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New method for high precision measurements of water inclusions in speleothems based laser absorption spectroscopy and its application

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Workshop on “Developments in isotope ratio measurements for gas analysis”, Bern, 10.10.2019

INTRODUCTION

What are speleothems?

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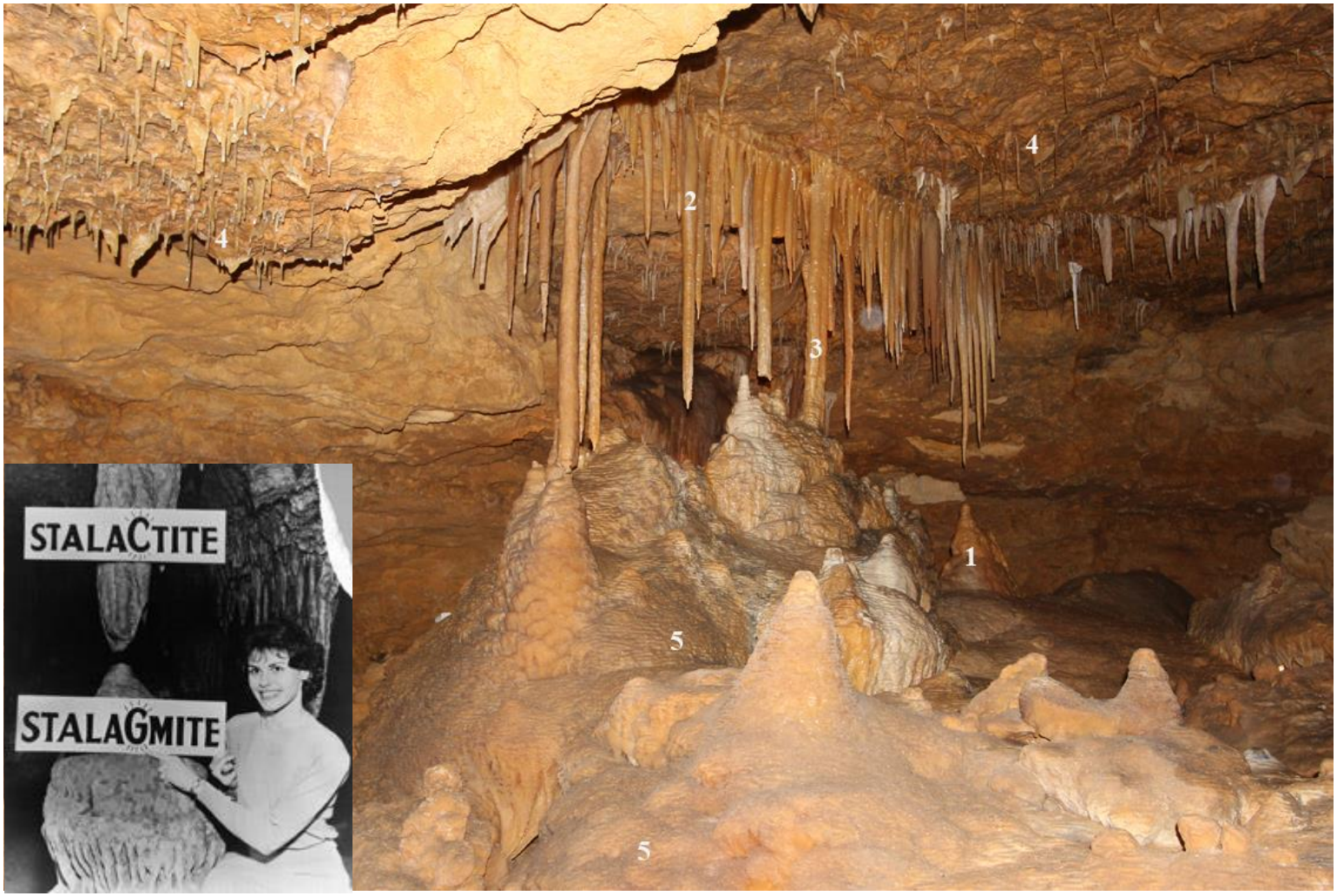

