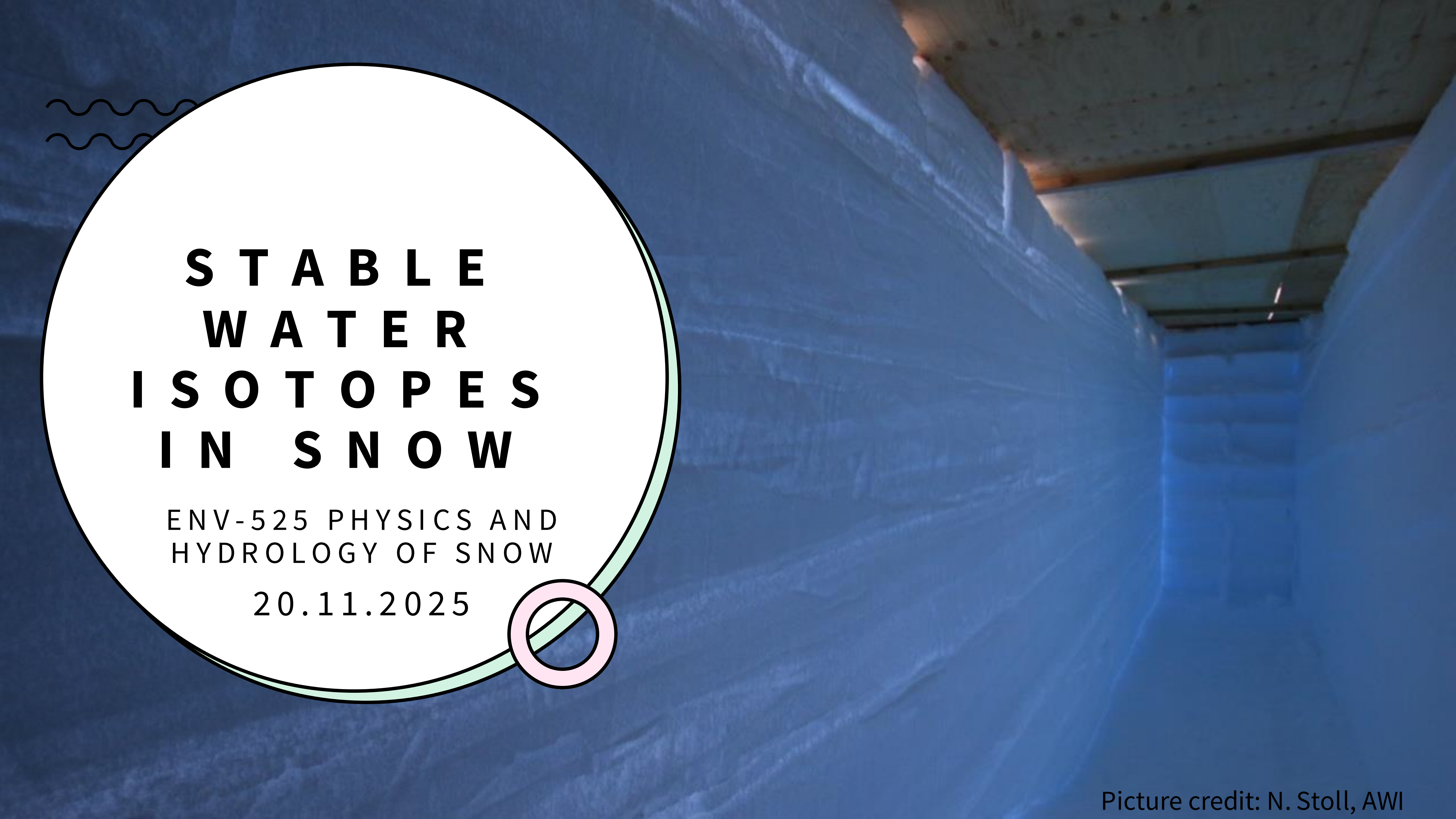


STABLE WATER ISOTOPES IN SNOW

ENV-525 PHYSICS AND HYDROLOGY OF SNOW

20.11.2025

Picture credit: N. Stoll, AWI

Why are we interested in Snow Isotopes

- Isotopic composition of snow and ice gives information on past dynamical processes
- Are used to determine temperatures of the past
- May help you to quantify important processes such as sublimation

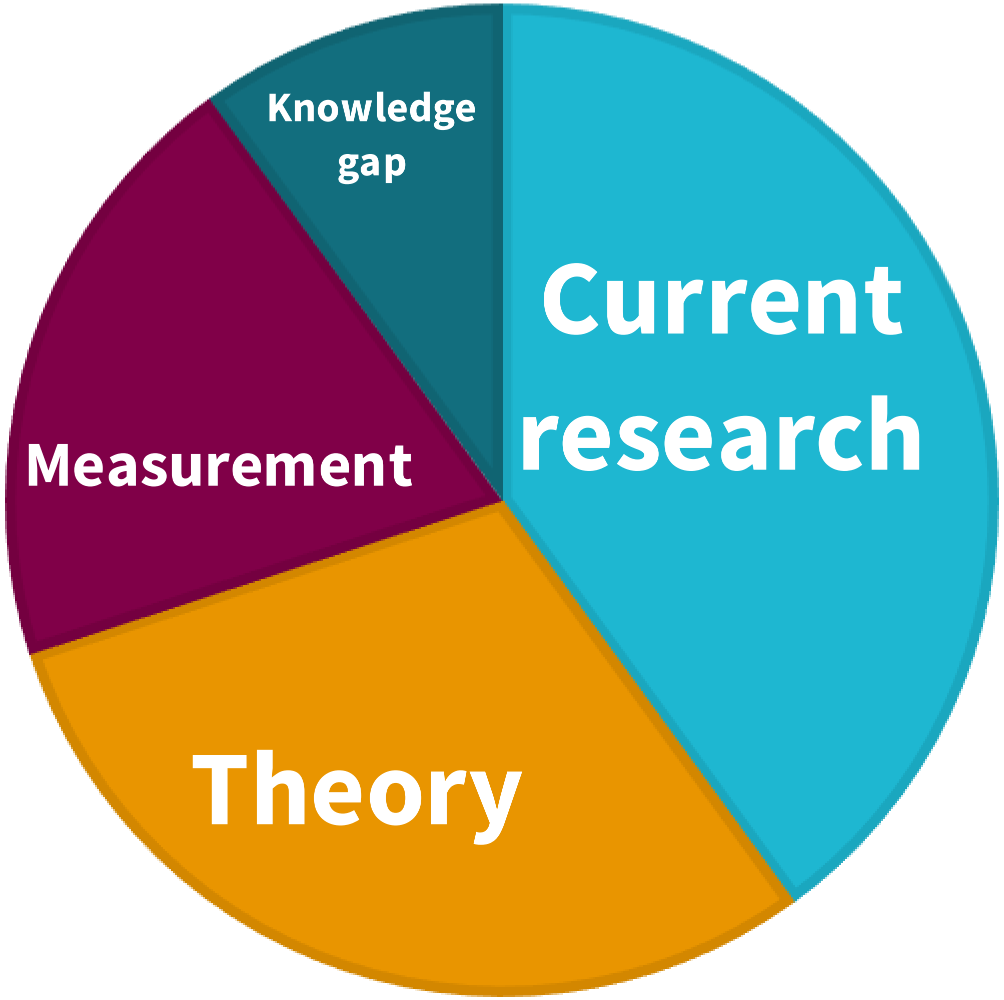
Slide credit: Sonja Wahl Sonja.Wahl@uib.no

TODAY'S LECTURE

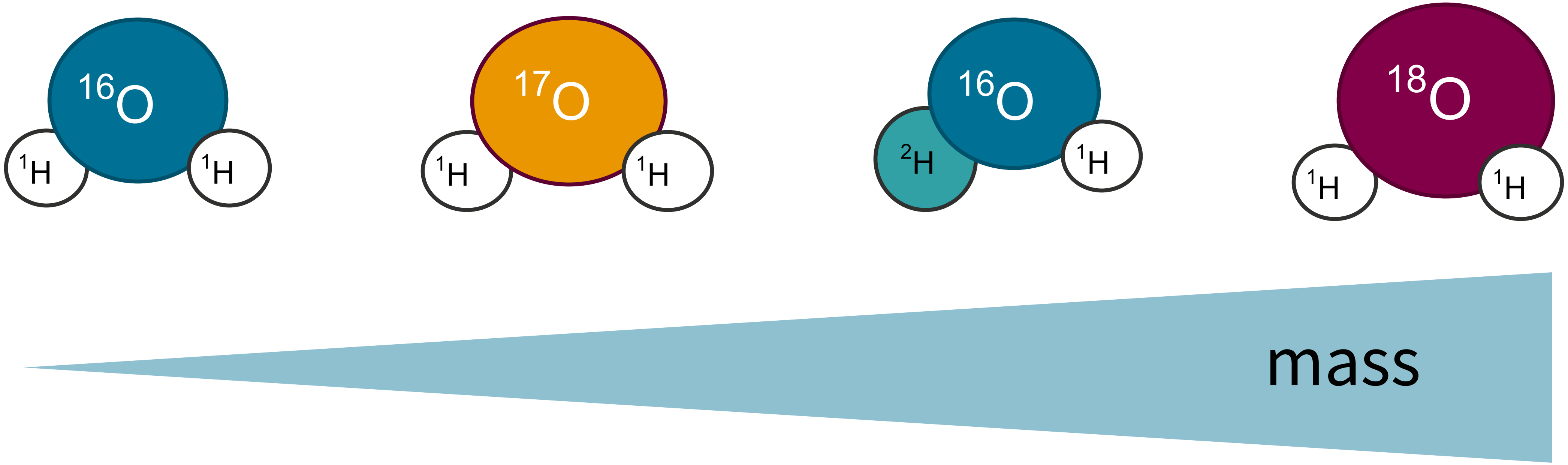
Stable Water Isotope Dynamics

Objectives

- Understanding the concept
- See application areas for snow/cryospheric studies
- Understand limitations



Stable water isotopologues (geochemistry)



Can you think of consequences of this mass difference for molecular characteristics?

Isotope differences, Horita et al. (2008)

HDO

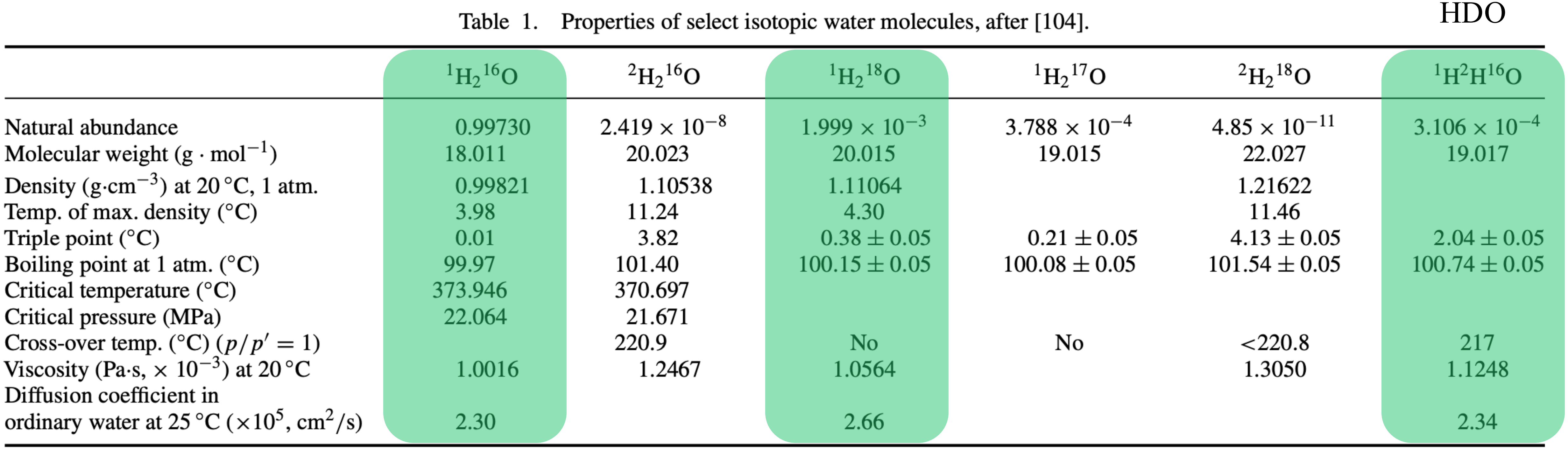
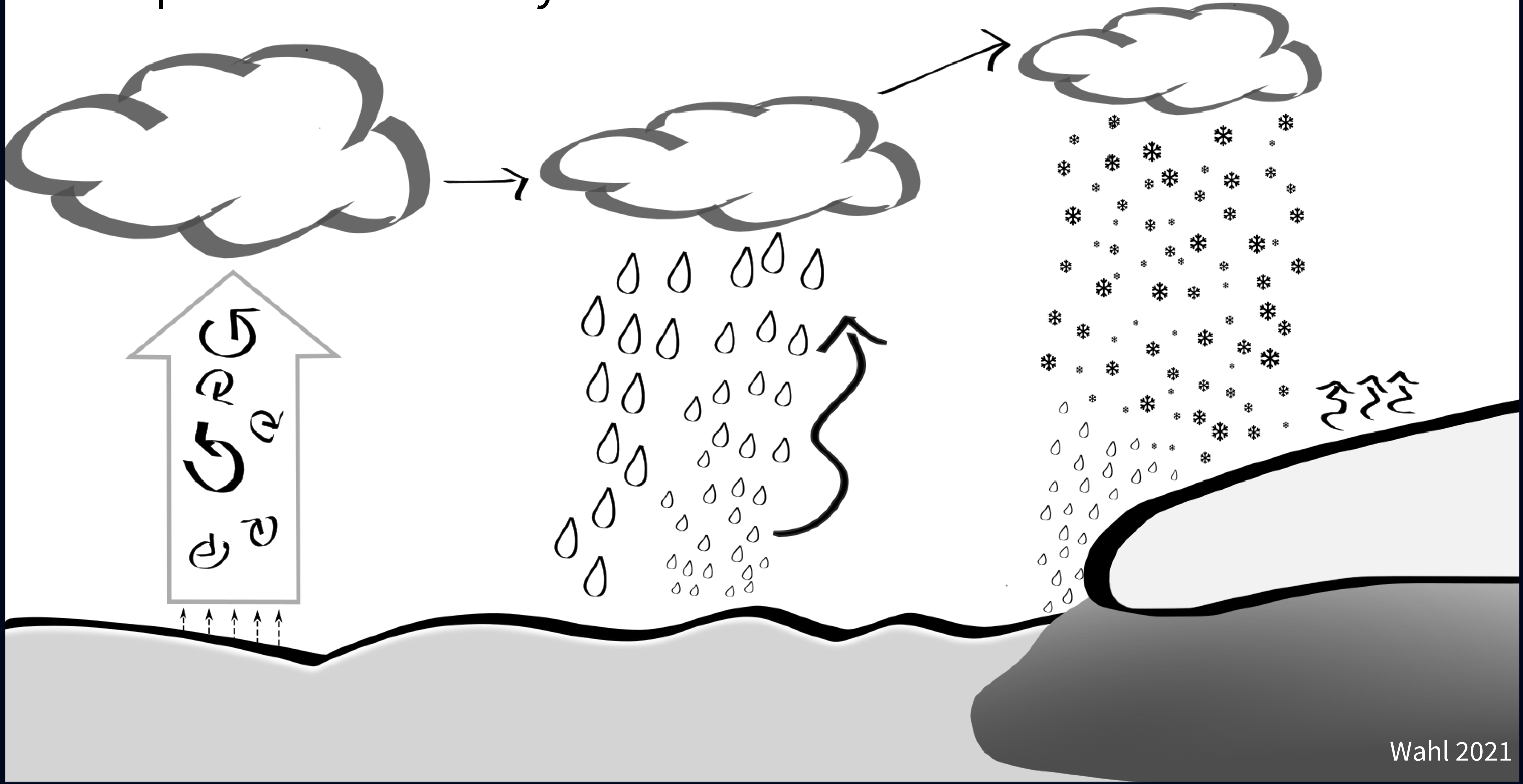


Table 1. Properties of select isotopic water molecules, after [104].

	$^1H_2{}^{16}O$	$^2H_2{}^{16}O$	$^1H_2{}^{18}O$	$^1H_2{}^{17}O$	$^2H_2{}^{18}O$	$^1H^2H^{16}O$
Natural abundance	0.99730	2.419×10^{-8}	1.999×10^{-3}	3.788×10^{-4}	4.85×10^{-11}	3.106×10^{-4}
Molecular weight ($g \cdot mol^{-1}$)	18.011	20.023	20.015	19.015	22.027	19.017
Density ($g \cdot cm^{-3}$) at 20 °C, 1 atm.	0.99821	1.10538	1.11064		1.21622	
Temp. of max. density (°C)	3.98	11.24	4.30		11.46	
Triple point (°C)	0.01	3.82	0.38 ± 0.05	0.21 ± 0.05	4.13 ± 0.05	2.04 ± 0.05
Boiling point at 1 atm. (°C)	99.97	101.40	100.15 ± 0.05	100.08 ± 0.05	101.54 ± 0.05	100.74 ± 0.05
Critical temperature (°C)	373.946	370.697				
Critical pressure (MPa)	22.064	21.671				
Cross-over temp. (°C) ($p/p' = 1$)		220.9	No	No	<220.8	217
Viscosity (Pa·s, $\times 10^{-3}$) at 20 °C	1.0016	1.2467	1.0564		1.3050	1.1248
Diffusion coefficient in ordinary water at 25 °C ($\times 10^5$, cm^2/s)	2.30		2.66			2.34

Diffusivity of isotopes in air at -10°C and 1atm
H_2O 0.1963 $cm^2\ s^{-1}$
HDO 0.1915 $cm^2\ s^{-1}$
$H_2{}^{18}O$ 0.1908 $cm^2\ s^{-1}$

