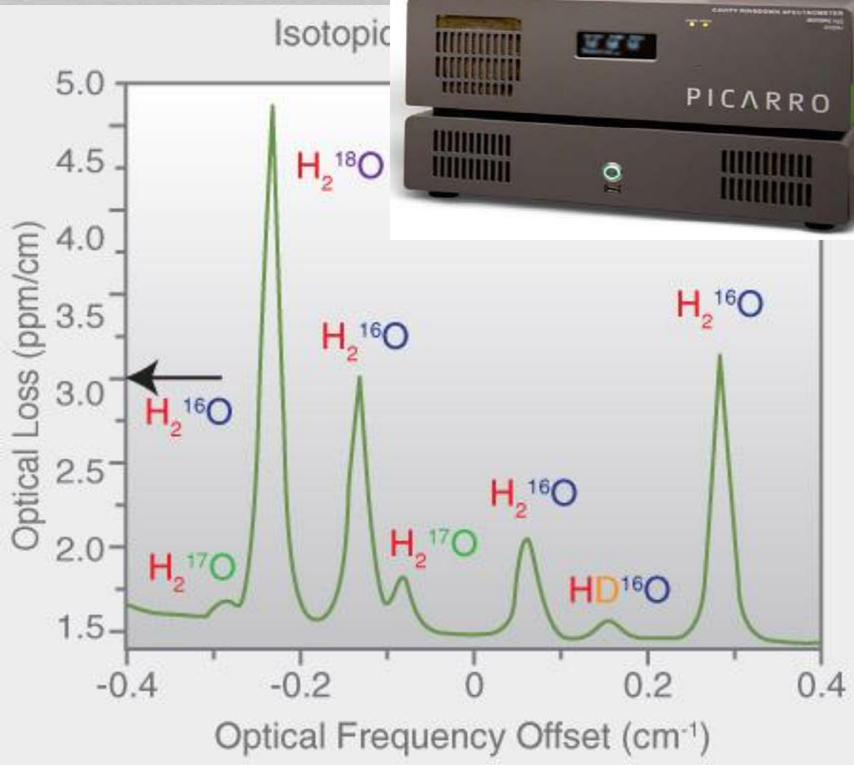
Methods of laboratory analysis of the stable water isotopes: Isotope-Ratio Mass-Spectrometry