Naracoorte Caves National Park, Australia

The water cycle and its connection to speleothems

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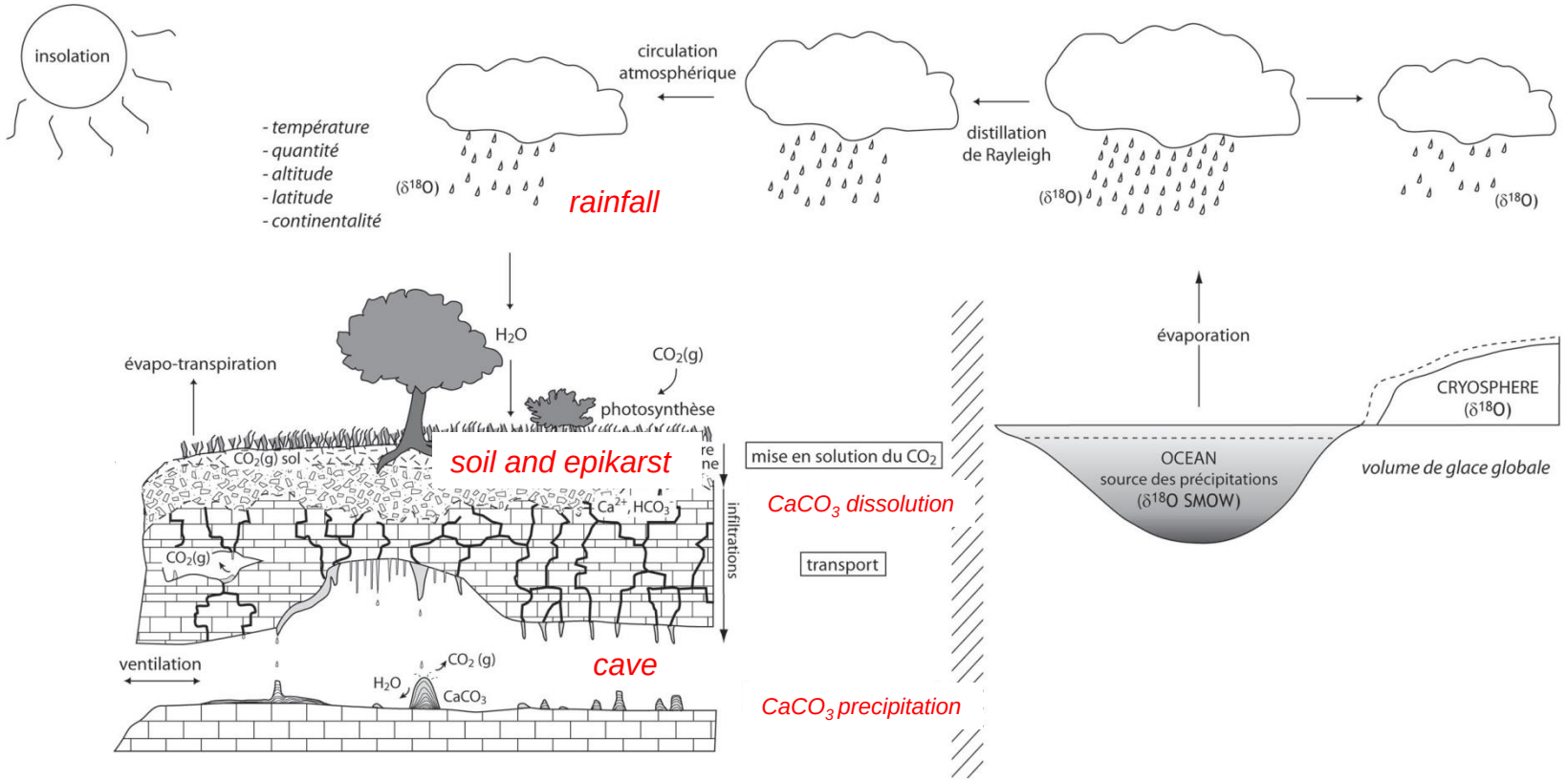

- Speleothem = recorder of the hydrological cycle

Couchoud, *Quaternaire*, 2008

Advantages of speleothems as paleoclimate archive

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- Growth for a **long time interval** during the Quaternary and earlier than 1 Ma (or older…).
- They can be **precisely dated** with laminae counting or U-Th decay method (up to 500,000 years). The precision can be better than 100 years for a sample aged of 129 ka *(Cheng et al., 2013).*
- They allow **multi-proxy study on one sample** such as: $\delta^{18}O$ and $\delta^{13}C$ of the calcite, δD, $\delta^{18}O$ of fluid inclusions, clumped isotopes, trace elements, nobles gases, etc.
- **They are well conserved** in cave environments and protected from erosion by physico-chemical processes occuring at the surface.
- They are found **all over the Globe.**