Isotopes in the Water Cycle

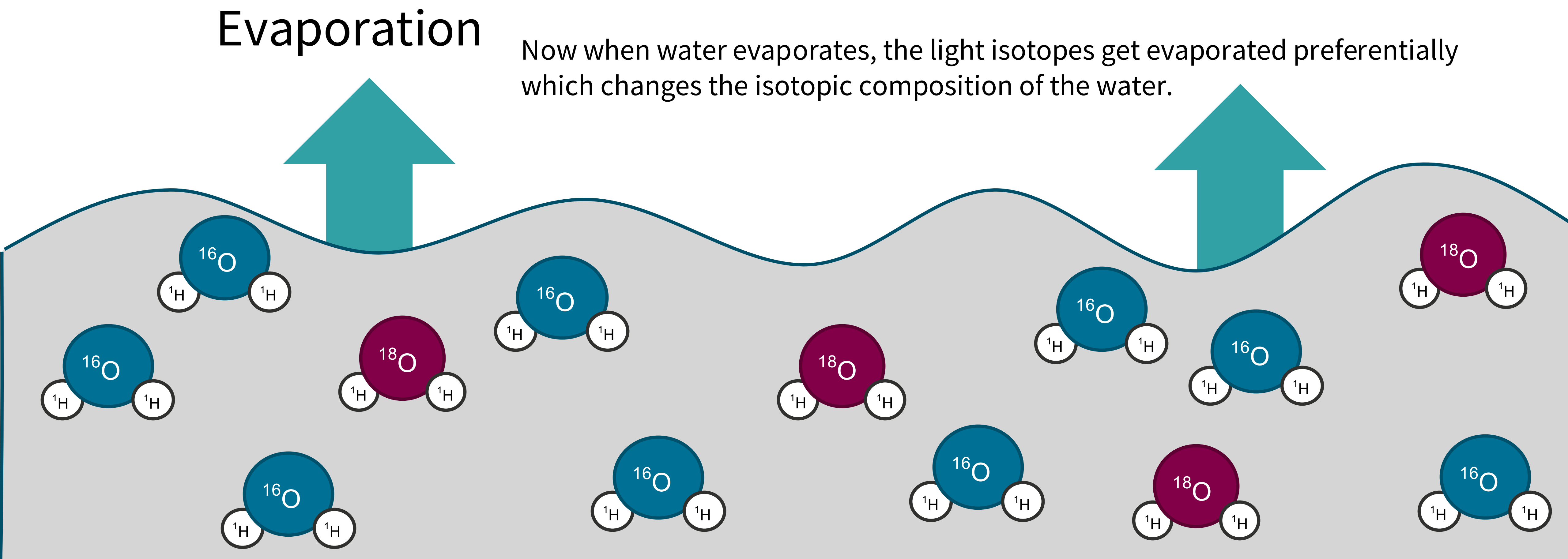


Wahl 2021

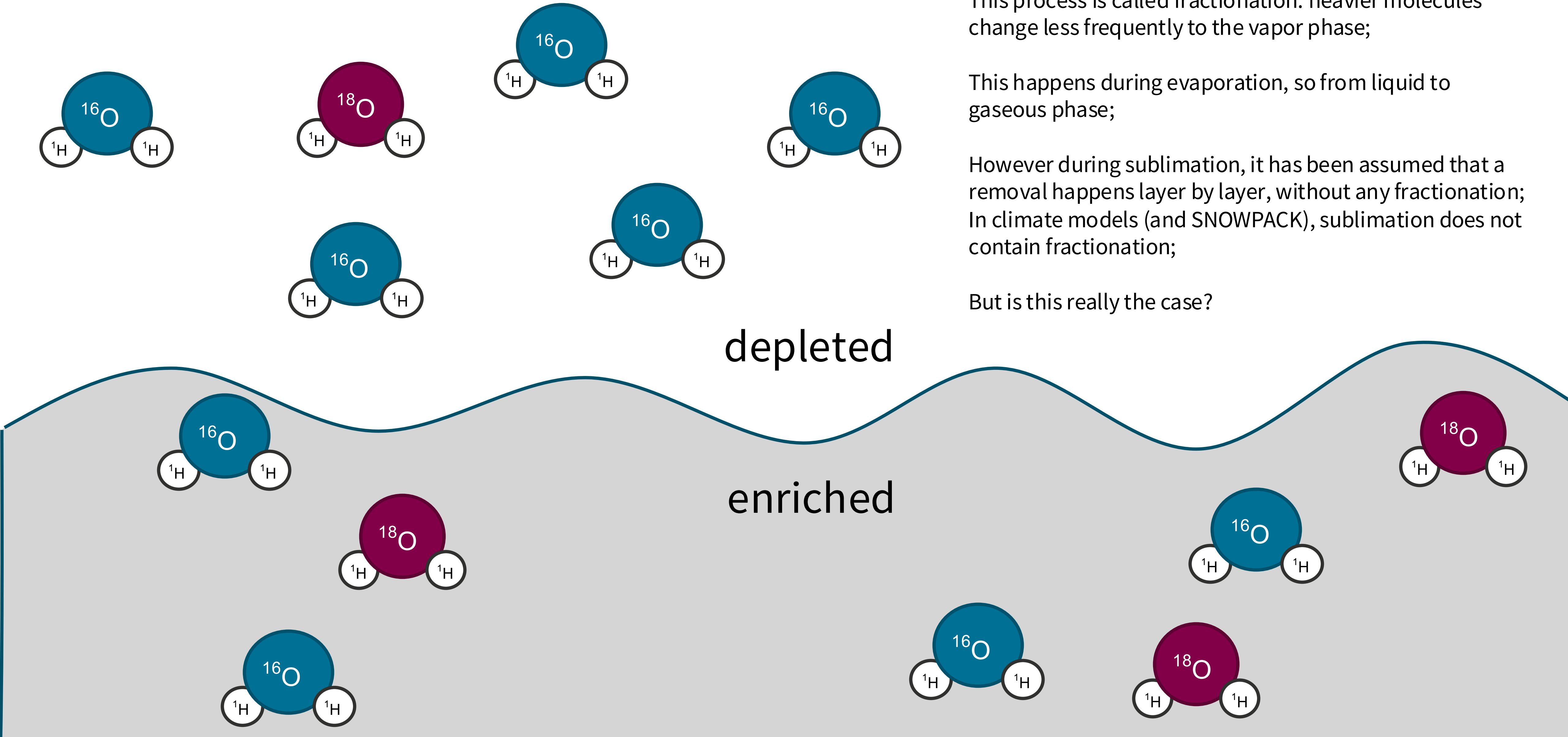
FRACTIONATION during phase change

We see here a water body that contains heavy and light water isotopes.
This means it has a certain isotopic composition.
The isotopic composition of a water sample is the ratio of heavy to light isotopes.

Now when water evaporates, the light isotopes get evaporated preferentially which changes the isotopic composition of the water.



FRACTIONATION during phase change



This process is called fractionation: heavier molecules change less frequently to the vapor phase;

This happens during evaporation, so from liquid to gaseous phase;

However during sublimation, it has been assumed that a removal happens layer by layer, without any fractionation; In climate models (and SNOWPACK), sublimation does not contain fractionation;

But is this really the case?

- # δ-notation (Craig 1965)

abundance

$$^{18}R = \frac{[H_2{}^{18}O]}{[H_2{}^{16}O]}$$

Is *R* a concentration?
Why not?

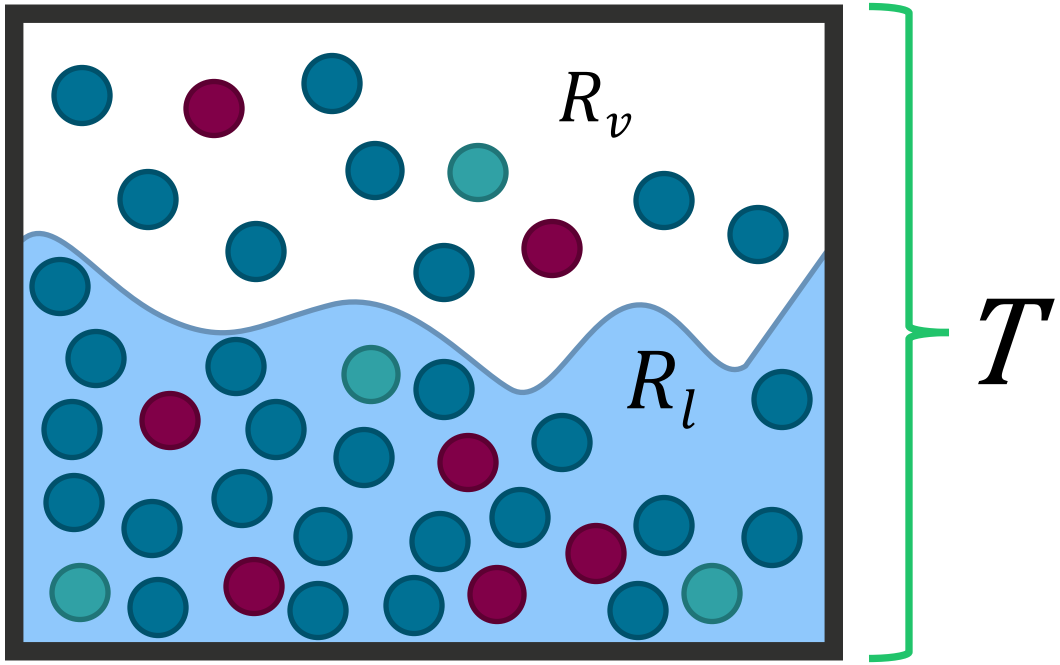
$$\delta^{18}\text{O} = \frac{^{18}R}{^{18}R_{VSMOW}} - 1$$

in ‰

VSMOW = Vienna Standard Mean Ocean Water

Isotopic fractionation

Equilibrium fractionation:



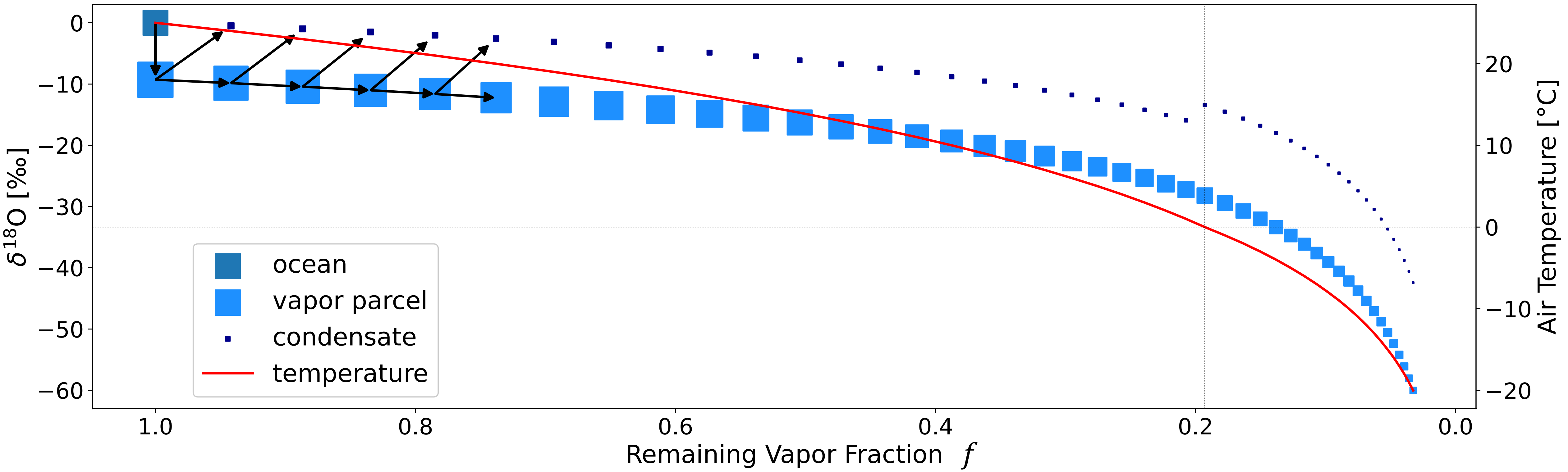
fractionation factor

$$\alpha_{\frac{l}{v}}(T) = \frac{R_l}{R_v}$$

>1, can also be defined as the reciprocal

What is the controlling isotope characteristic?

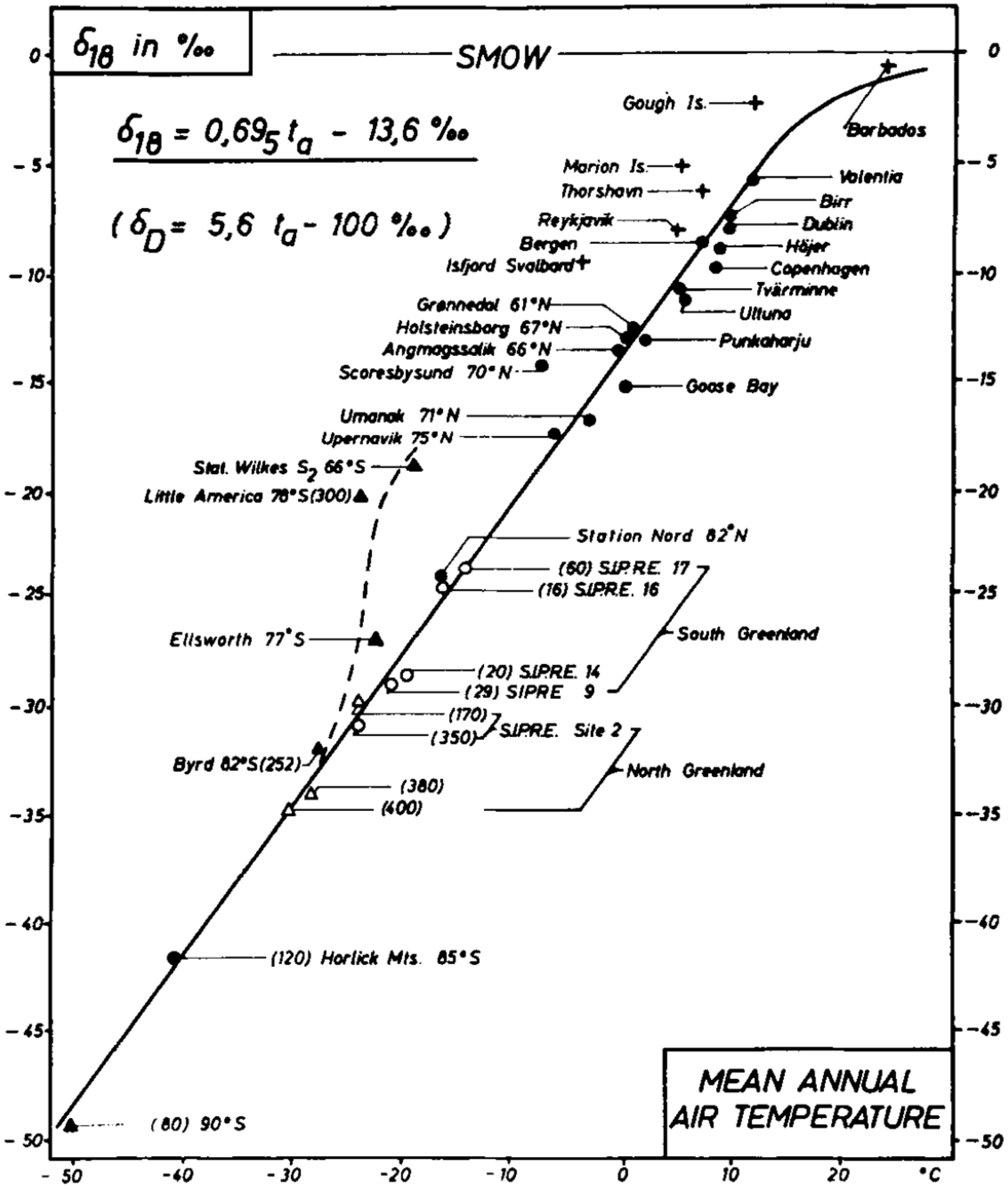
○ Rayleigh Distillation = eq. fractionation



Rayleigh model for vapor: $R_v = R_0 f^{\alpha(T)-1}$

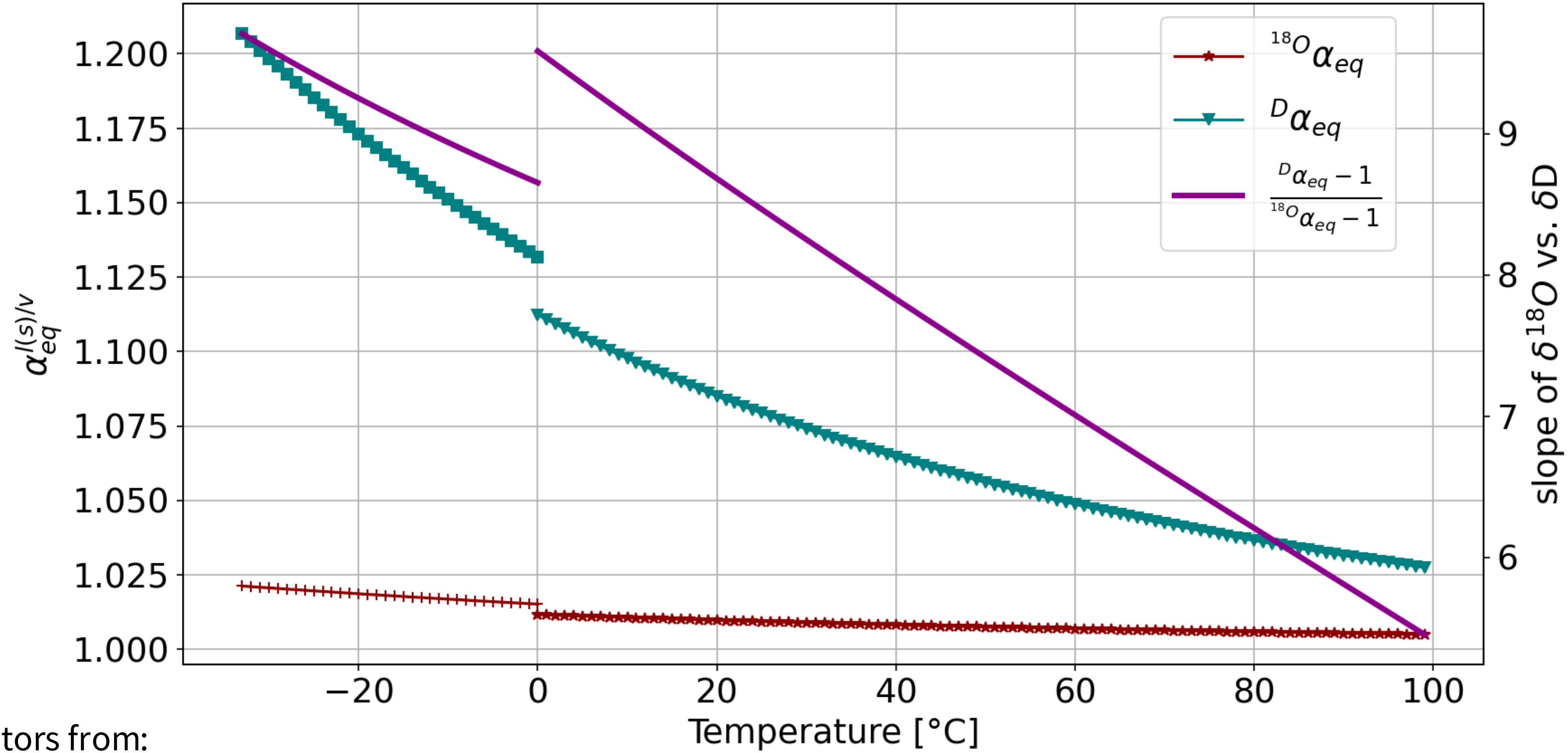
- Isotopes in precipitation

Dansgaard (1964)