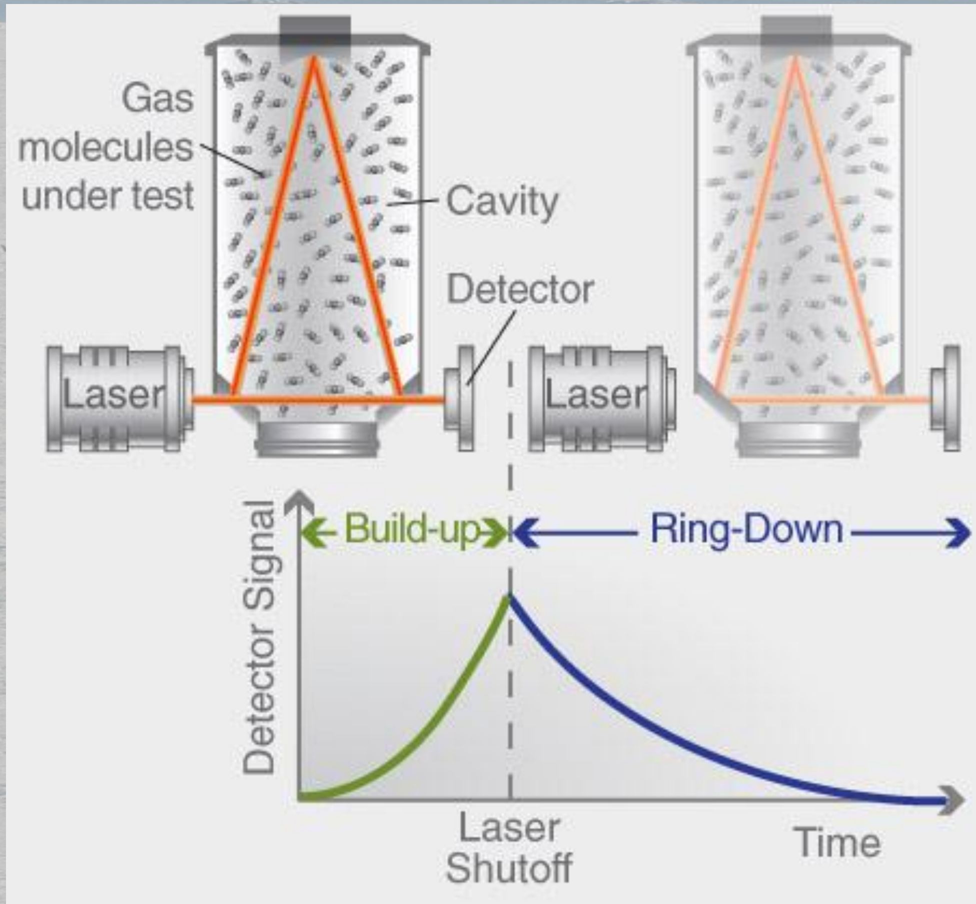






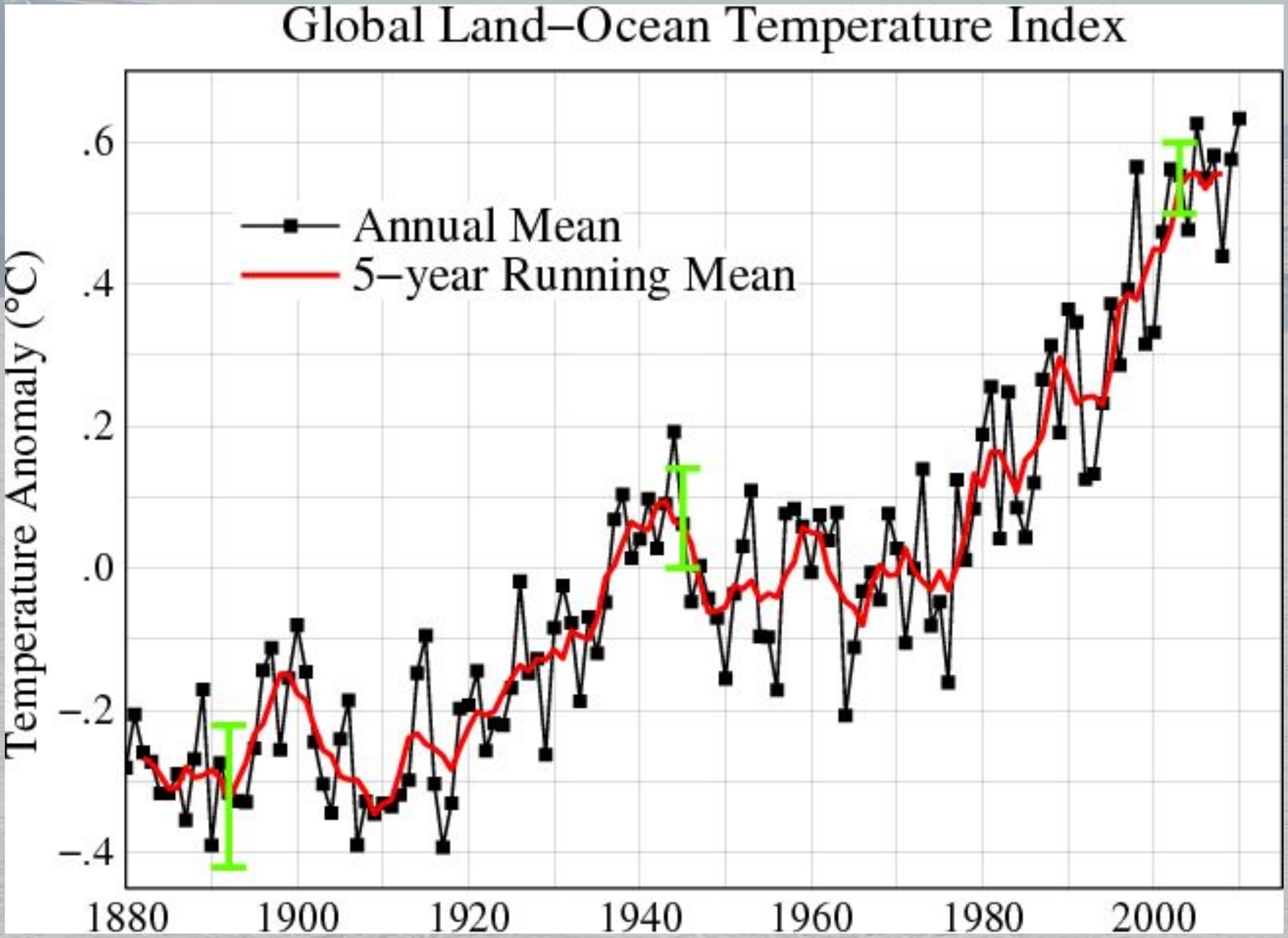
Methods of laboratory analysis of the stable water isotopes: Laser Spectroscopy