Repartition of carbonate rocks

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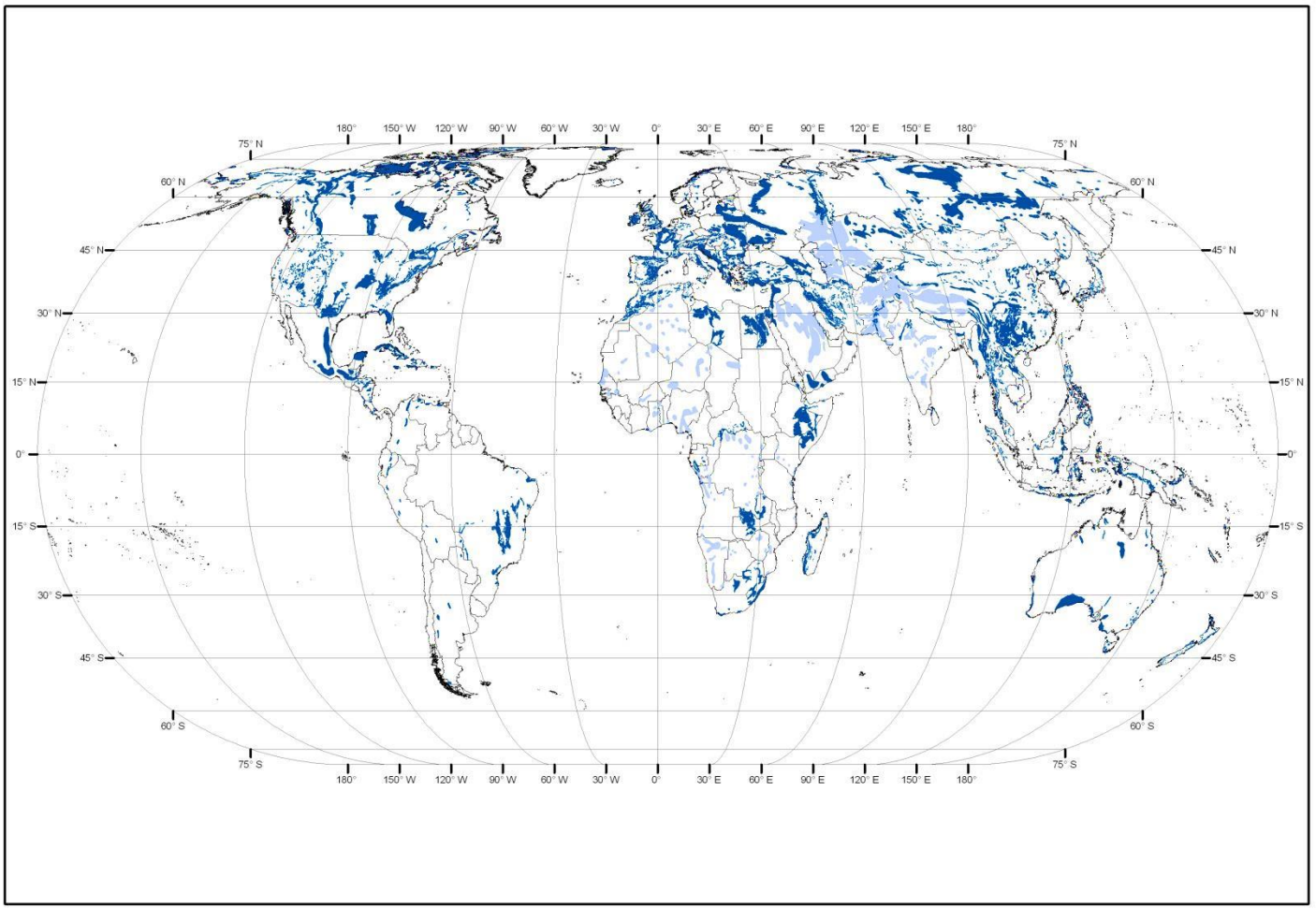