Equilibrium fractionation factors

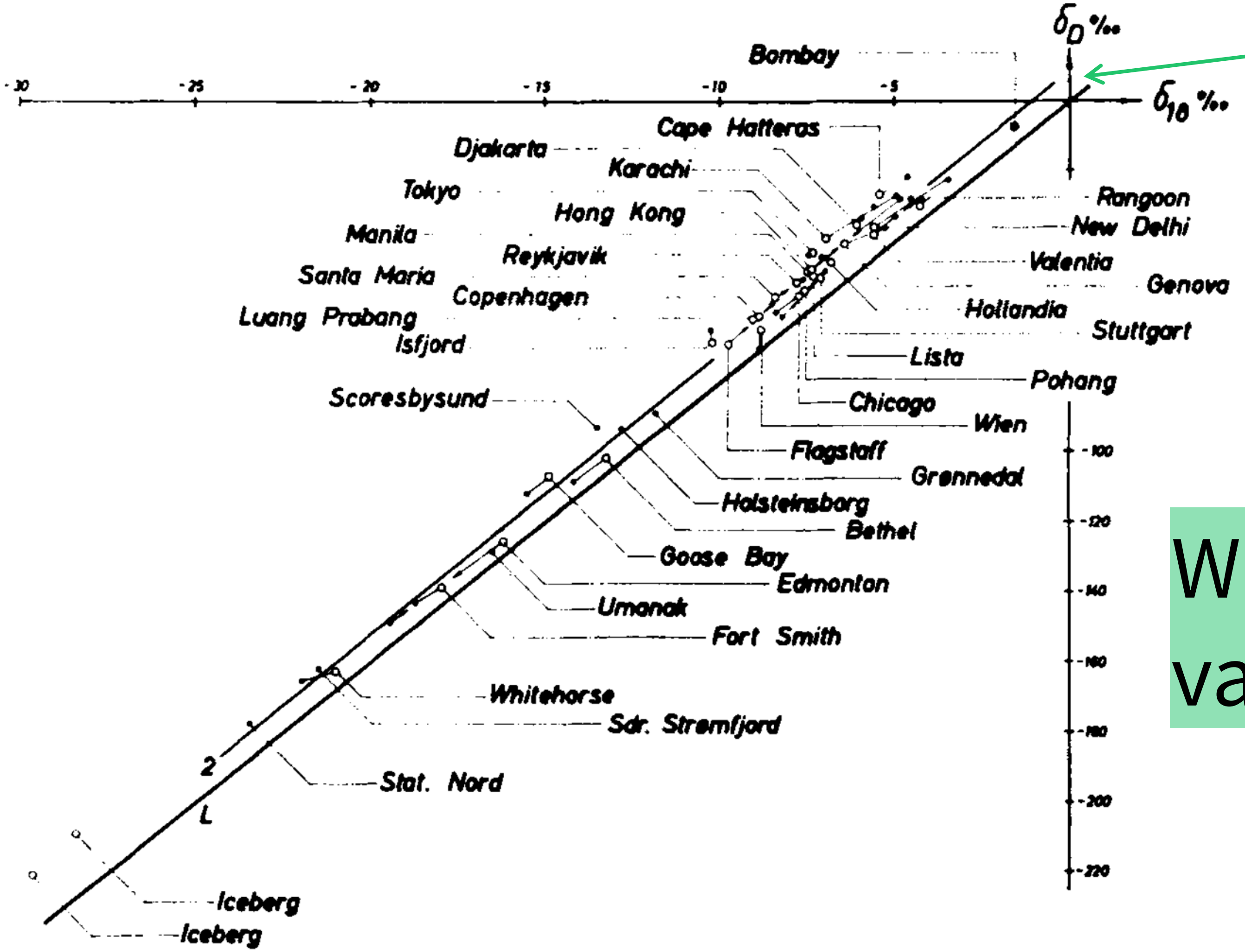
Stronger temperature dependence for HDO



Fractionation factors from:
Majoube (1971 a,b), Merlivat & Nief (1967)

Deuterium-excess, d-excess, xs, dxs

Dansgaard (1964)



Global Meteoric Water Line (GMWL)

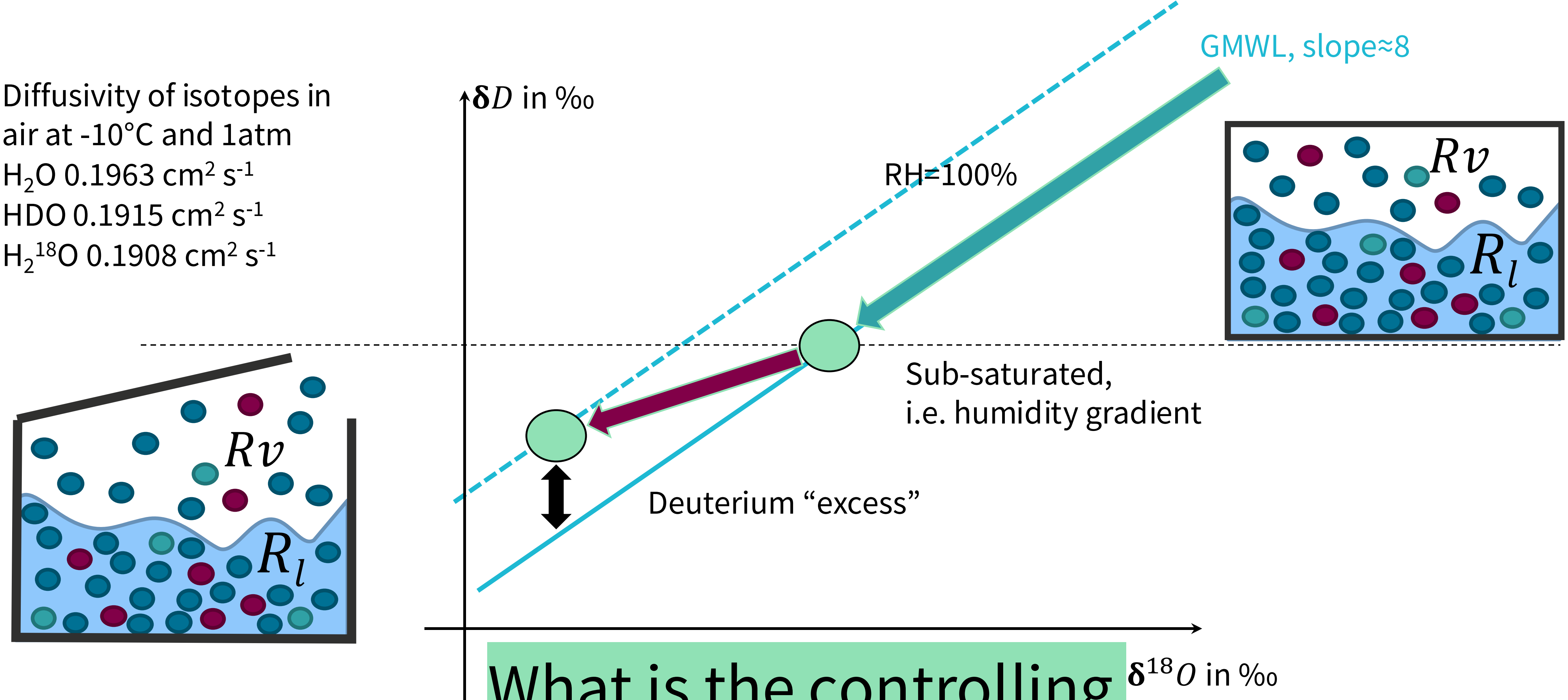
Slope ≈ 8

What is the d-excess value of the GMWL?

$$\text{d-excess} = \delta D - 8 \bullet \delta^{18}\text{O}$$

Vapor d-excess during evaporation

Diffusivity of isotopes in air at -10°C and 1atm
H_2O 0.1963 $cm^2\ s^{-1}$
HDO 0.1915 $cm^2\ s^{-1}$
$H_2{}^{18}O$ 0.1908 $cm^2\ s^{-1}$



What is the controlling isotope characteristic?

○ Effective fractionation factor during non-equilibrium conditions

$$R_{v} = \alpha_{eff} \cdot R_{l}$$

Equilibrium fractionation factor

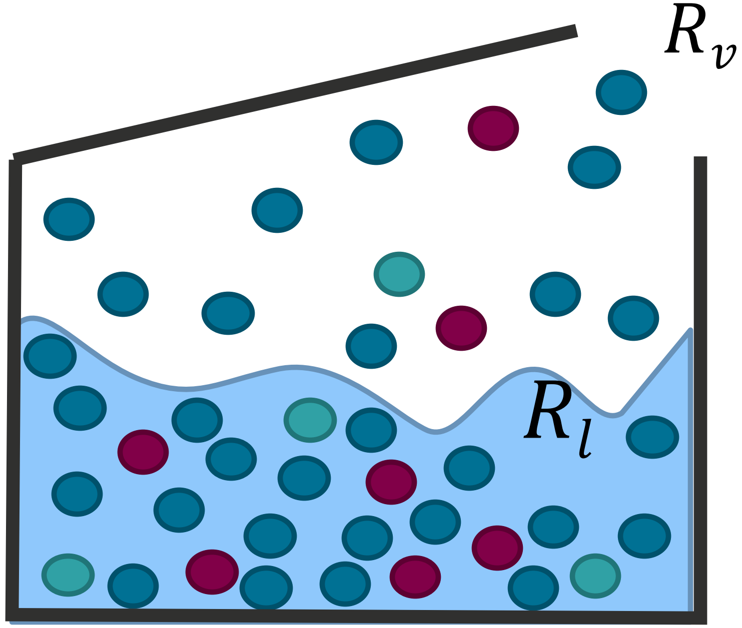
Kinetic fractionation factor

$$\alpha_{eff} = \alpha_{eq}(T) \cdot \alpha_{kin}(h)$$

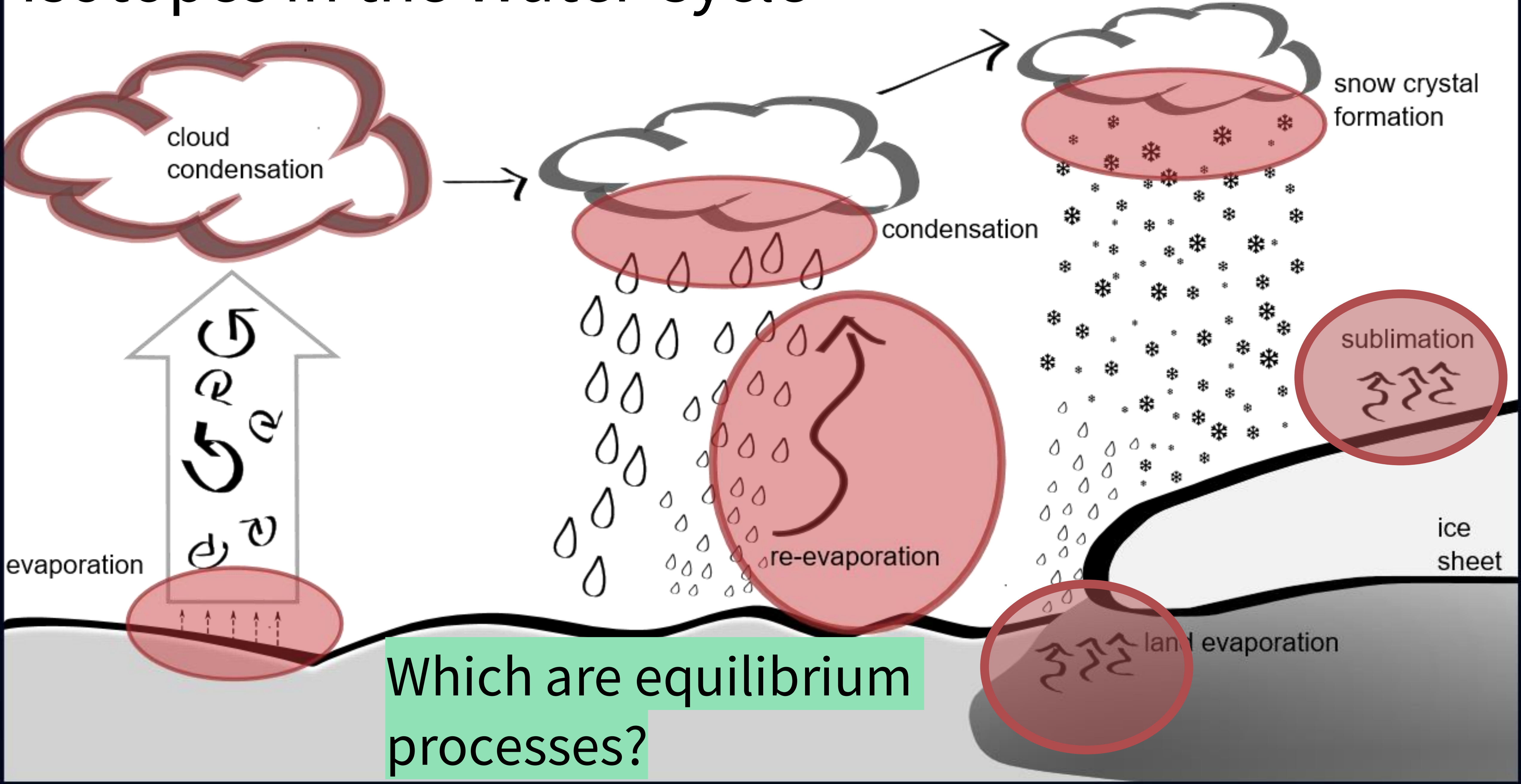
$\alpha_{eq}(T)$ is a function of Temperature (T)

$\alpha_{kin}(h)$ is a function of sub-saturation (h)

→ Different molecular diffusivities create fractionation

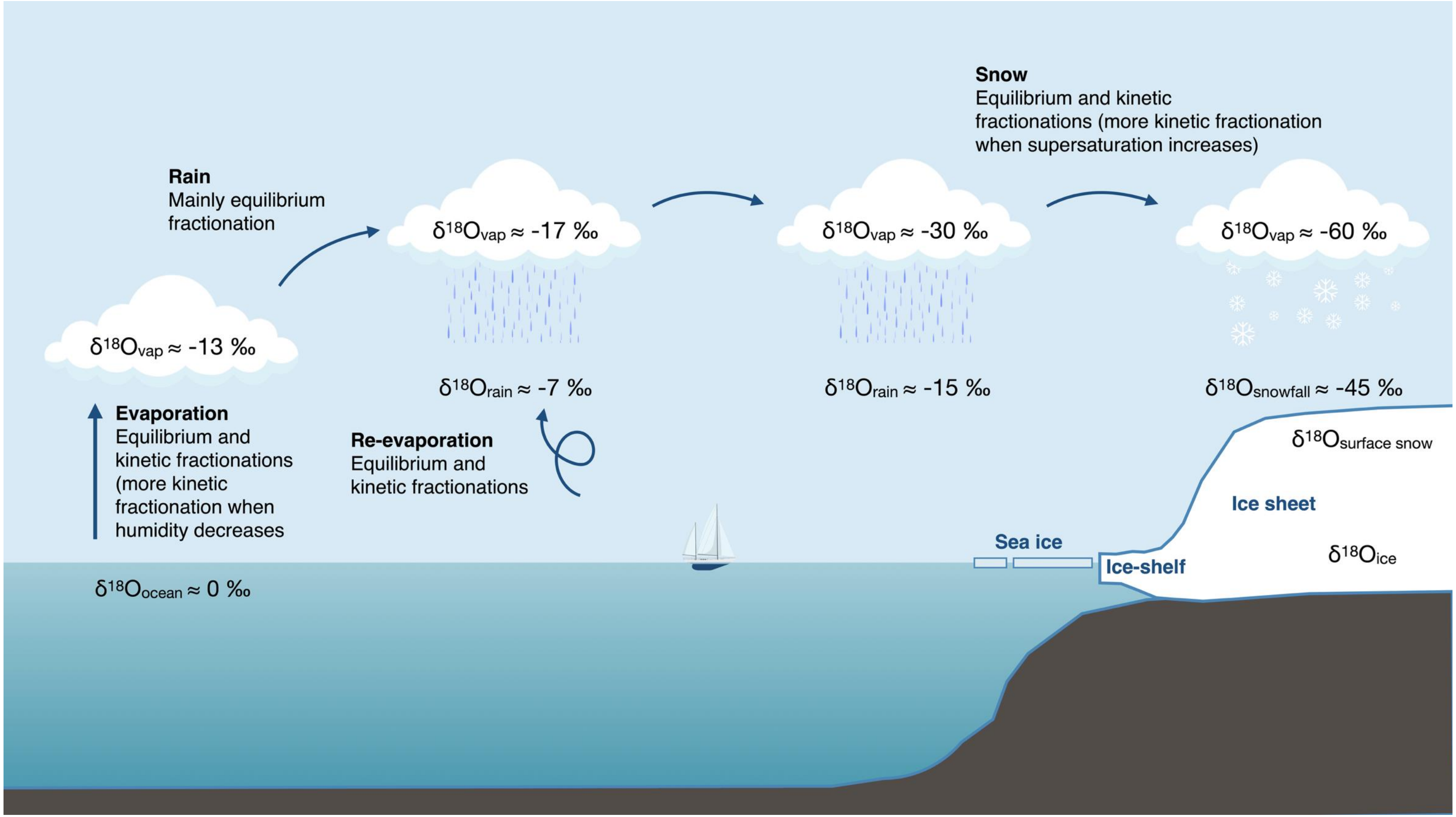


Isotopes in the Water Cycle



Which are equilibrium processes?

Isotopes in the Water Cycle



From Dutrievoz, PhD Thesis

So what?

- Isotopic composition of a water parcel is integrated signal of phase change (and mixing) processes
- δ^{18}O and δD signals strongly temperature dependent
- D-excess signal …

  …preserved during equilibrium processes

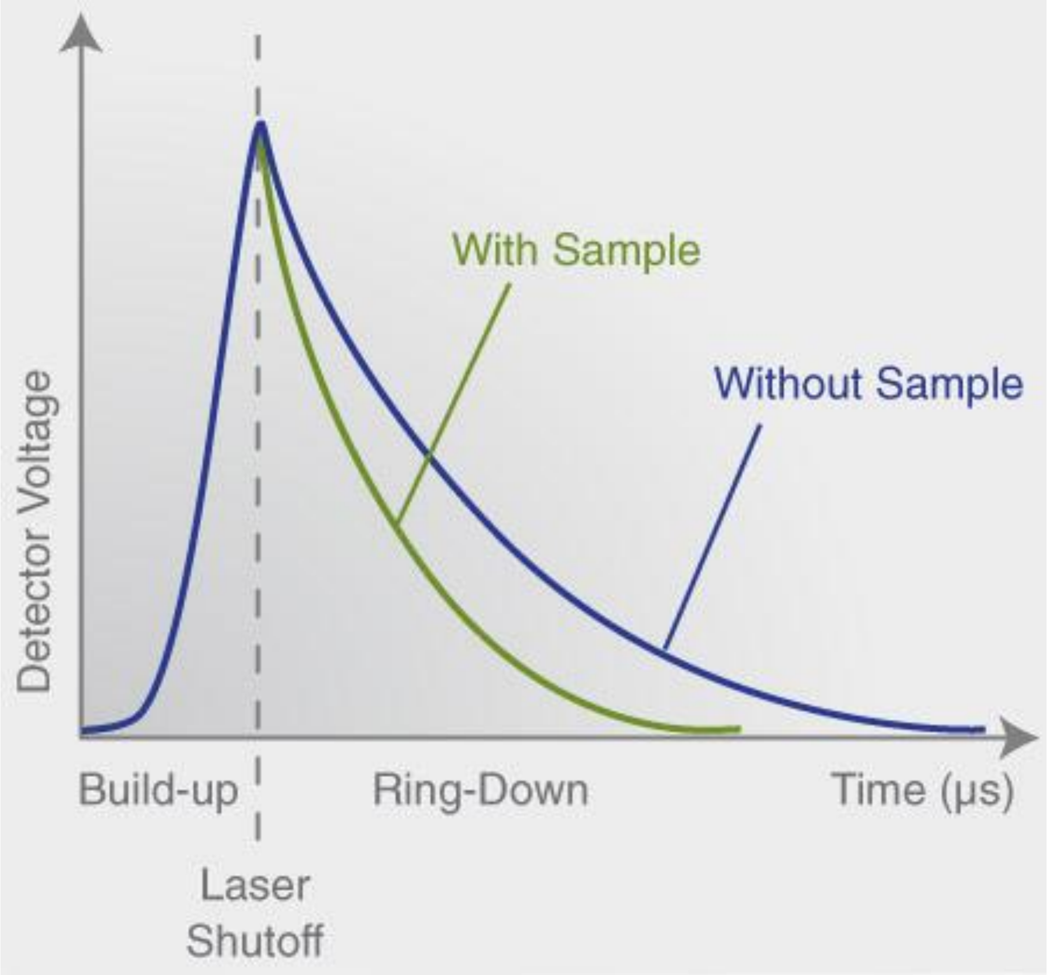
  …changes are a sign of non-equilibrium processes

Measurement of stable water isotopes

- Indirectly: **Isotope Ratio Mass Spectrometry**
  - separation by mass in electromagnetic field
  Advantage: very precise ($\delta^{18}O = 0.004‰, \delta D = 0.09‰, Luz\ et\ al.\ 2009$)
  Disadvantage: no vapor measurements, costly, slow
  chemical reaction of water sample to gases