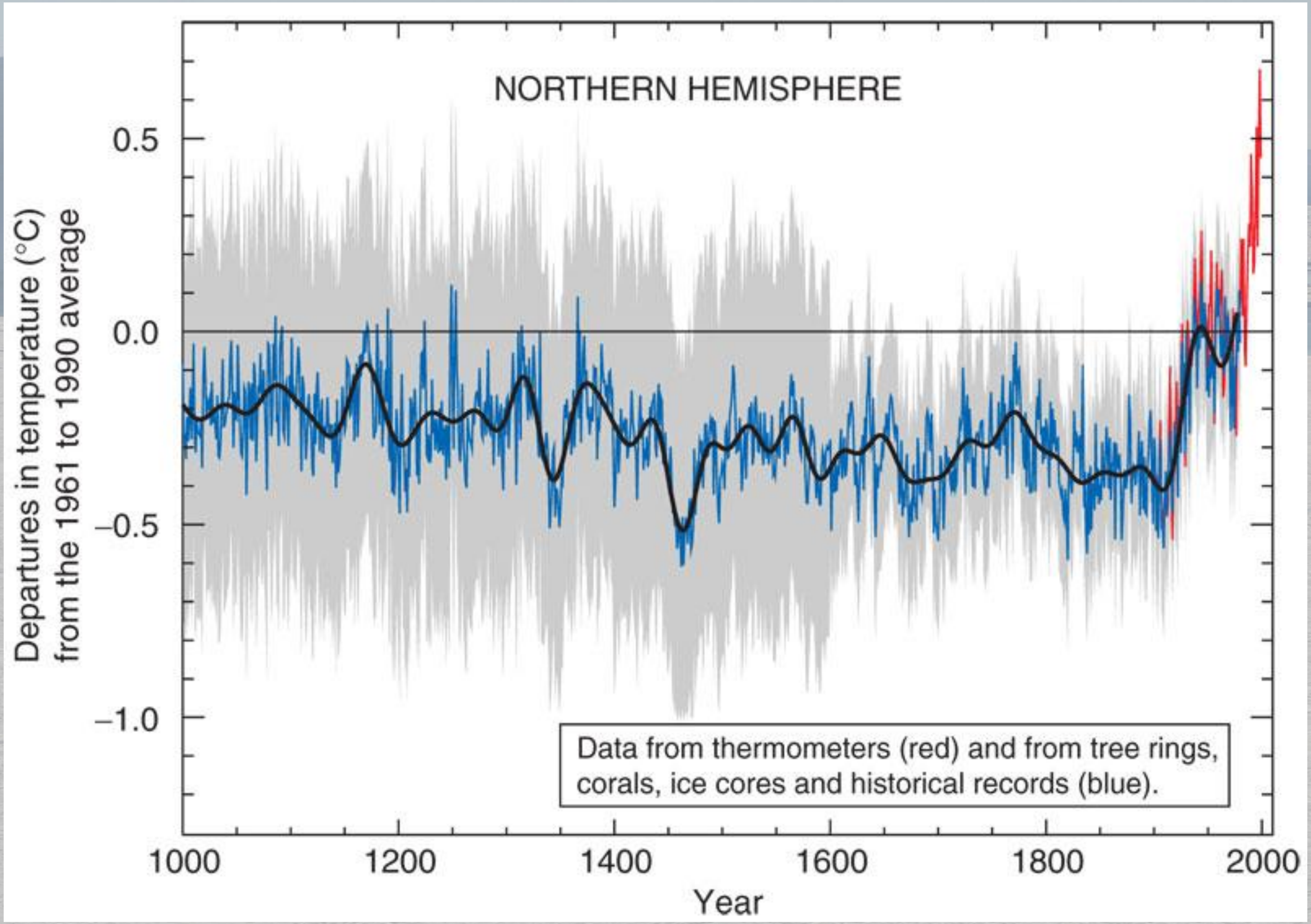


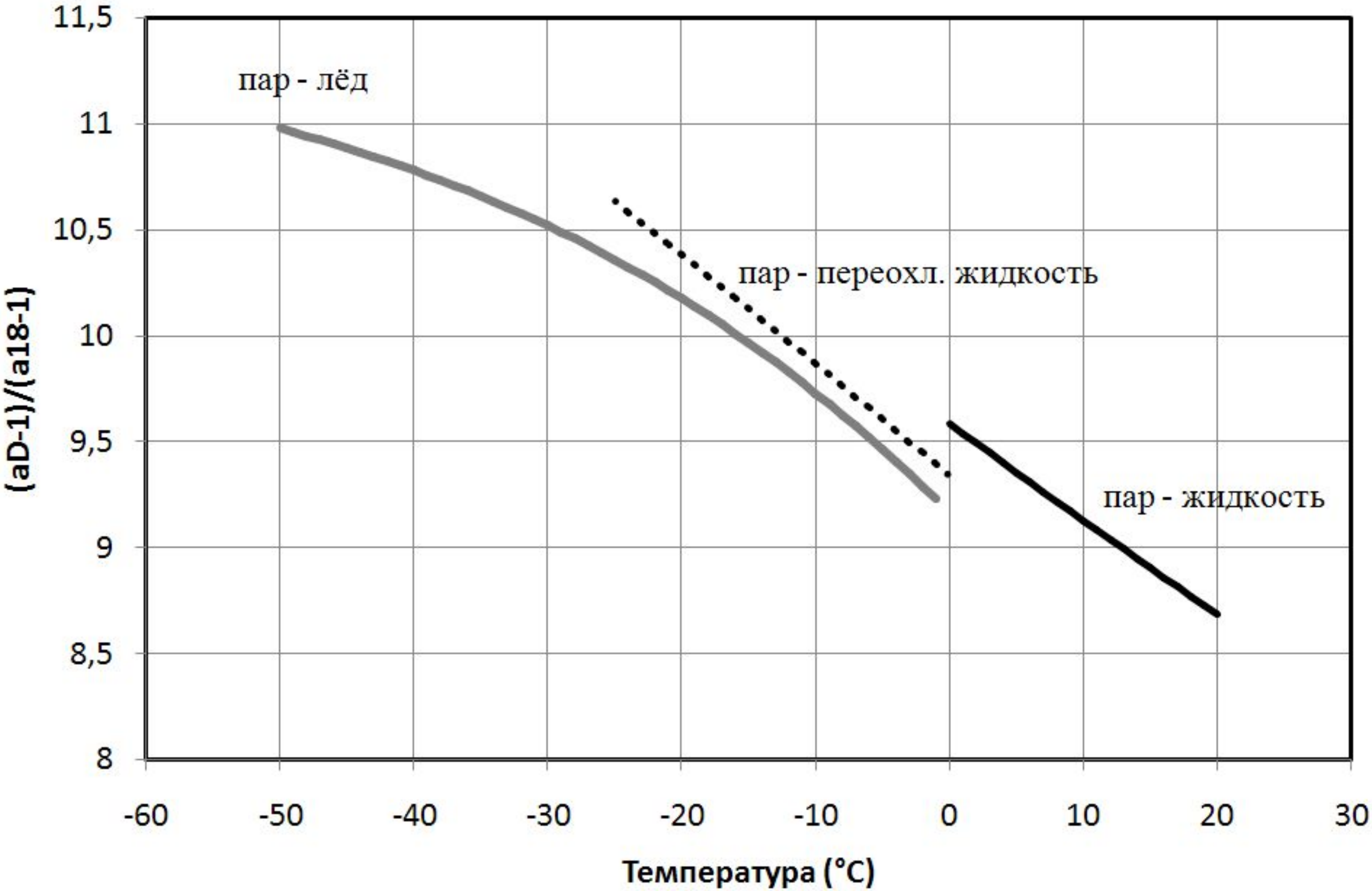
Thank you!