http://web.env.auckland.ac.nz/our_research/karst/

STALCLIM project

Investigated caves in Switzerland

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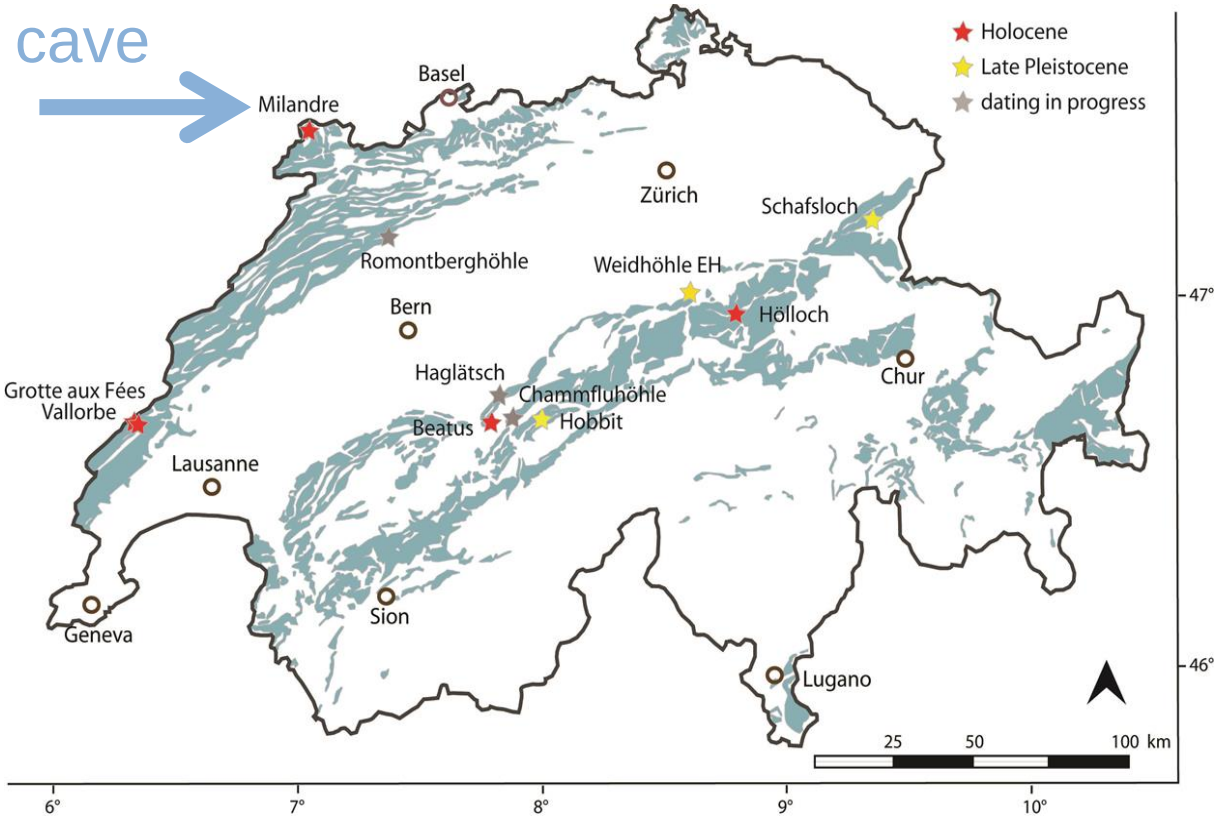
Milandre cave