- Directly: **Optical Spectroscopy**
  - absorption characteristics of different isotopes
  Advantage: in-situ measurements of vapor possible, “cheap”, fast
  Disadvantage: high calibration effort, difficult at low humidity
  Precision vapor: 10min avg: $\delta^{18}O < 0.23‰$; $\delta D < 2.4‰$ (Galewsky et al. 2016)
  Precision liquid: 👍 $\delta^{18}O < 0.1‰$; $\delta D < 1‰$

Cavity Ring-Down Spectroscopy (CRDS)



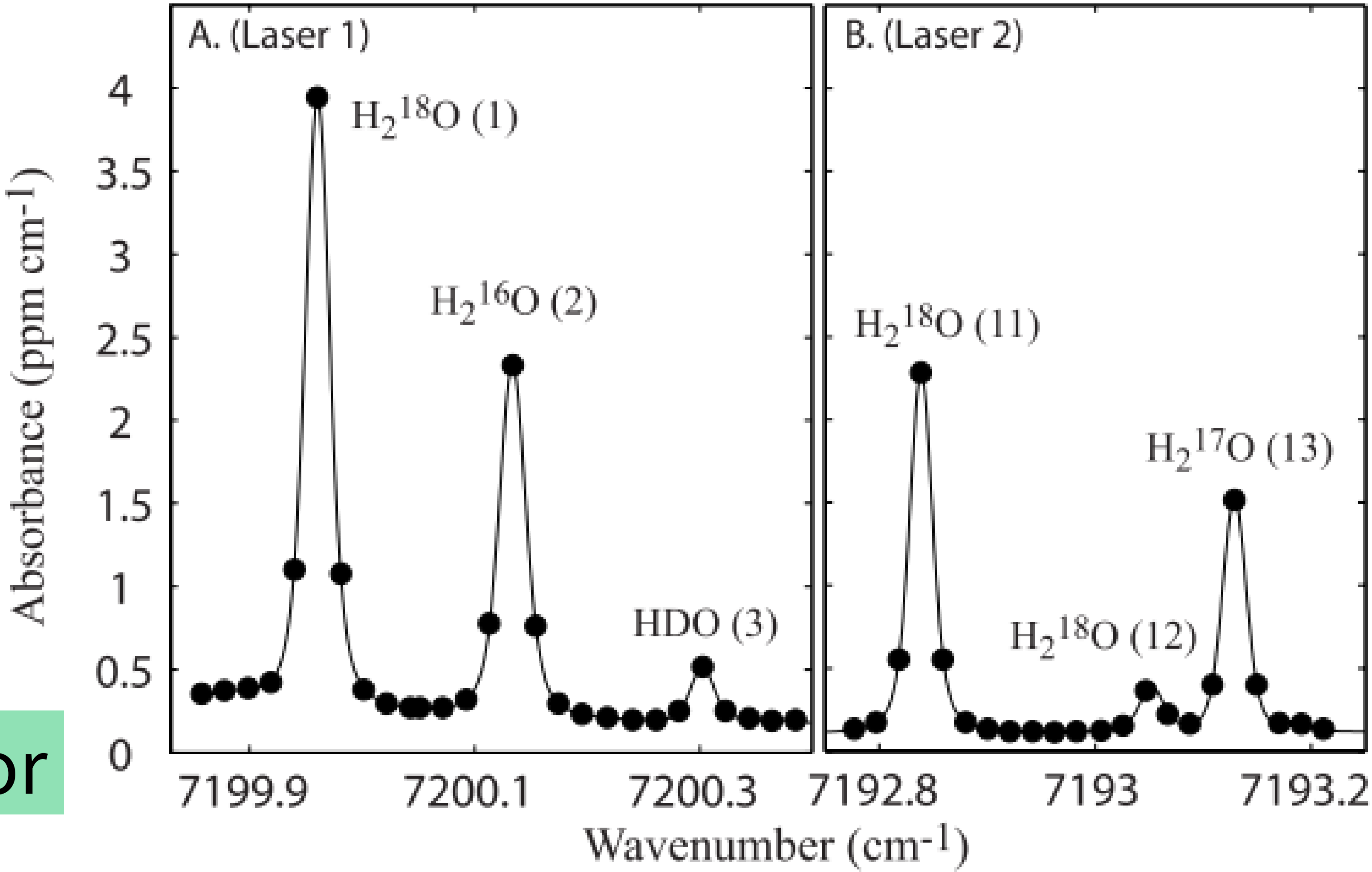
Absorption proportional to molecule abundance

CRDS method – absorption spectra

$$^{18}R = \frac{A(\mathrm{H_2{}^{18}O(11)})}{A(\mathrm{H_2{}^{16}O(2)})},$$

A = integrated peak

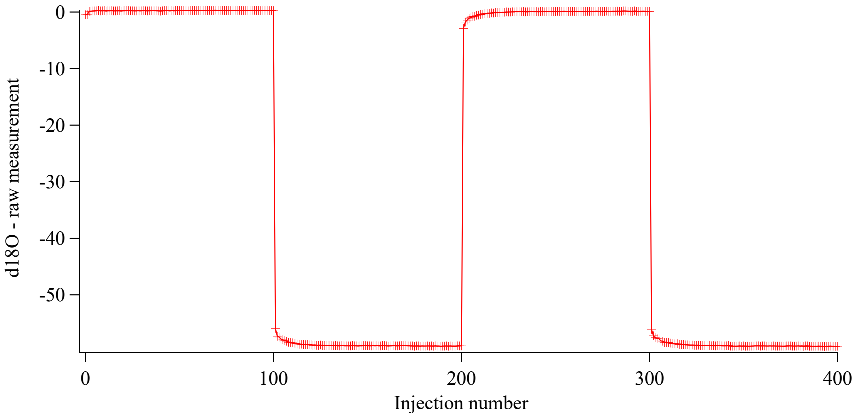
Can you think of a problem when you want to measure vapor isotopes in winter?

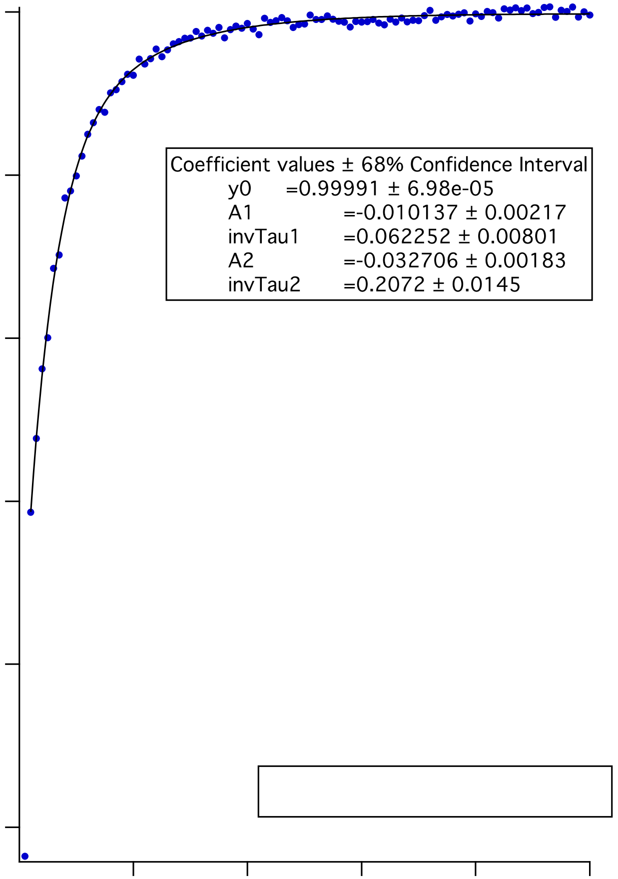


(Steig et al., 2014)

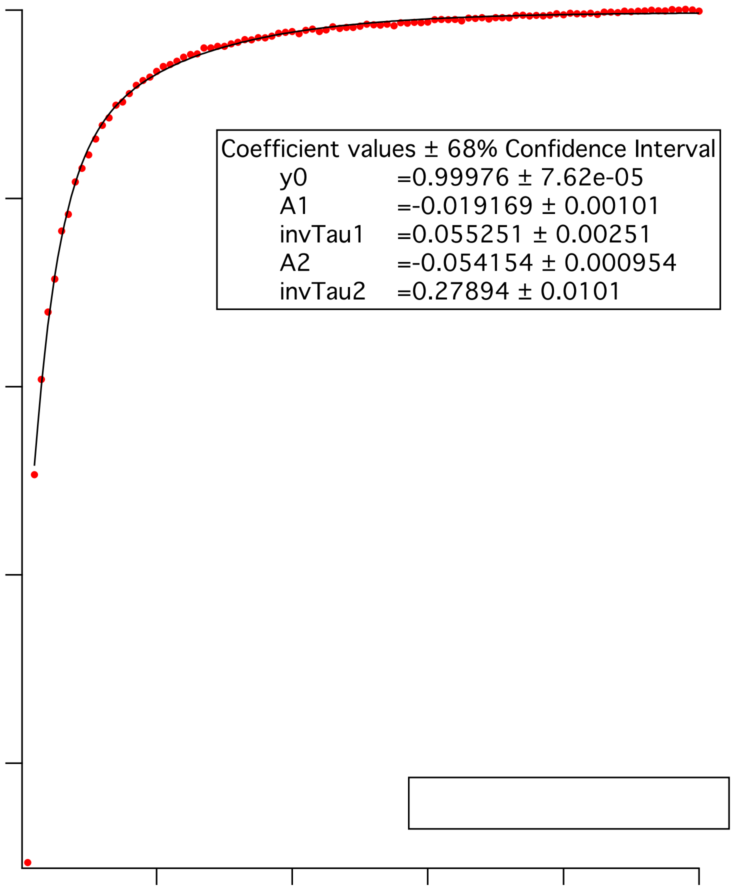
Picarro calibration – memory effect

Water is a sticky molecule…





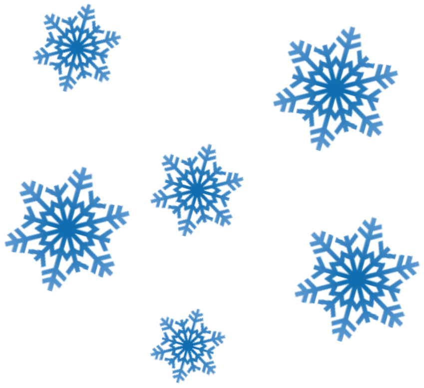
Coefficient values ± 68% Confidence Interval
y0 =0.99991 ± 6.98e-05
A1 =-0.010137 ± 0.00217
invTau1 =0.062252 ± 0.00801
A2 =-0.032706 ± 0.00183
invTau2 =0.2072 ± 0.0145

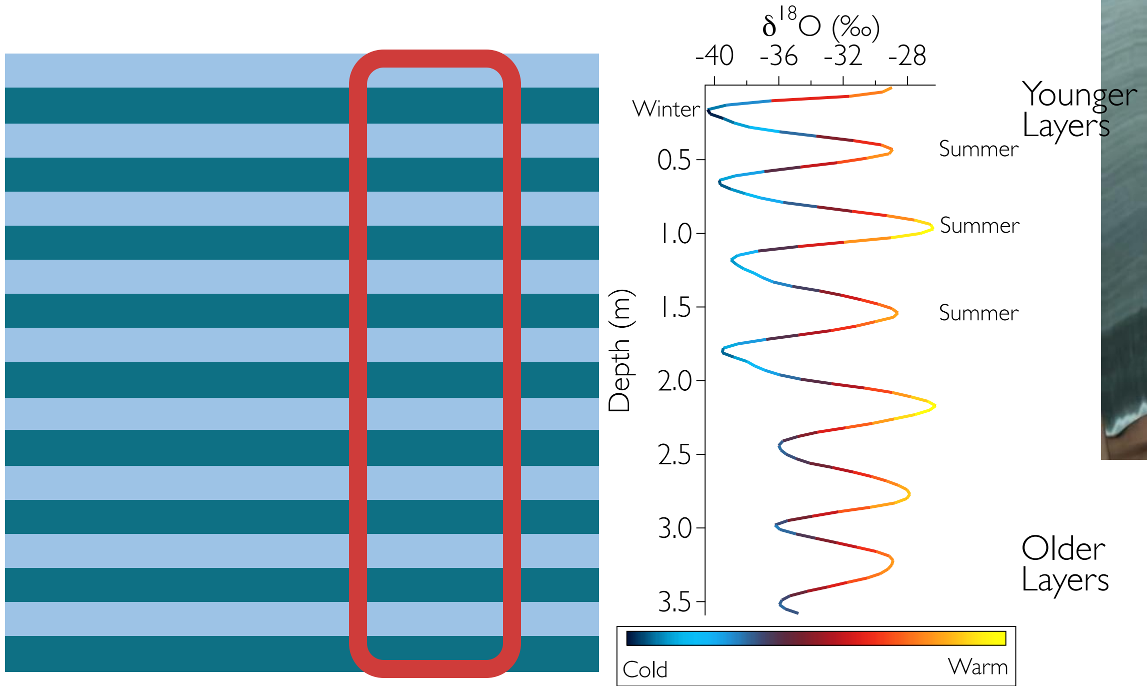


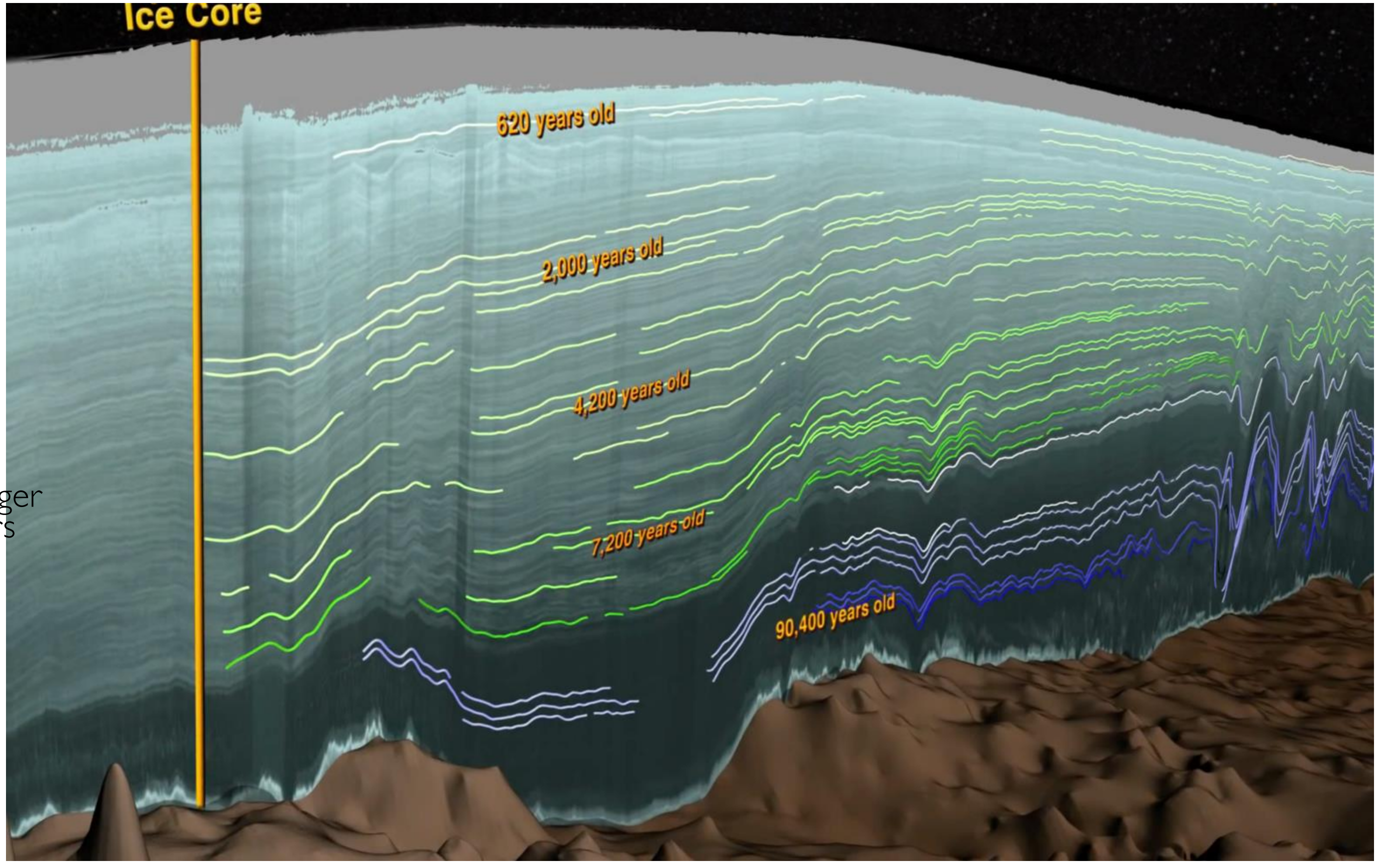
Coefficient values ± 68% Confidence Interval
y0 =0.99976 ± 7.62e-05
A1 =-0.019169 ± 0.00101
invTau1 =0.055251 ± 0.00251
A2 =-0.054154 ± 0.000954
invTau2 =0.27894 ± 0.0101

What does this mean for isotope measurements?