E-mail to: ekaykin@aari.ru

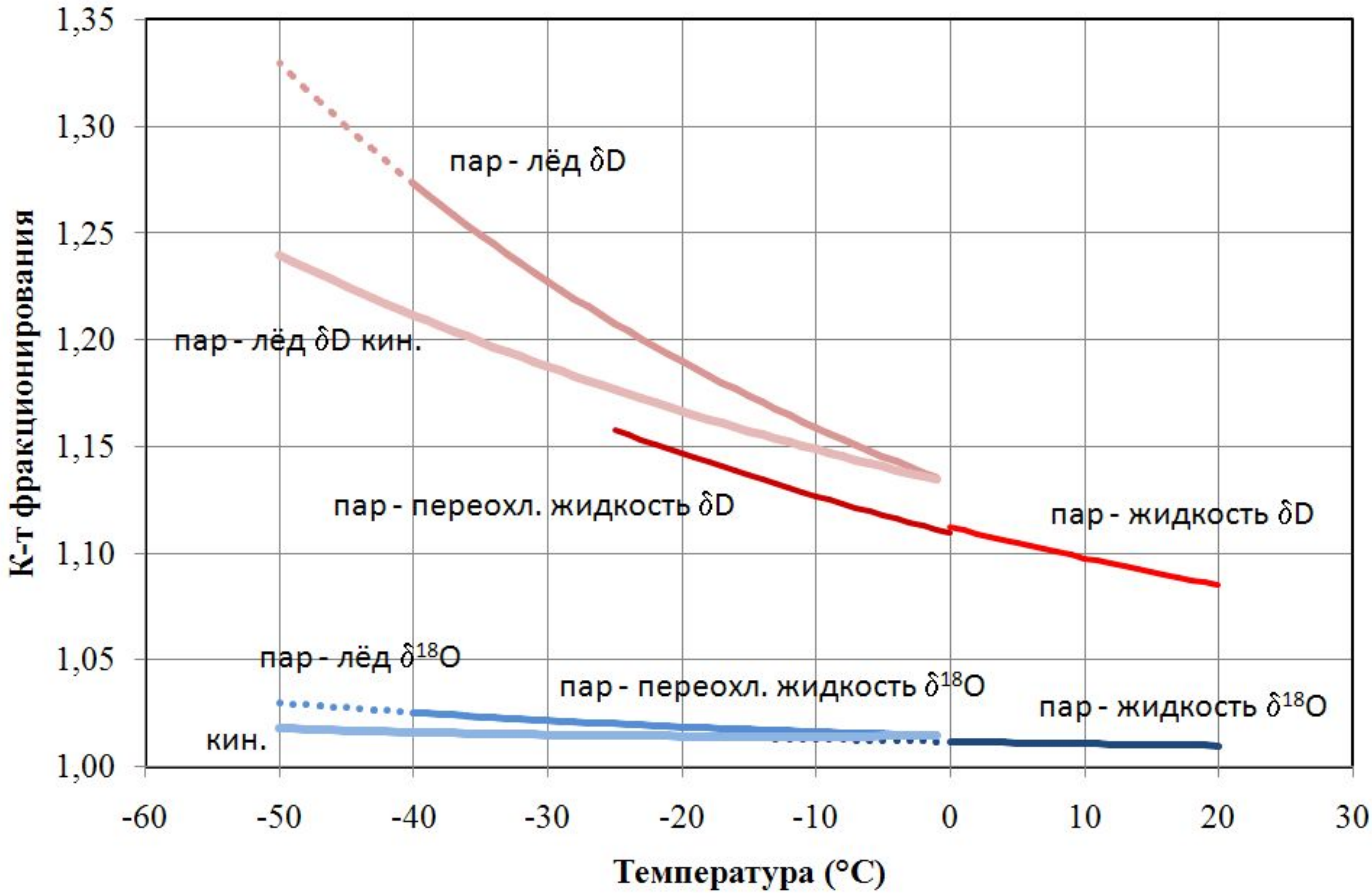


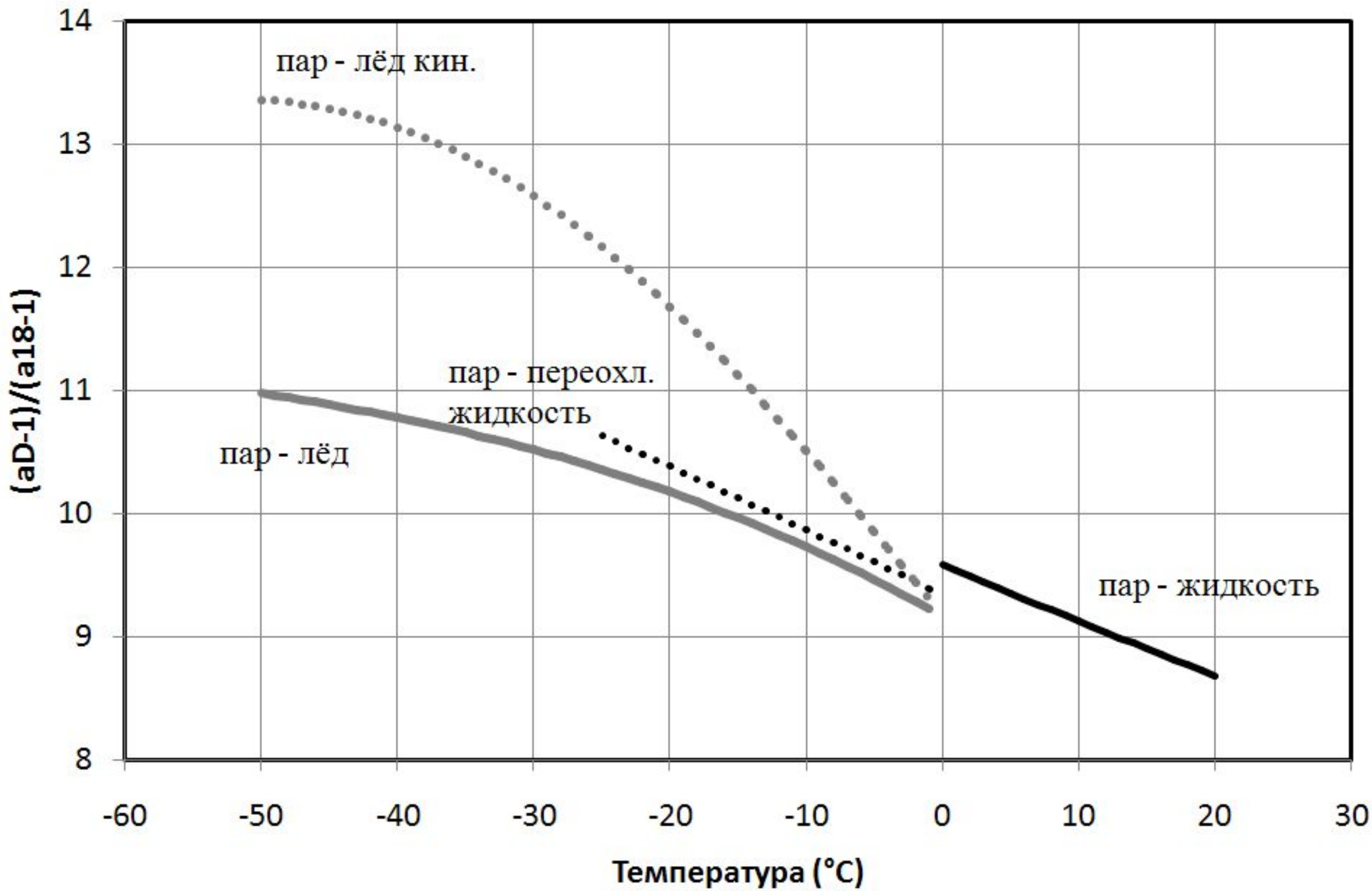
Global Land−Ocean Temperature Index
Annual Mean
5−year Running Mean
Temperature Anomaly (°C)
.6
.4
.2
.0
−.2
−.4
1880
1900
1920
1940
1960
1980
2000