Isotopes in firn and ice cores – climate proxies





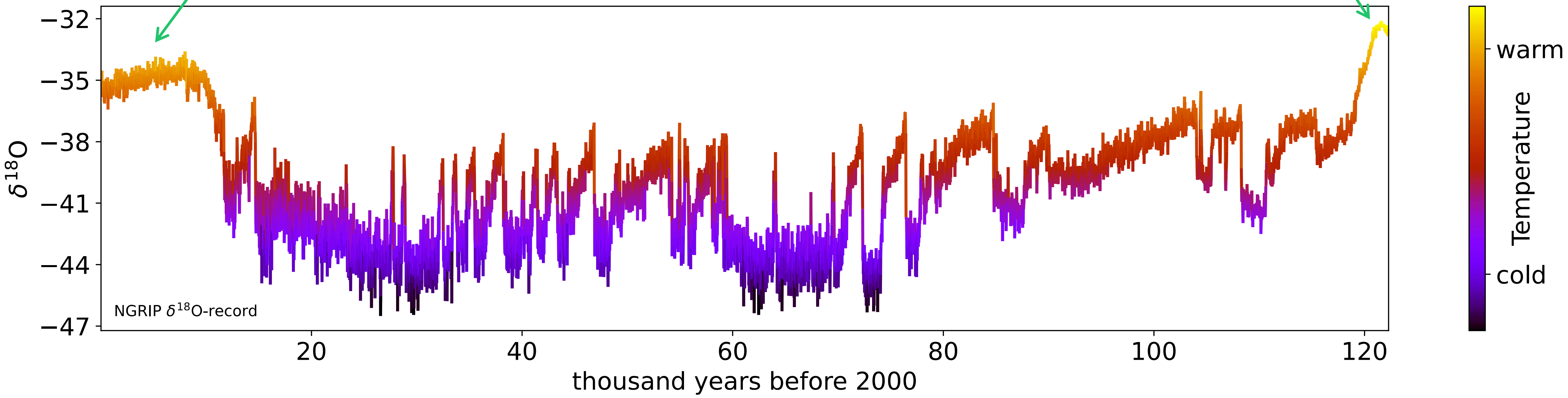


NASA | Greenland's Ice Layers Mapped in 3D
(http://svs.gsfc.nasa.gov/goto?4249)

Paleothermometer = δ-signal → Temperature

Holocene = Current warm period

Eemian = Last warm period

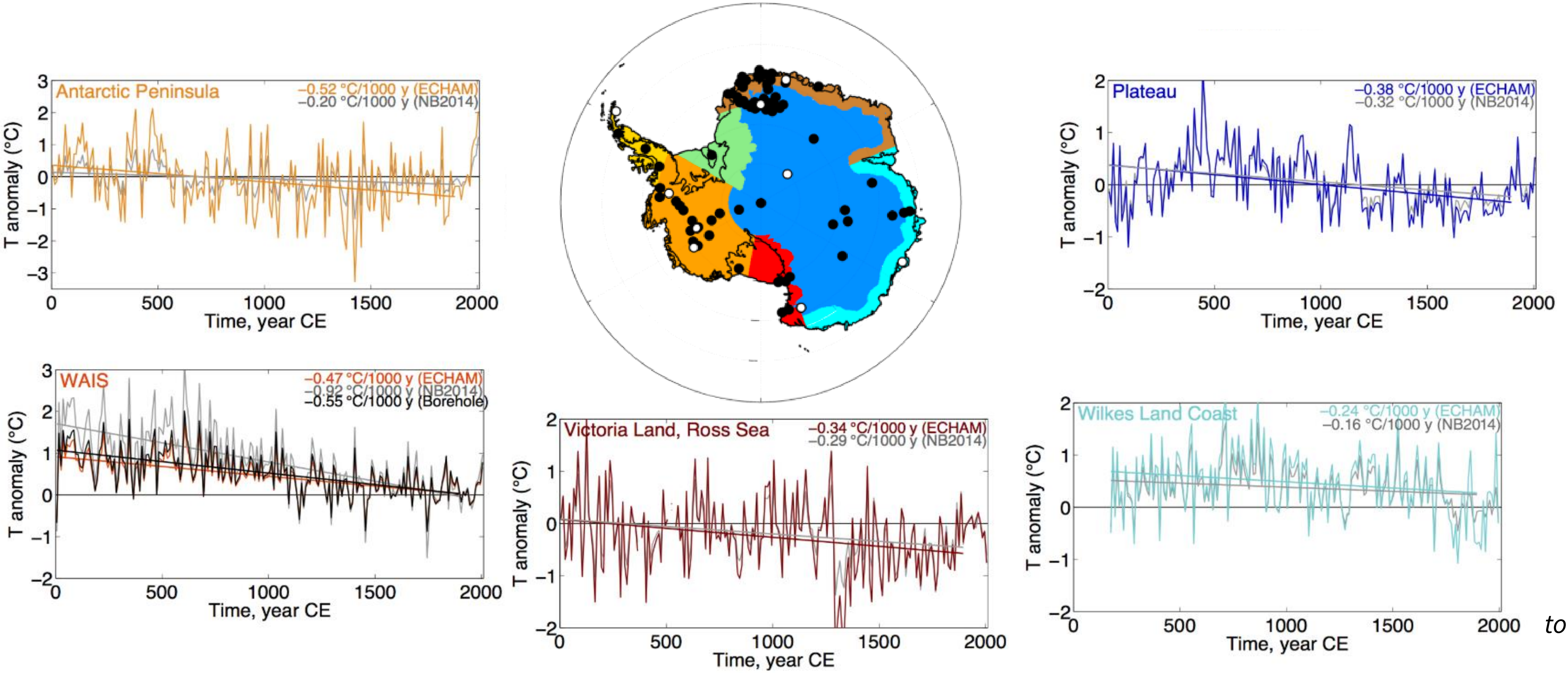


Last glacial period

Isotopes in firn and ice cores – climate proxies

Holocene cooling in all of Antarctica

Trend 0-1900 CE

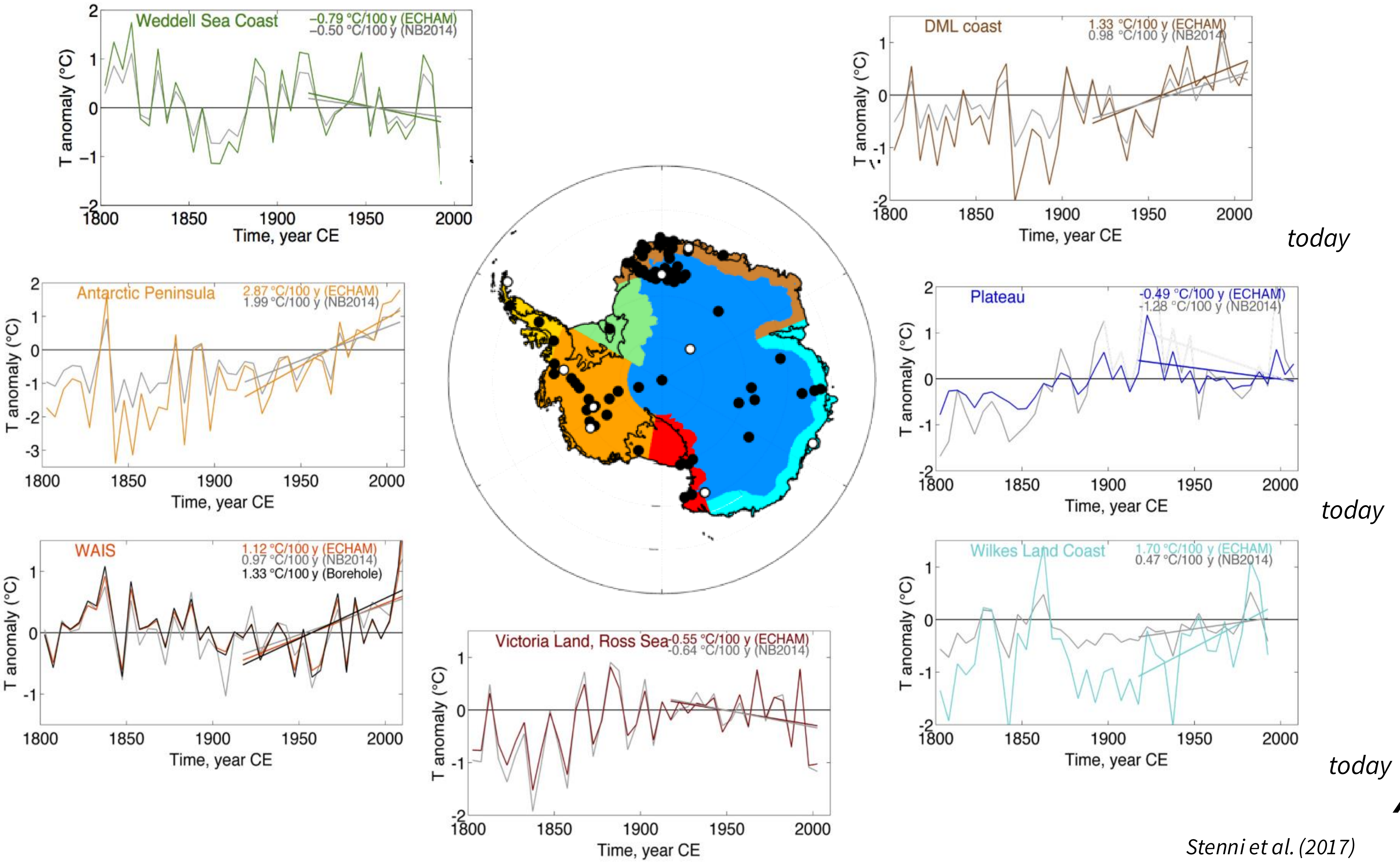


today

today

Stenni et al. (2017)

Isotopes in ice cores – climate variability



today

today

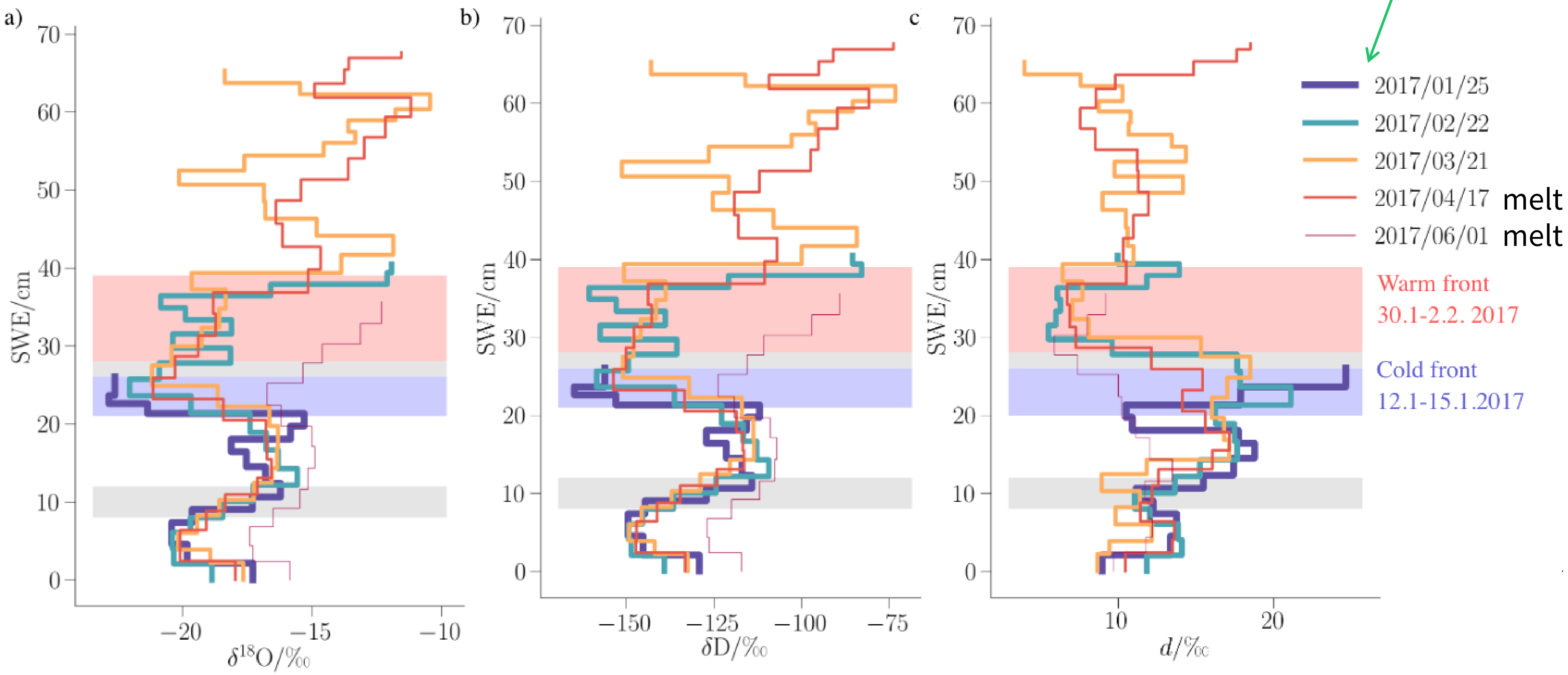
today

Stenni et al. (2017)

○ Seasonal Snowpack, Weissfluhjoch

Aemisegger & Trachsel et al. (2022)

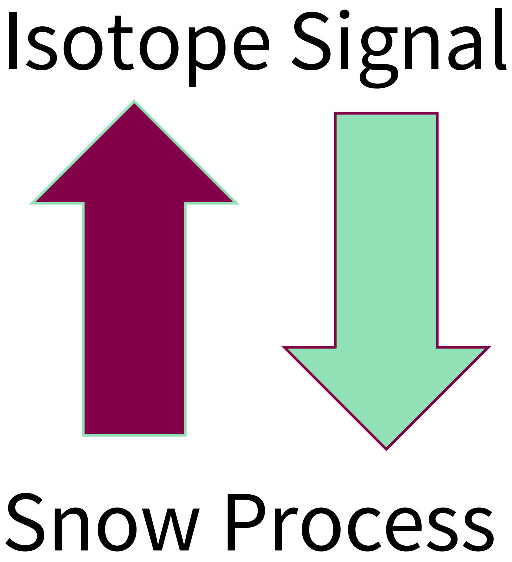
Snow profiles taken:



melt

melt

○ Isotopes and (polar) Snow – current research



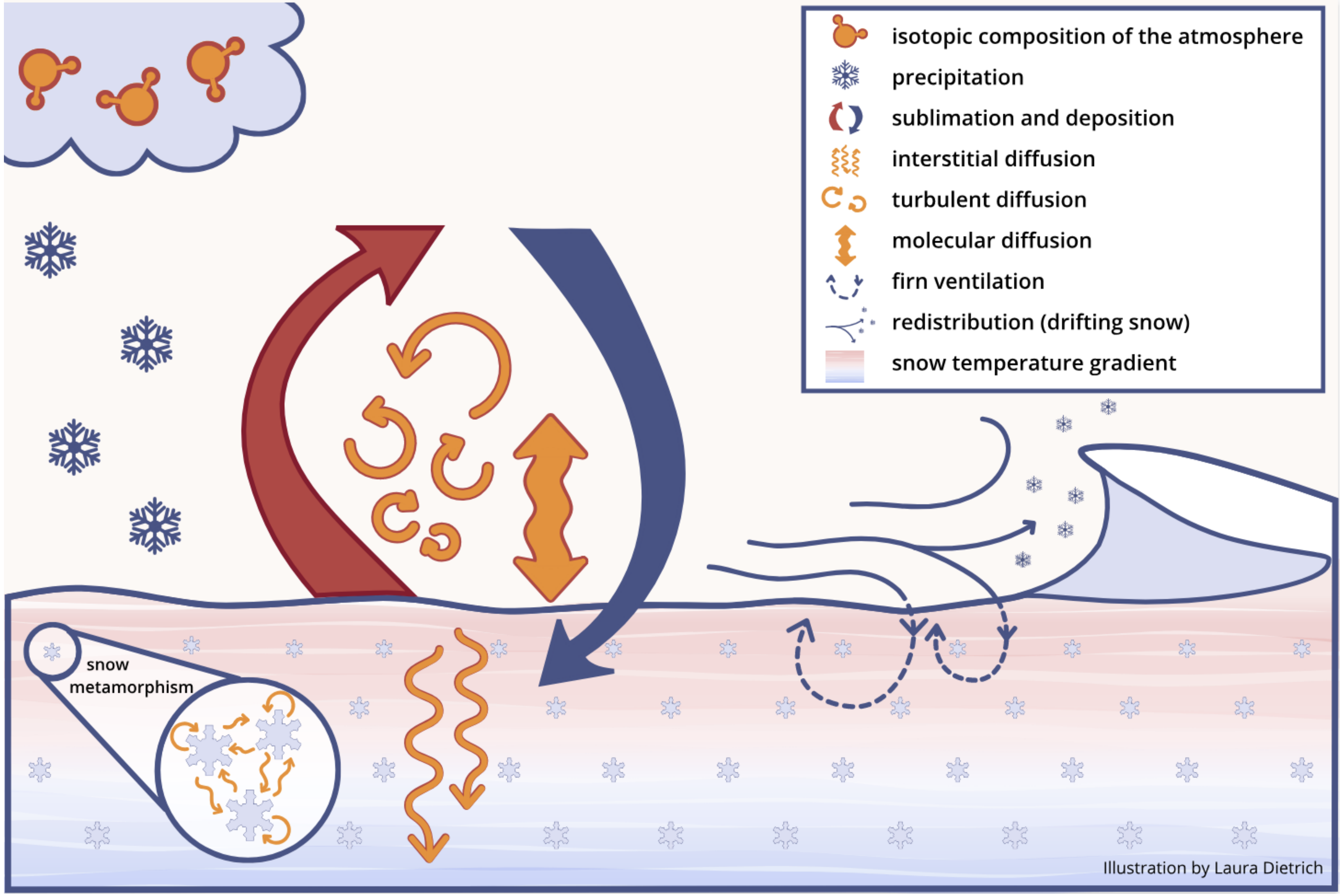
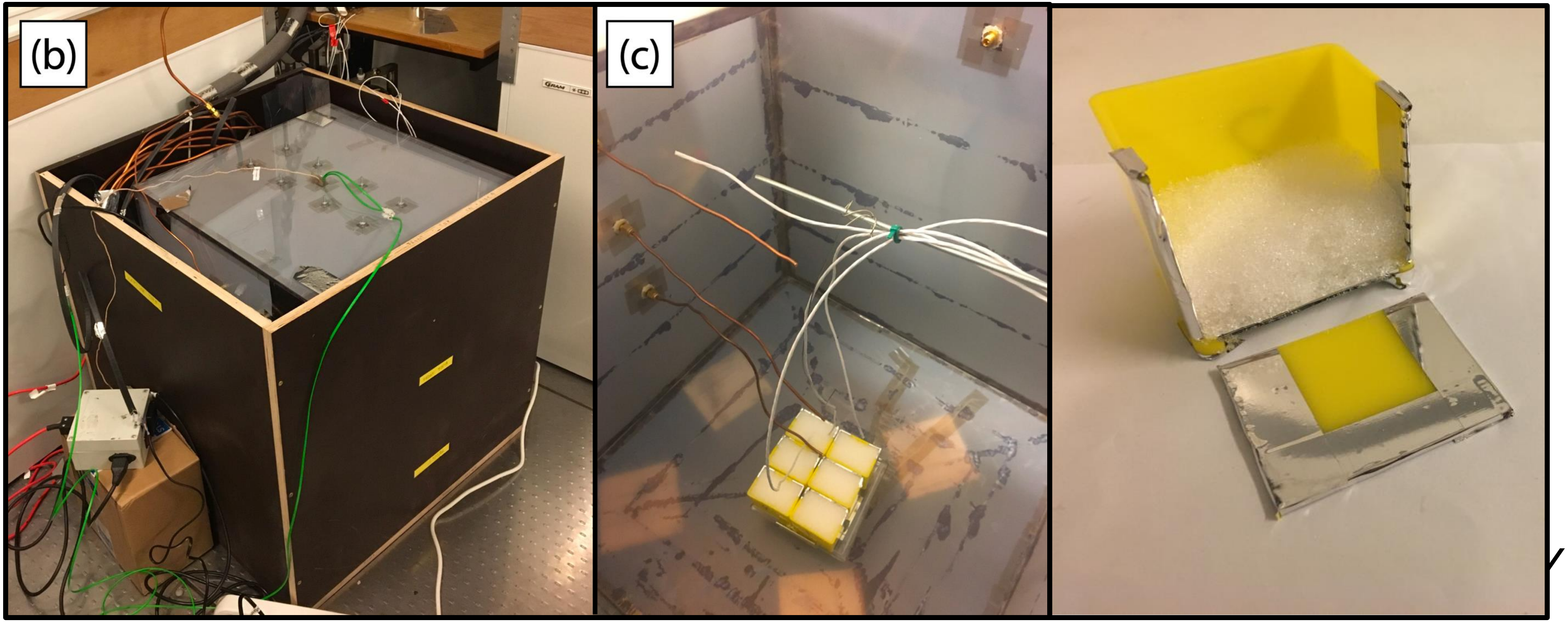


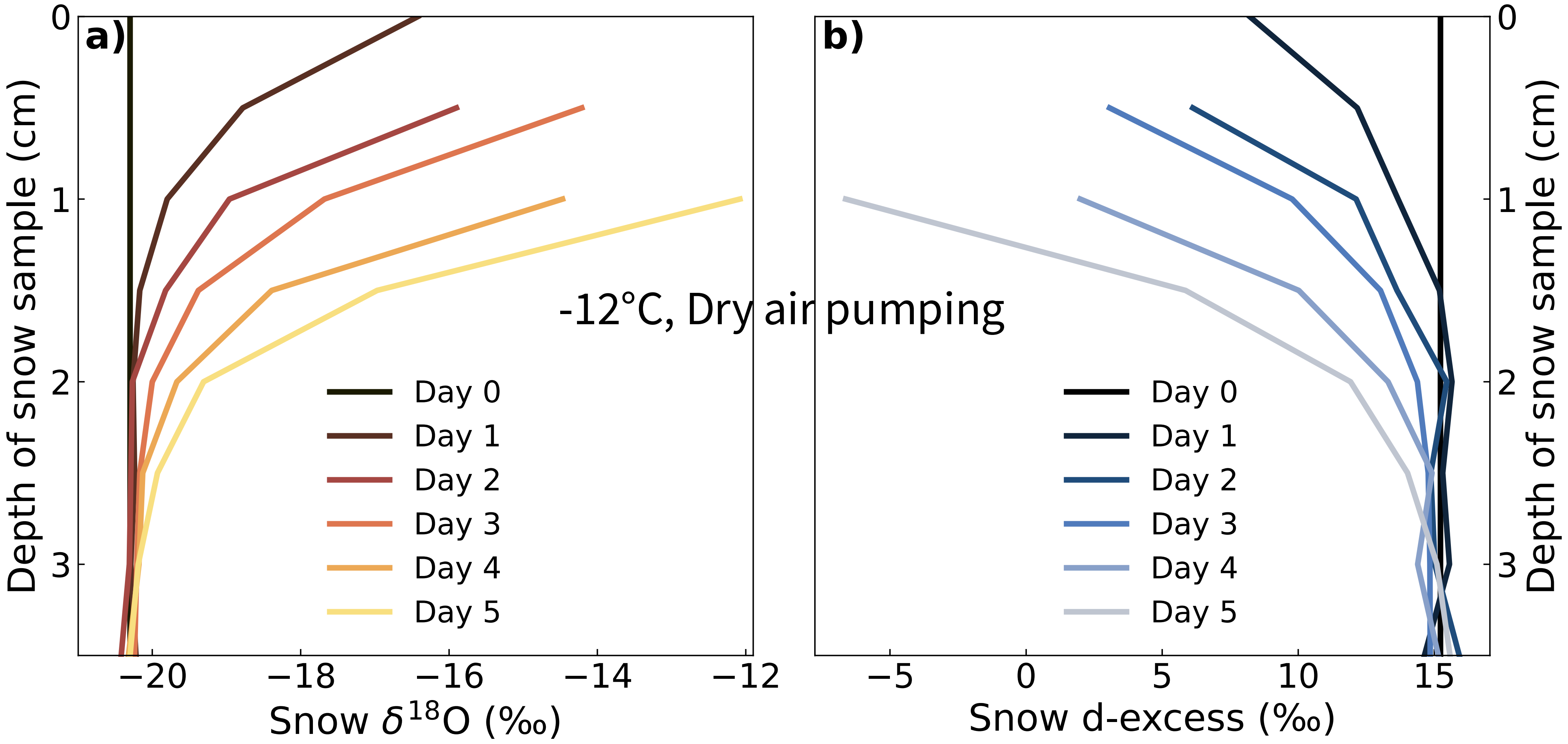
Illustration by Laura Dietrich

Effects of sublimation on snow isotope signal



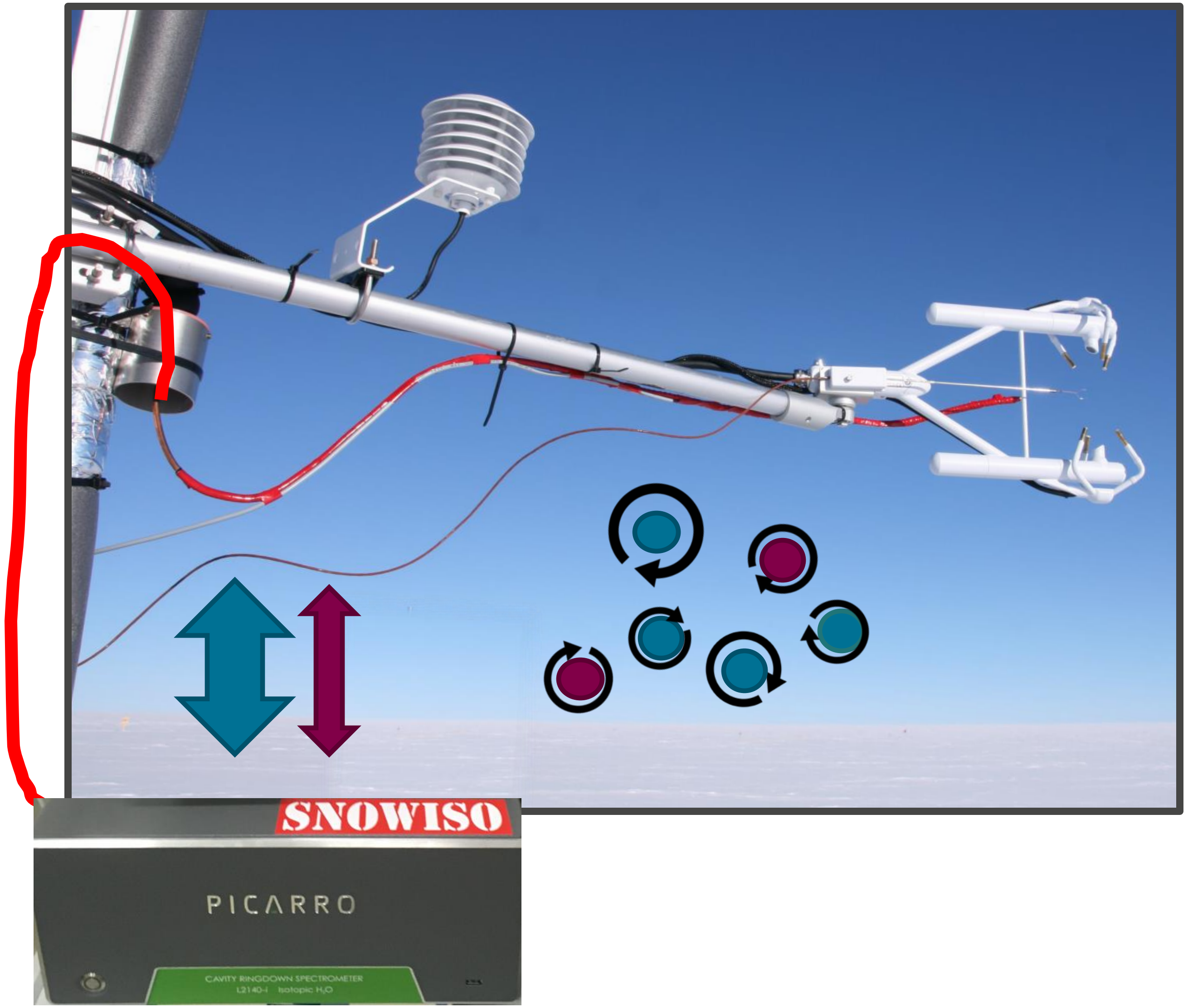
Hughes et al. (2021)

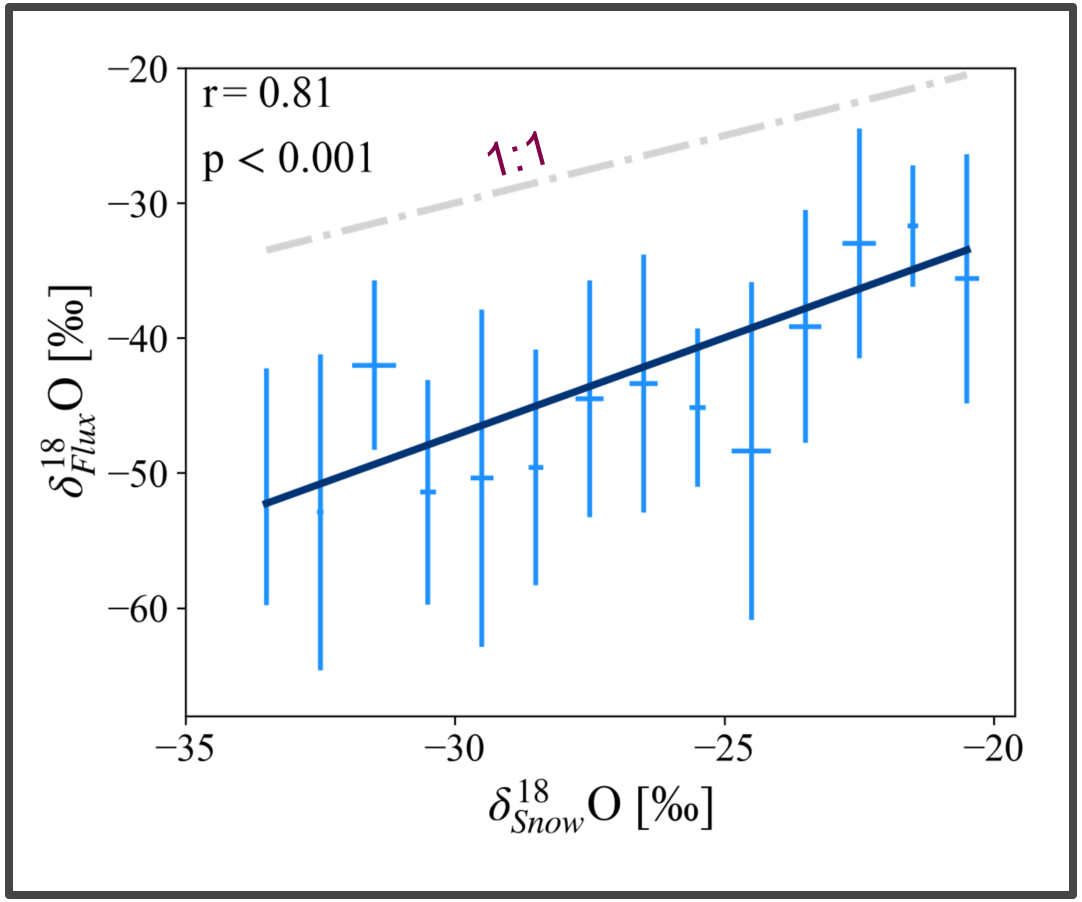
Laboratory experiments on sublimation influence


-12°C, Dry air pumping

In the lab, forced sublimation (blowing dry air into a box with snow) shows a clear fractionation effect;
The d-excess points to kinetic fractionationing Hughes et al. (2021)

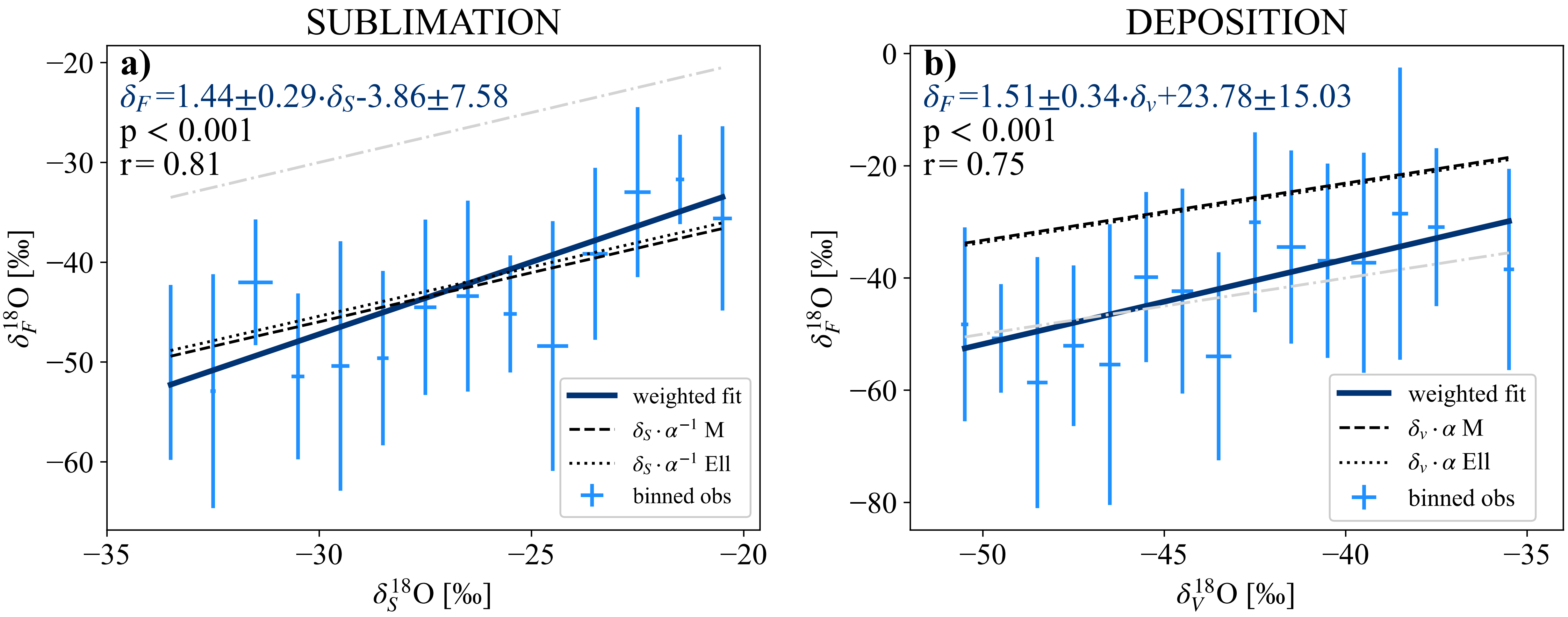
Isotopic composition of humidity flux





Wahl et al. (2021)

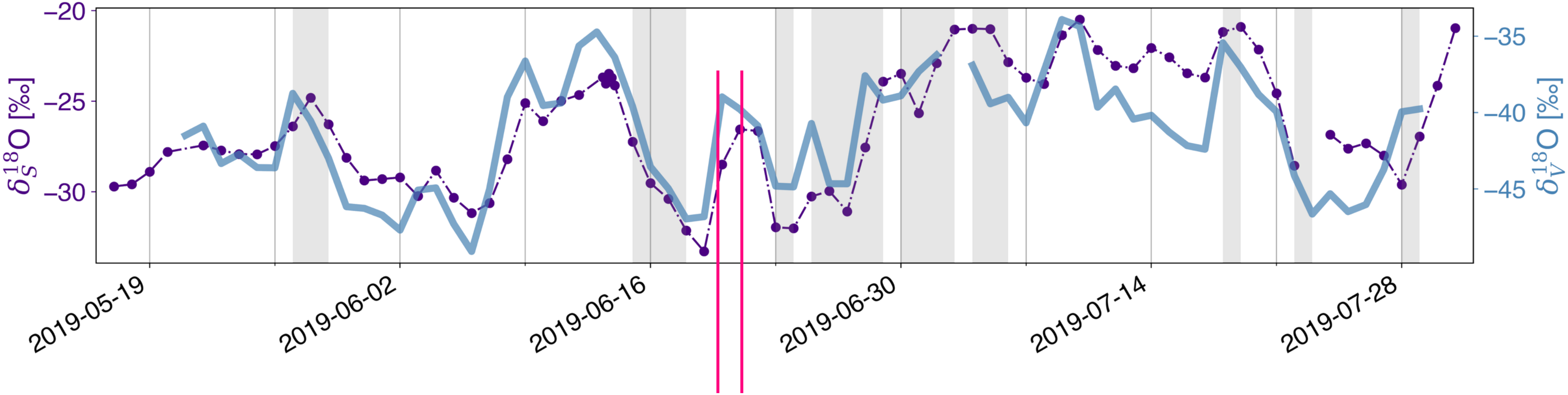
Direct measurements of humidity flux isotopic composition



Dased curves show equilibrium fractionation models, grey curve is 1:1 line. On x-axis is the snow (a) or vapor (b) delta value and on the y-axis the one of the flux. These measurements show that sublimation achieves a fractionation effect, while this is not so clear for deposition, contrary to old theories. Wahl et al. (2021)

○ Snow surface isotope signal variability

Observations of day-to-day changes in snow isotopic composition



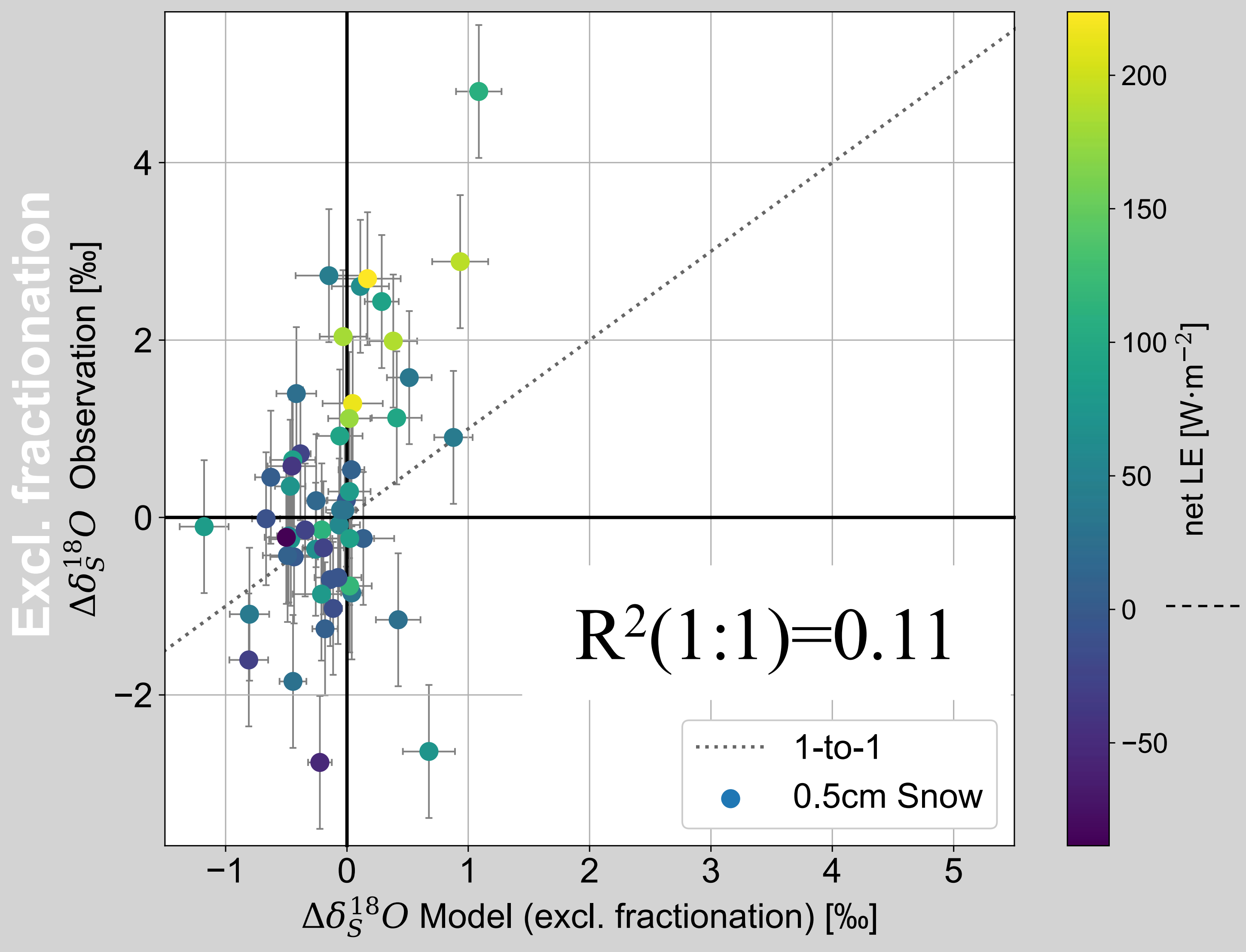
Strong temporal dynamics of isotopic composition due to following processes:

$\Delta\delta^{18}O$

- Changing vapor composition in the air
- Sublimation and deposition of vapor
- New snowfall events
- Potential melt

Modeling the snow surface isotope signal under different sublimation regimes

No fractionation during sublimation



We can get an idea on the importance of sublimation fractionation when modelling the surface snow composition with current equilibrium models.