NORTHERN HEMISPHERE
Departures in temperature (°C) from the 1961 to 1990 average
0.5
0.0
−0.5
−1.0
Data from thermometers (red) and from tree rings, corals, ice cores and historical records (blue).
1000
1200
1400
1600
1800
2000
Year

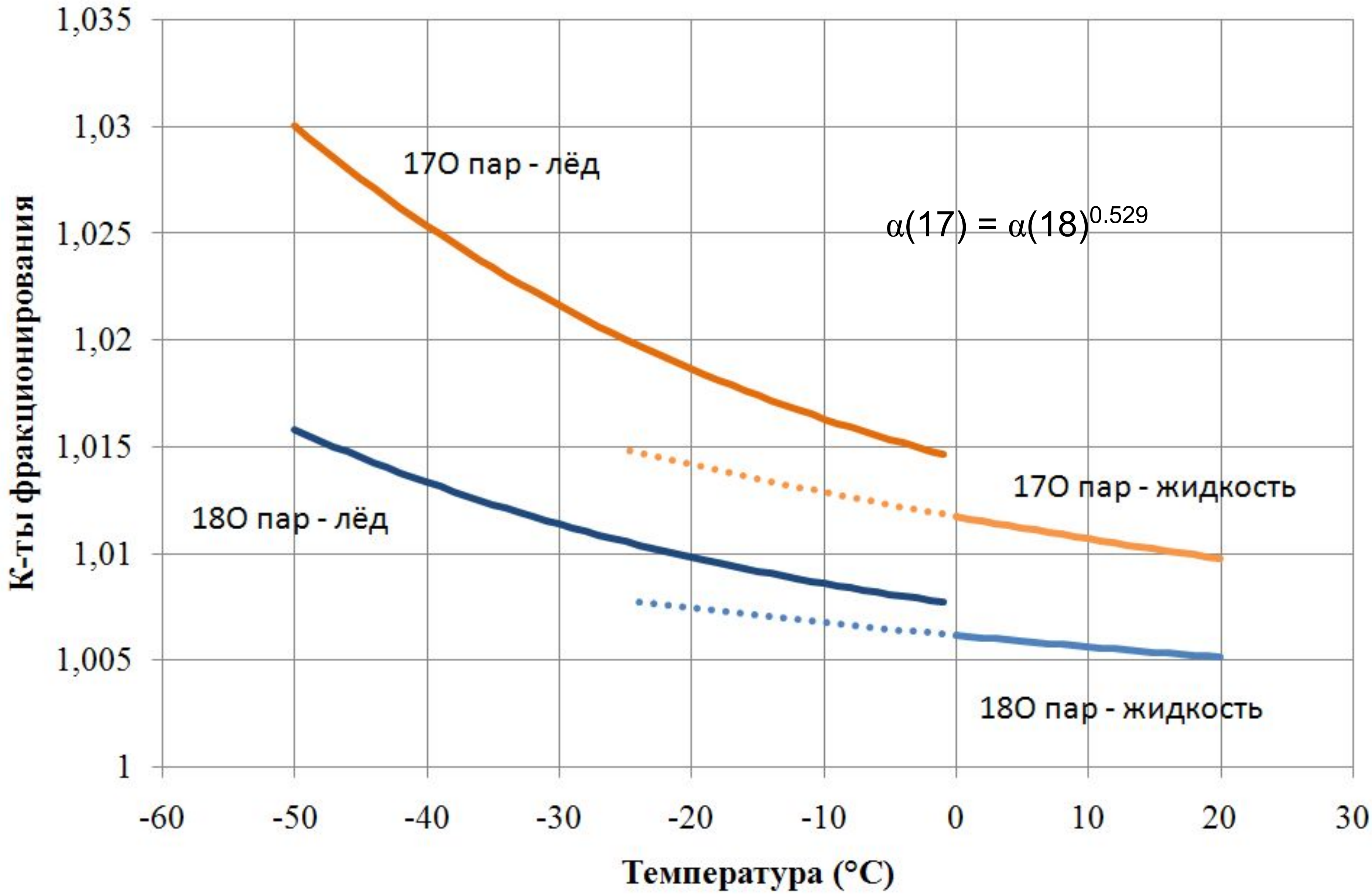


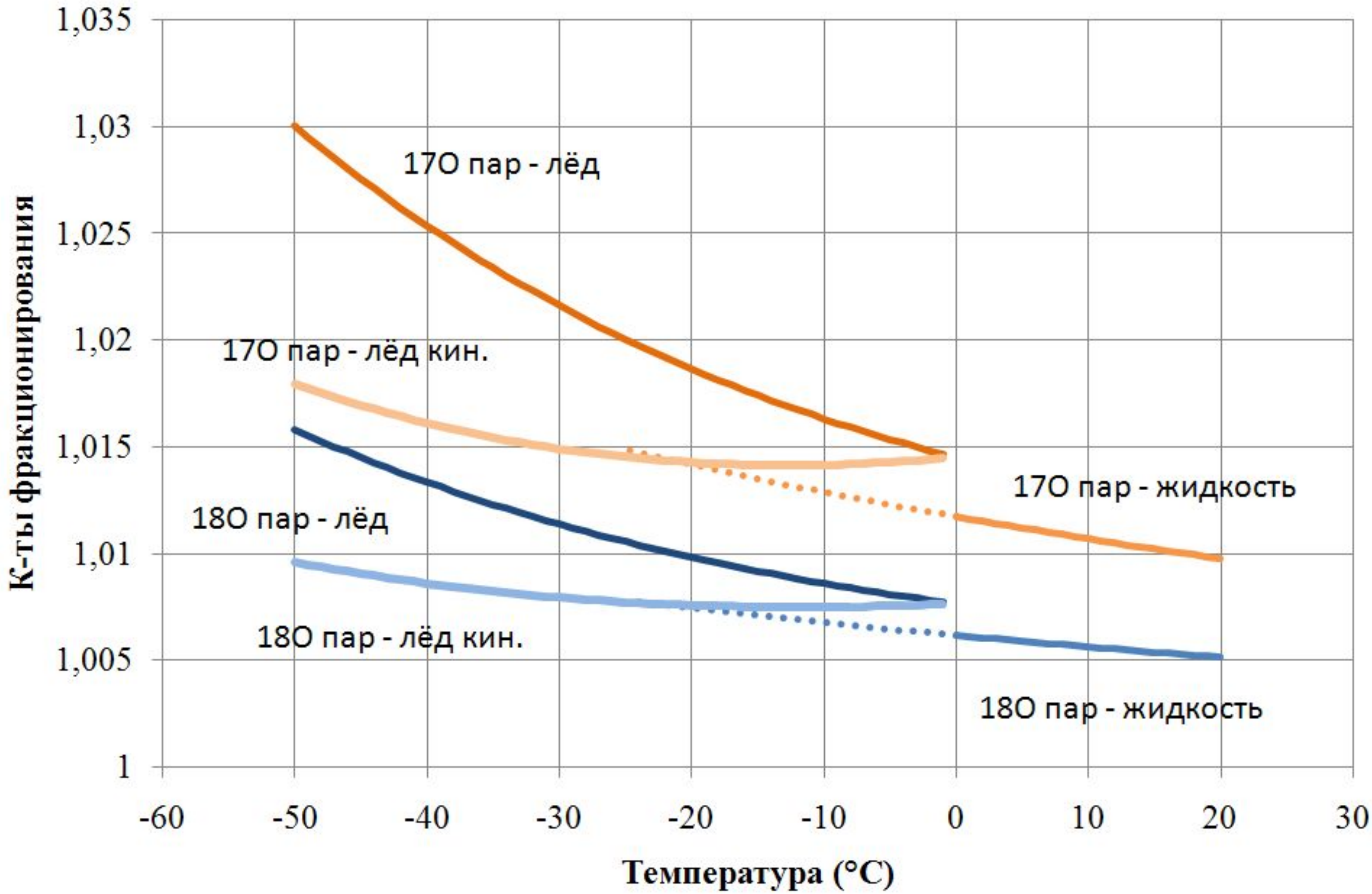
11,5
11
10,5
10
9,5
9
8,5
8
(aD-1)/(a18-1)
пар - лёд
пар - переохл. жидкость
пар - жидкость
-60
-50
-40
-30
-20
-10
0
10
20
30
Температура (°C)