Sublimation

↑

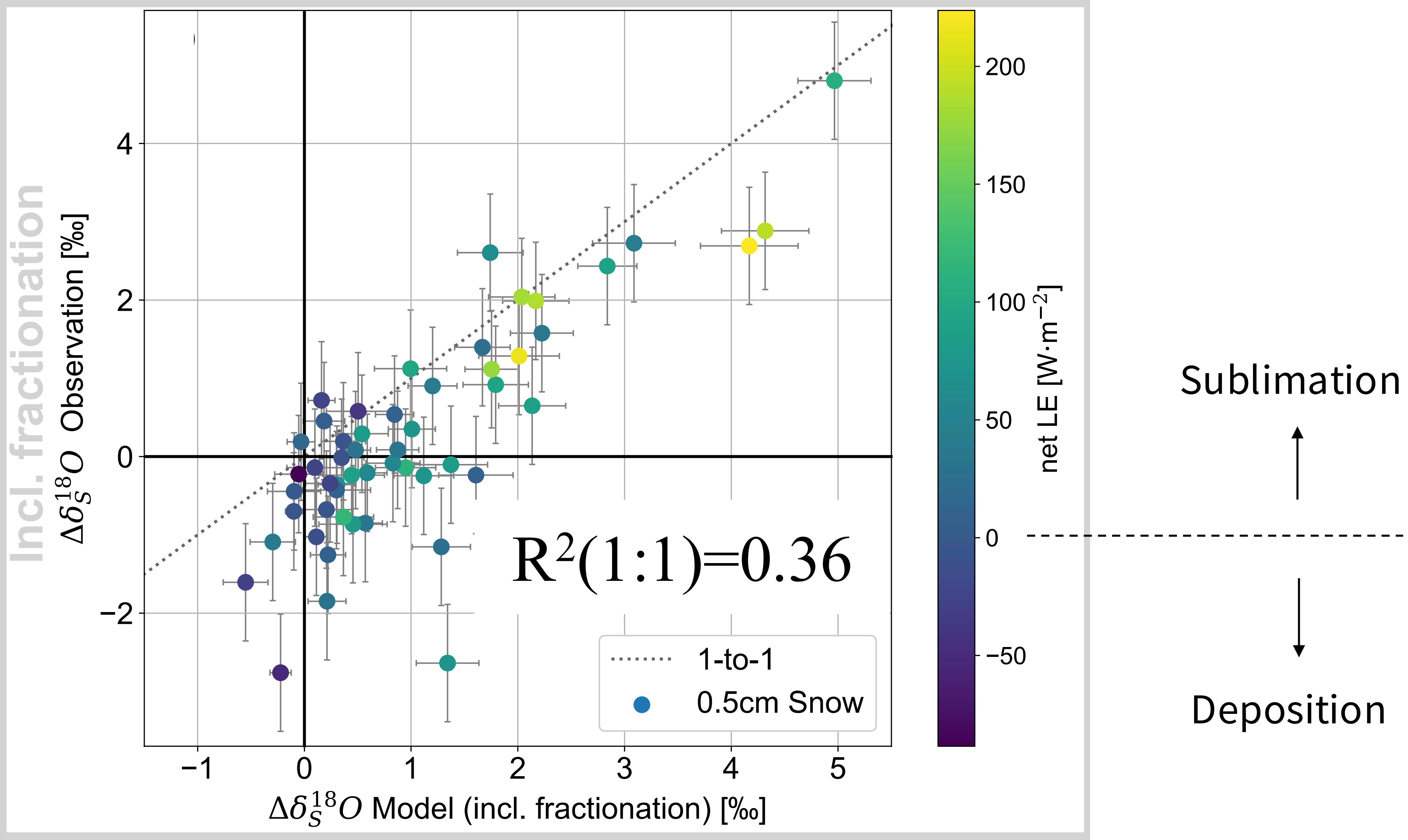
↓

Deposition

Wahl et al. (2022)

Modeling the snow surface isotope signal under different sublimation regimes

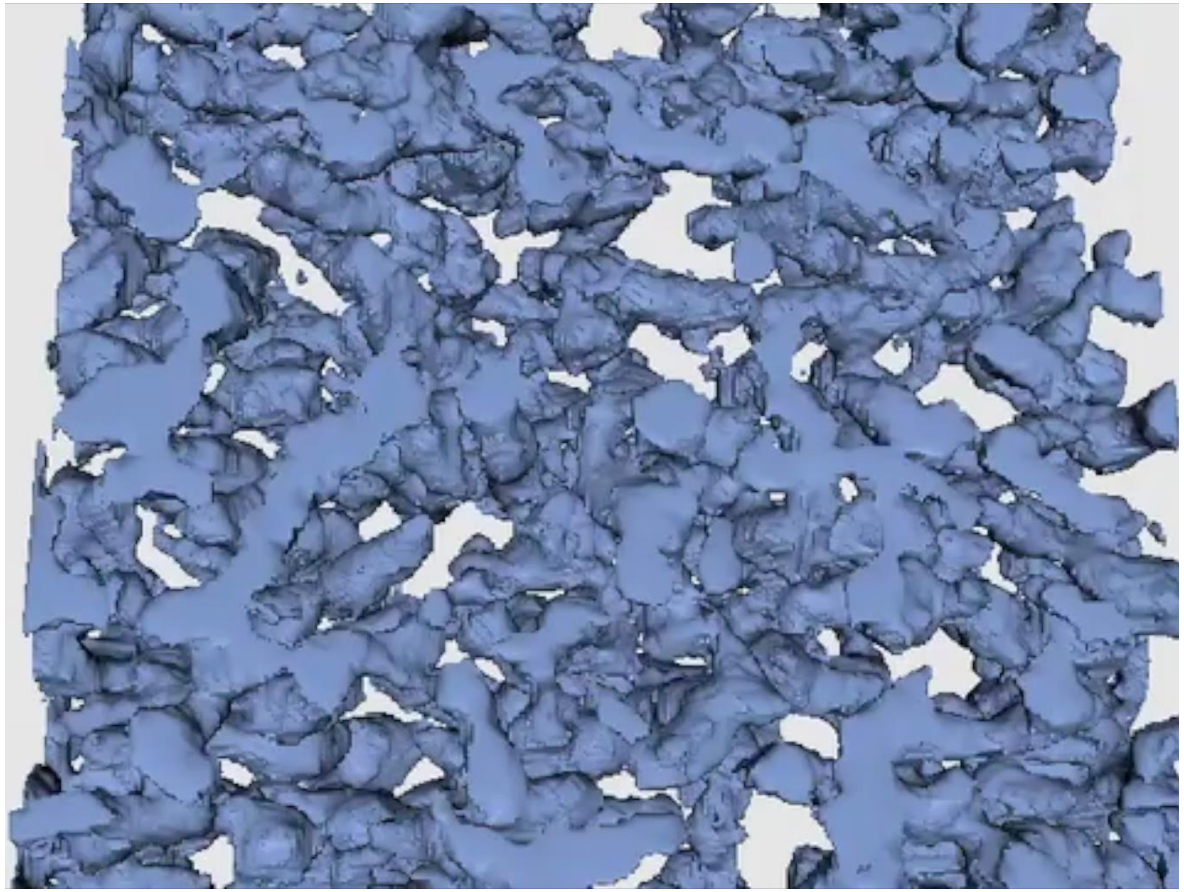
Fractionation during sublimation



Snow-Atmosphere humidity exchange can explain 36% of the observed day-to-day variability.

Wahl et al. (2022)

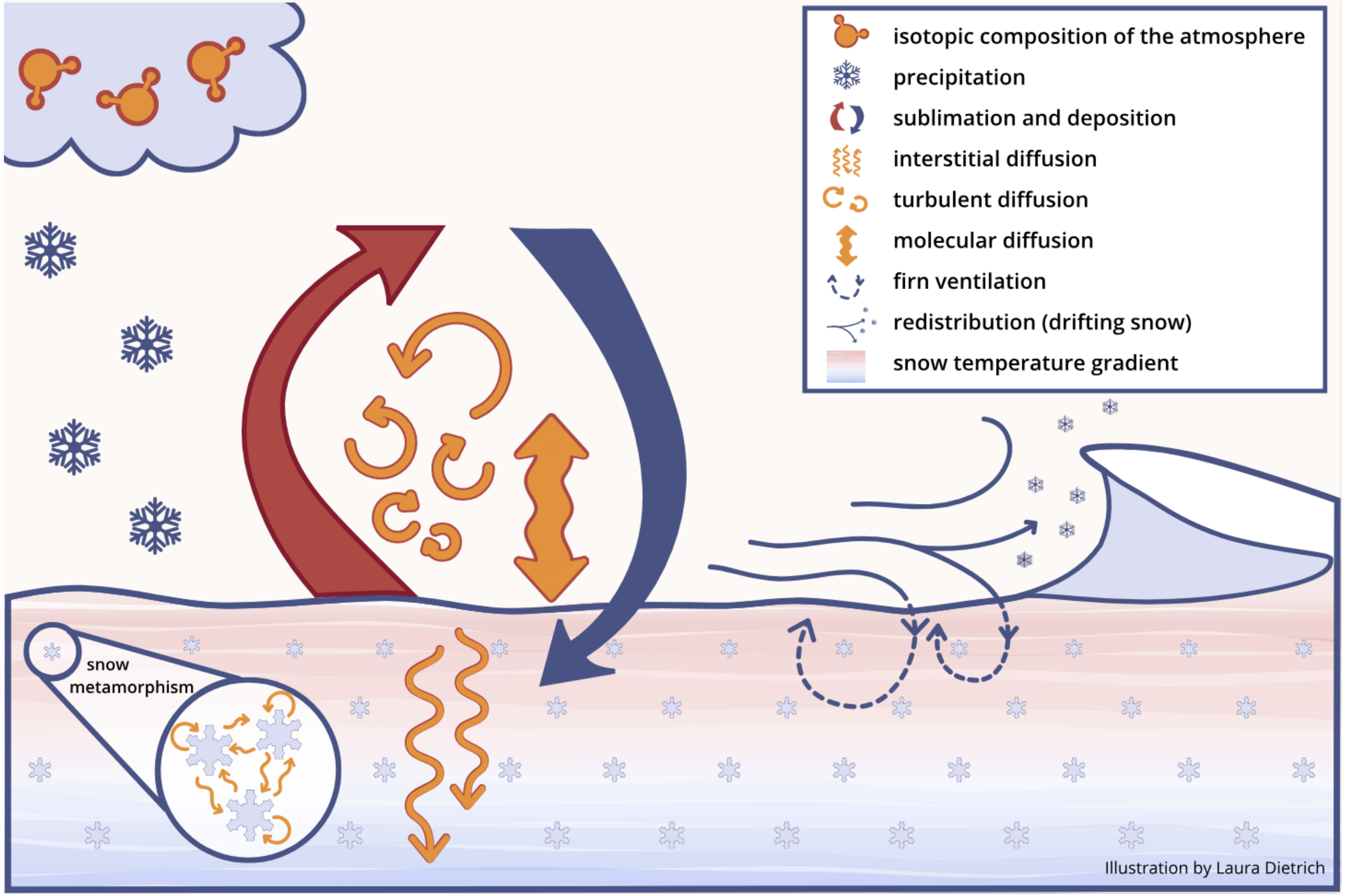
Snow Metamorphism ↔ Isotope Signal



Pinzer et al. (2012)

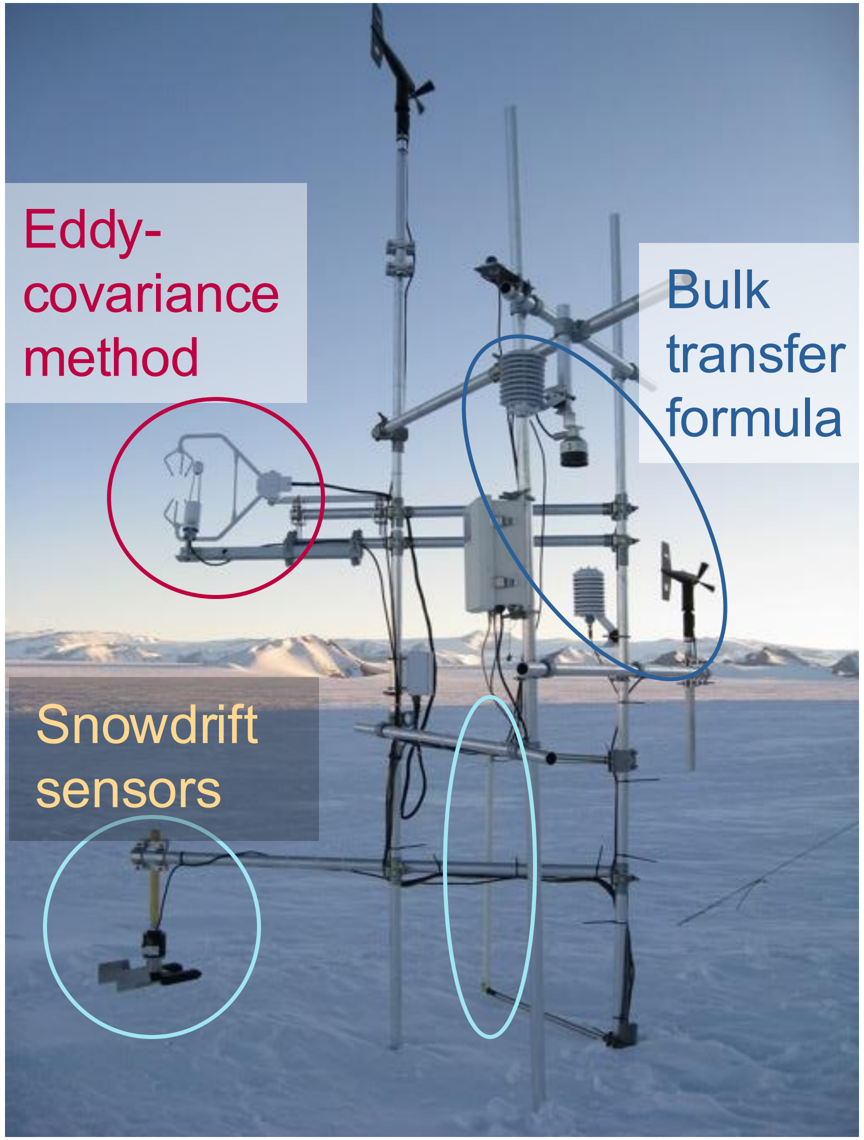
What happens with the isotope signal under snow metamorphism?

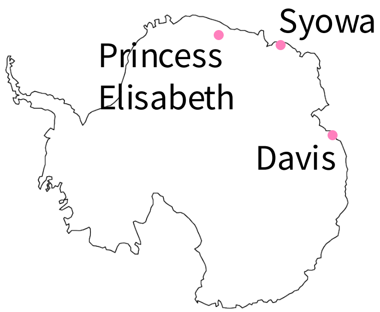
Isotopes and Snow – Knowledge Gap



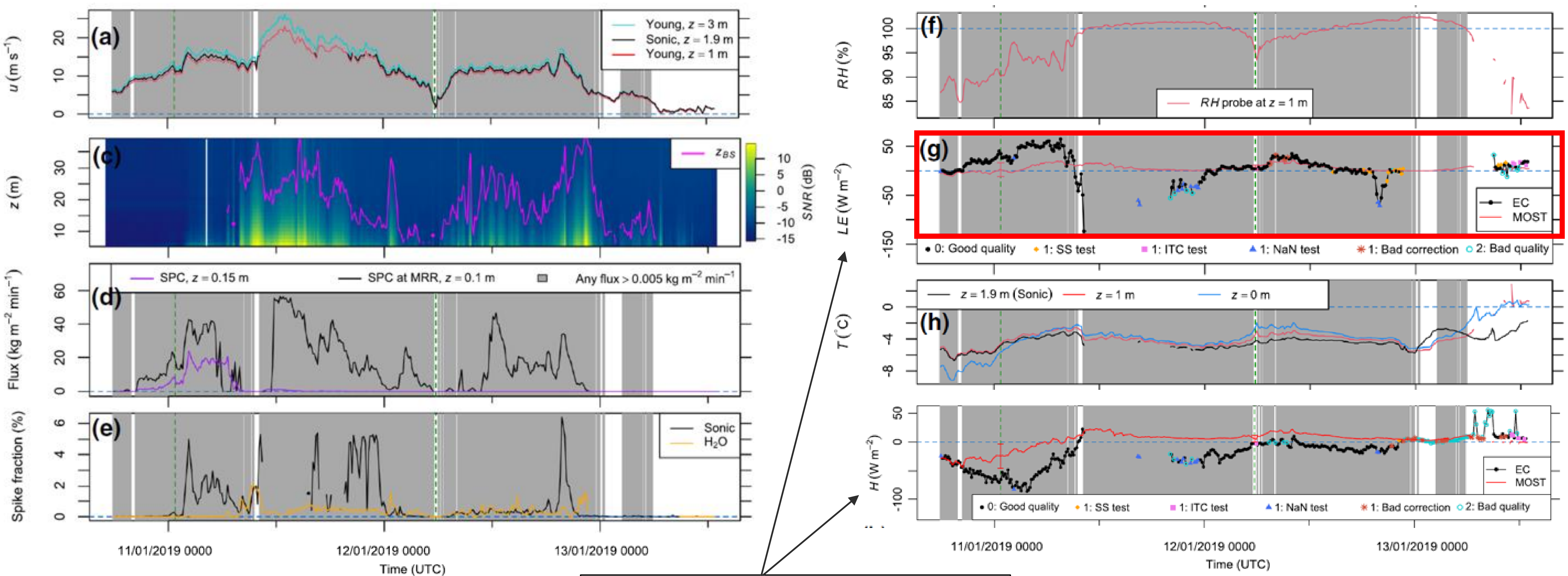
Closing the Gap – Metamorphism during Snow Transport

What do we do? – 1) Small Scale Measurements





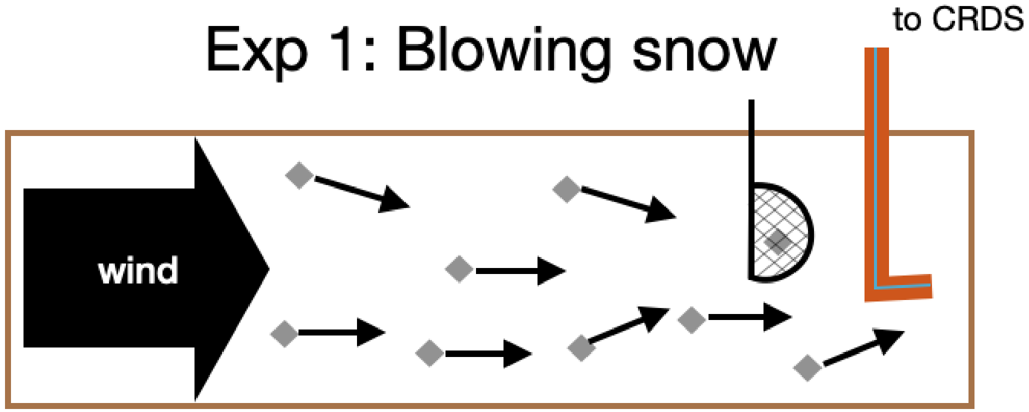
Storm event at Syowa, Antarctica



Below a height of 2 m.

Sigmund et al. BLM, 2021

Current work at SLF in Davos: Drifting/blowing snow signature in isotope signal?



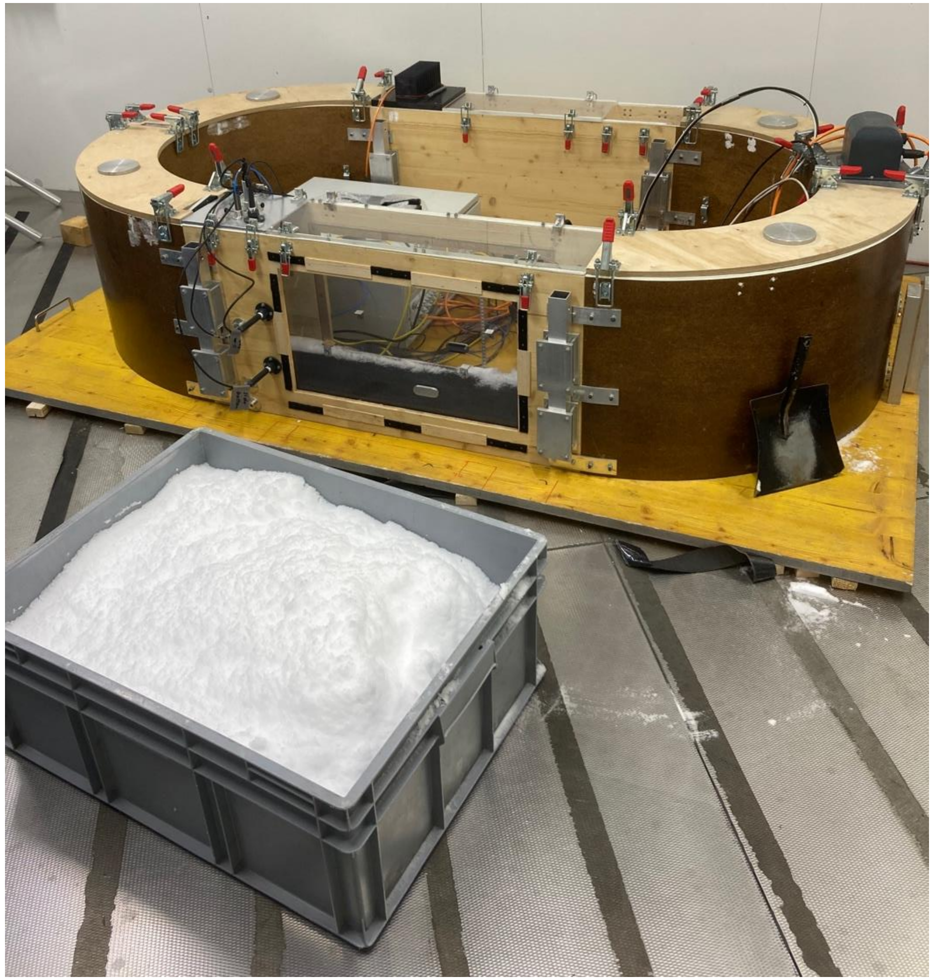
Increased sublimation during blowing snow events…

… can we measure isolated sublimation signal?

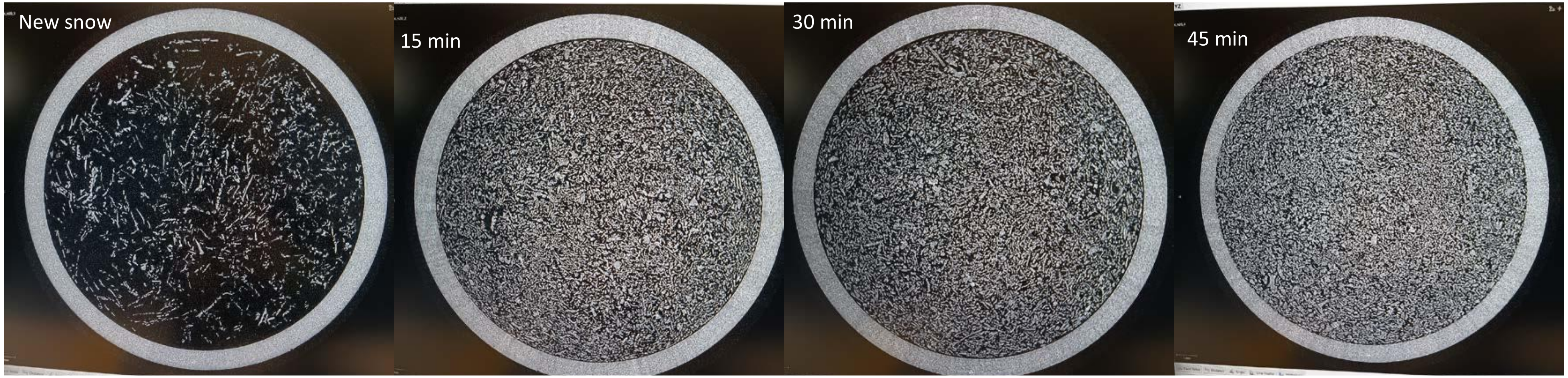
Ring-Wind Tunnel Experiments

Simulating wind-blown snow in lab

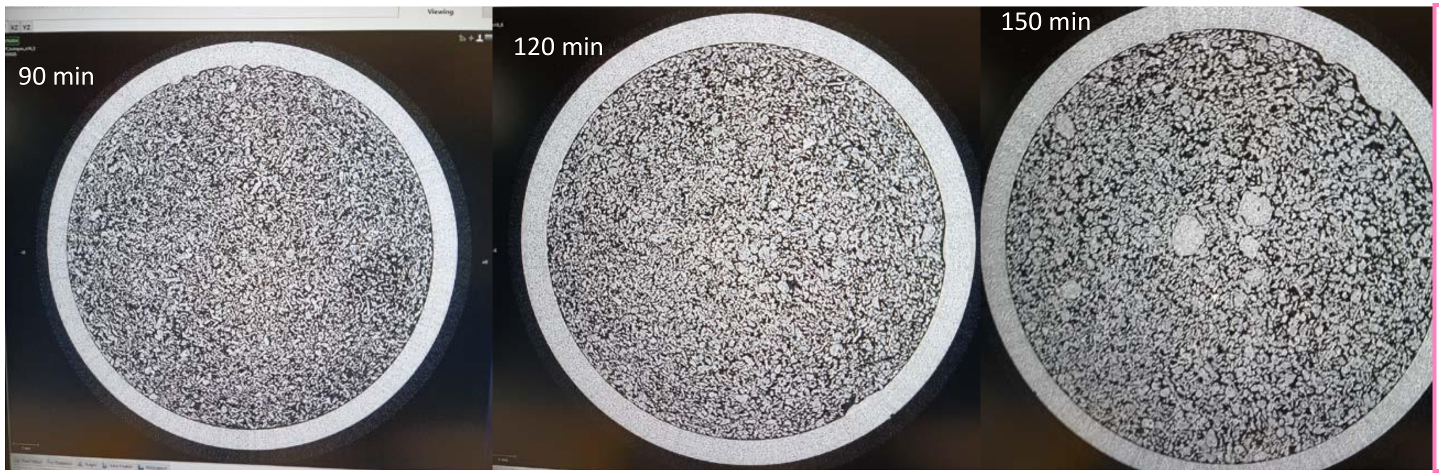
- Start with nature identical snow
  (Schleef et al. 2014)
- Aeolian transport of snow
- Repeated sampling of:
  - Airborne snow
    - CT: Particle size & SSA, isotopic composition
  - Water vapor (continuously)
    - Humidity, isotopic composition
  - Meteorological variables
    - Temperature, wind speed, RH



Snow Particle Analyses



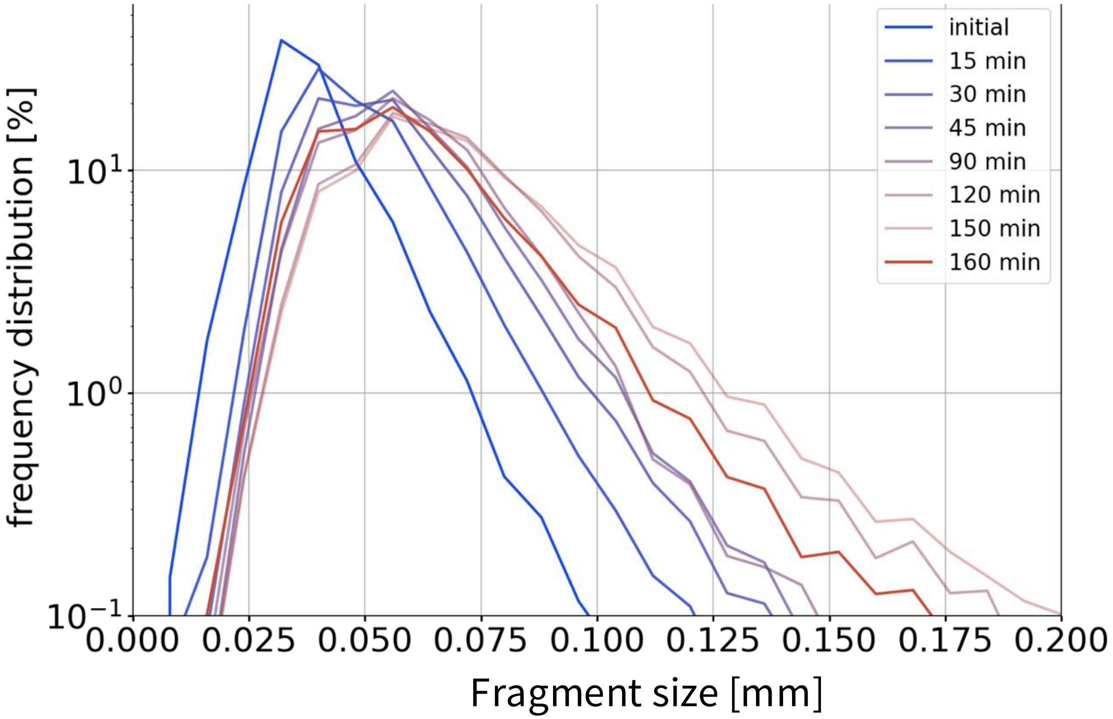
dendritic → rounded

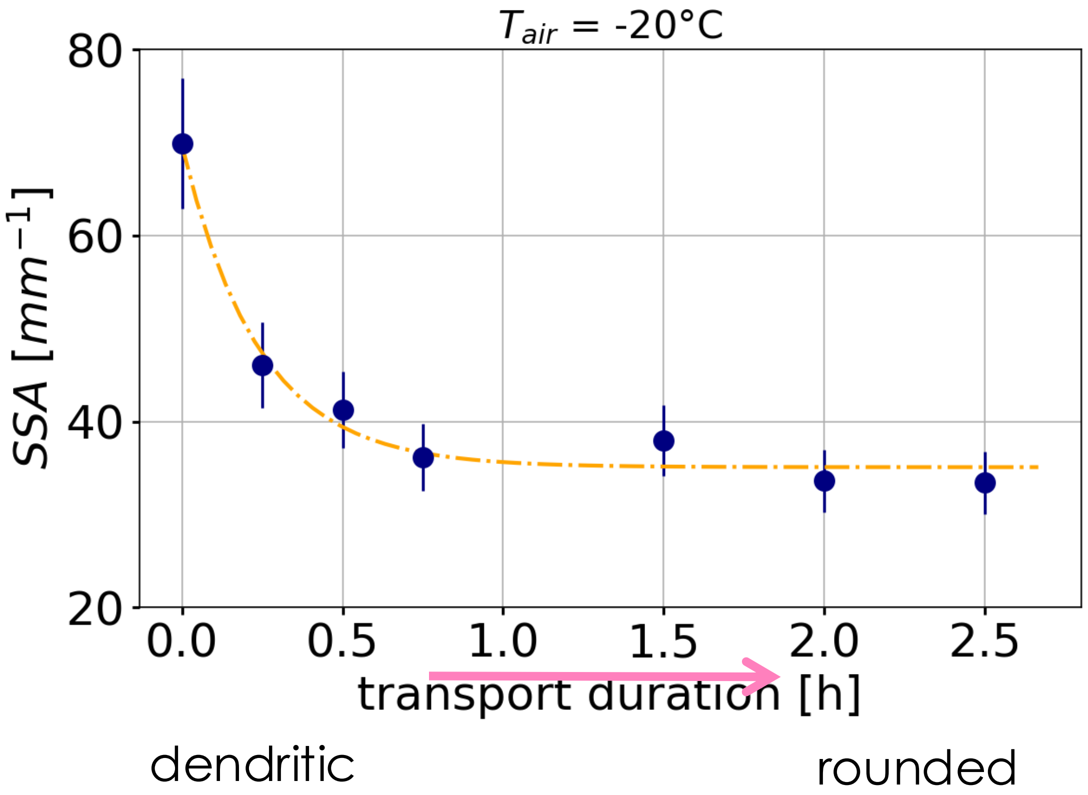


Micro-CT scans of airborne snow

Snow Particle Analyses

- Particle size distribution
- SSA (Specific Surface Area) evolution





Which processes are at work?

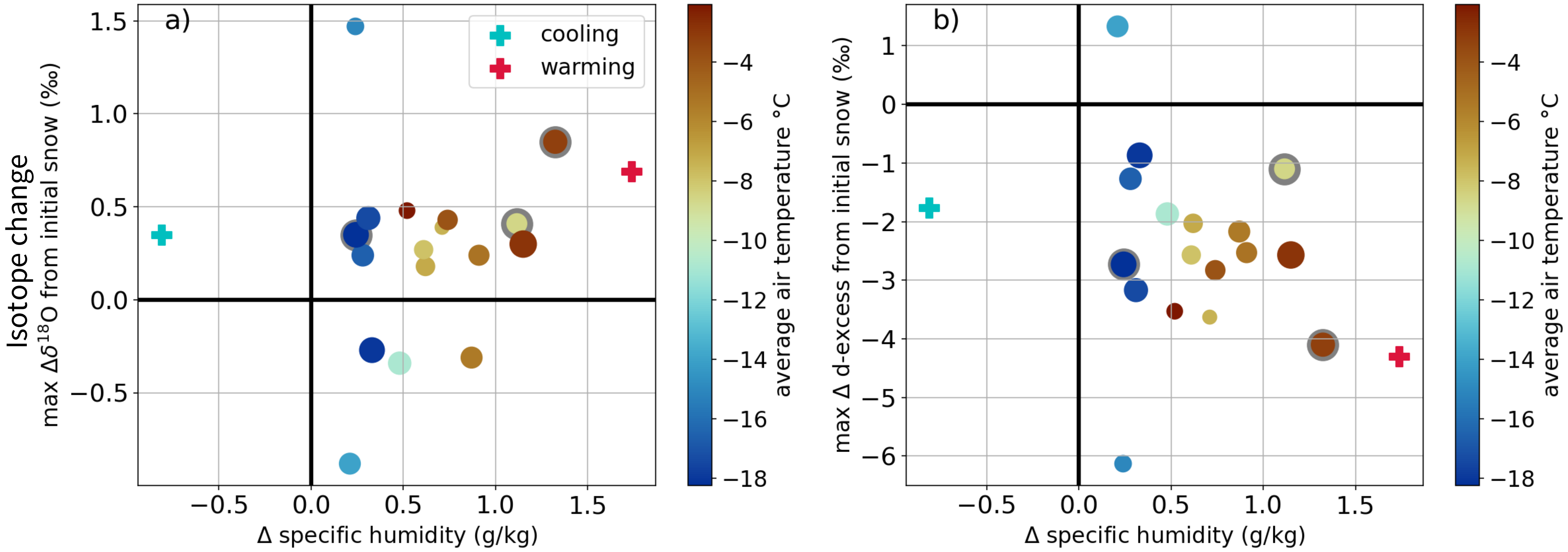
Mechanical? (fragmentation & abrasion & clustering)

Metamorphic? (sublimation and vapor deposition)

Results – Change in Snow Isotope Signal

δ^{18}O

d-excess

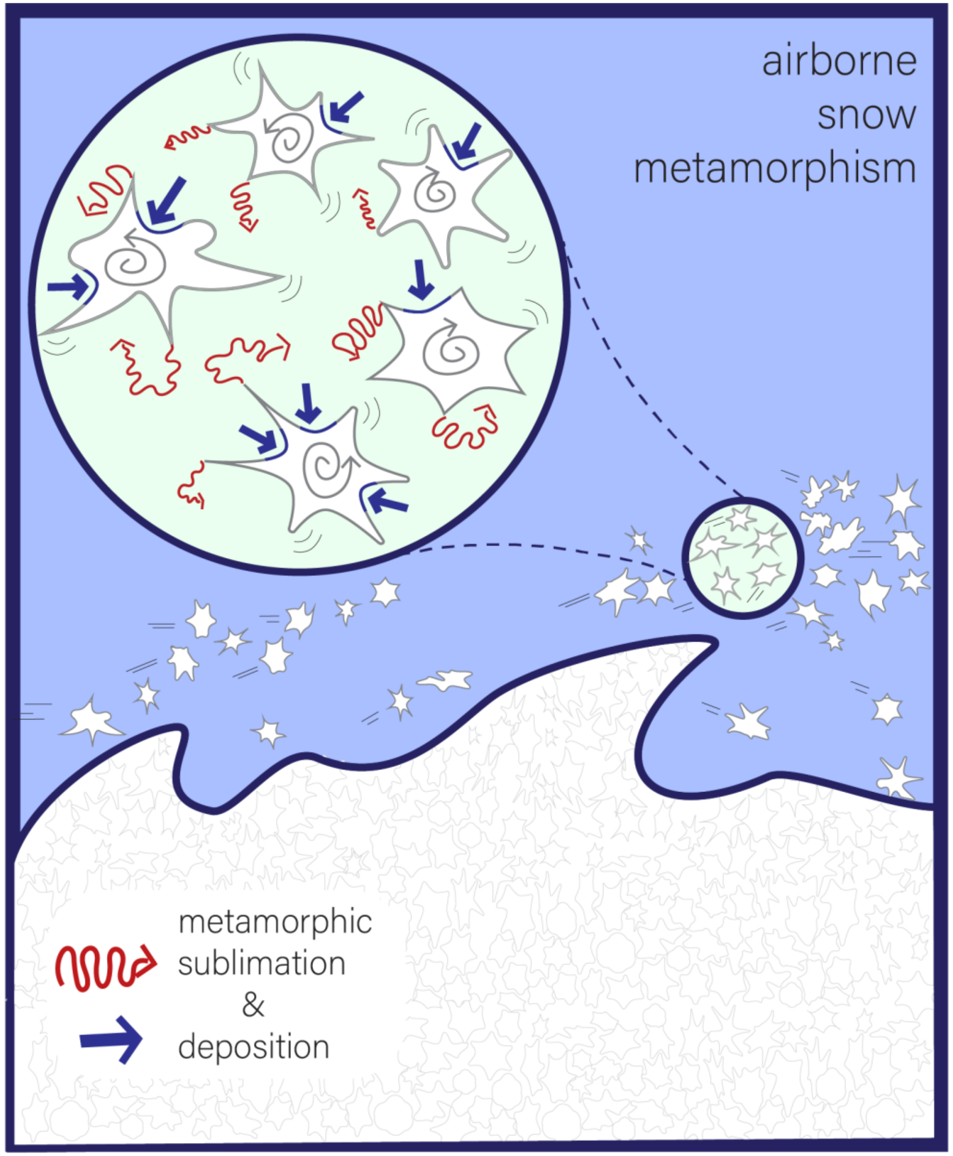


“ net sublimated snow "

“ net sublimated snow "

Conclusions

- Snow particle growth
  + SSA decrease
  + Isotope change
  → **Airborne**
  Snow Metamorphism
- Snow sublimation and redeposition on the airborne particles
- **Blowing snow events leave an isotopic fingerprint in the snow** isotopic composition



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