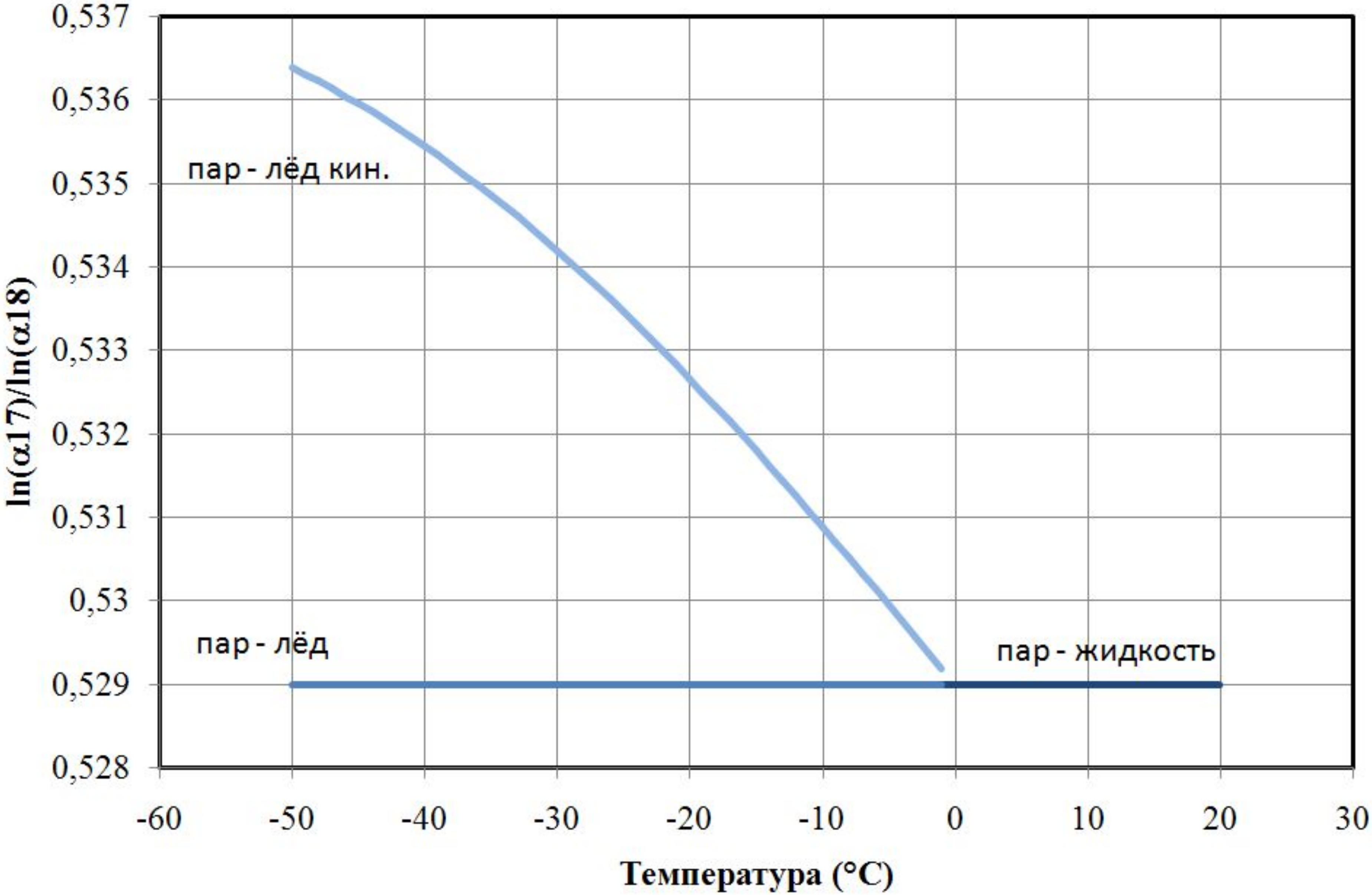

1,35
1,30
1,25
1,20
1,15
1,10
1,05
1,00
К-т фракционирования
-60
-50
-40
-30
-20
-10
0
10
20
30
Температура (°С)
пар - лёд δD
пар - лёд δD кин.
пар - переохл. жидкость δD
пар - жидкость δD
пар - лёд δ18O
пар - переохл. жидкость δ18O
пар - жидкость δ18O
кин.



пар - лёд кин.
пар - переохл.
жидкость
пар - лёд
пар - жидкость
(aD-1)/(a18-1)
Температура (°C)
14
13
12
11
10
9
8
-60
-50
-40
-30
-20
-10
0
10
20
30


1,035
1,03
1,025
1,02
1,015
1,01
1,005
1
-60
-50
-40
-30
-20
-10
0
10
20
30
К-ты фракционирования
Температура (°C)
17O пар - лёд
α(17) = α(18)^0.529
17O пар - жидкость
18O пар - лёд
18O пар - жидкость


1,035
1,03
1,025
1,02
1,015
1,01
1,005
1
К-ты фракционирования
-60
-50
-40
-30
-20
-10
0
10
20
30
Температура (°C)
17O пар - лёд
17O пар - лёд кин.
17O пар - жидкость
18O пар - лёд
18O пар - лёд кин.
18O пар - жидкость



0,537
0,536
0,535
0,534
0,533
0,532
0,531
0,53
0,529
0,528
ln(α17)/ln(α18)
пар - лёд кин.
пар - лёд
пар - жидкость
-60
-50
-40
-30
-20
-10
0
10
20
30
Температура (°C)