A. Häuselmann , *PhD thesis,* 2015

Milandre cave settings

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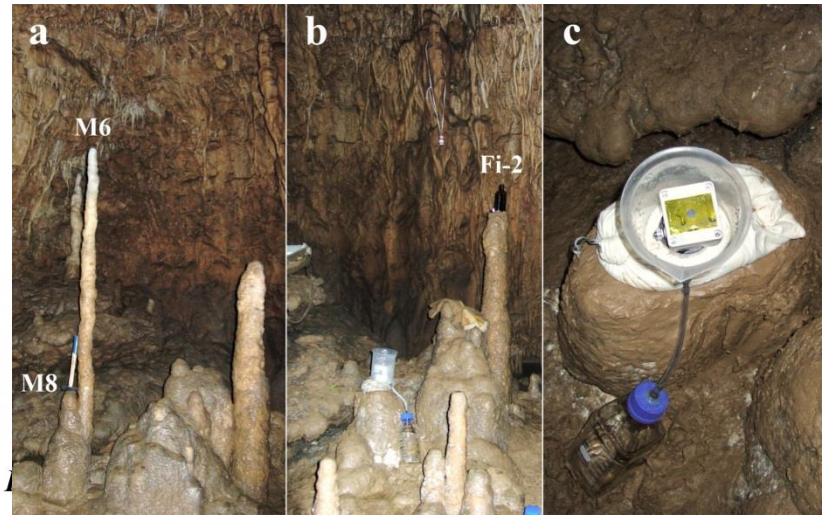

Monitoring study:
- Cave MAT = MAT outside
- Changes in δD_{fi} are closely related to δD_{dw} that is influenced by temperature-controlled δD_p

Affolter et al., *Quaternary Science Reviews*, 2015

From cave to analysis
Sample selection & transport

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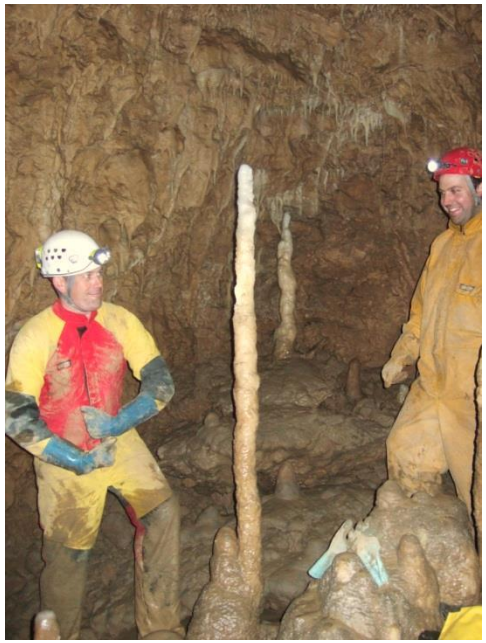
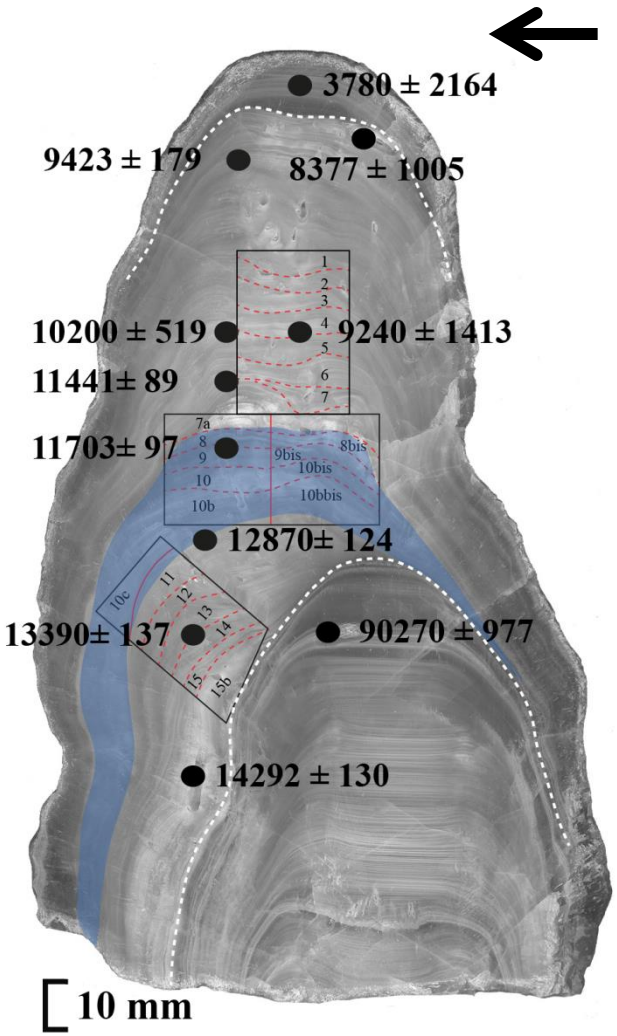


Milandre Cave, Switzerland

Dating of fluid inclusion samples



M8 stalagmite

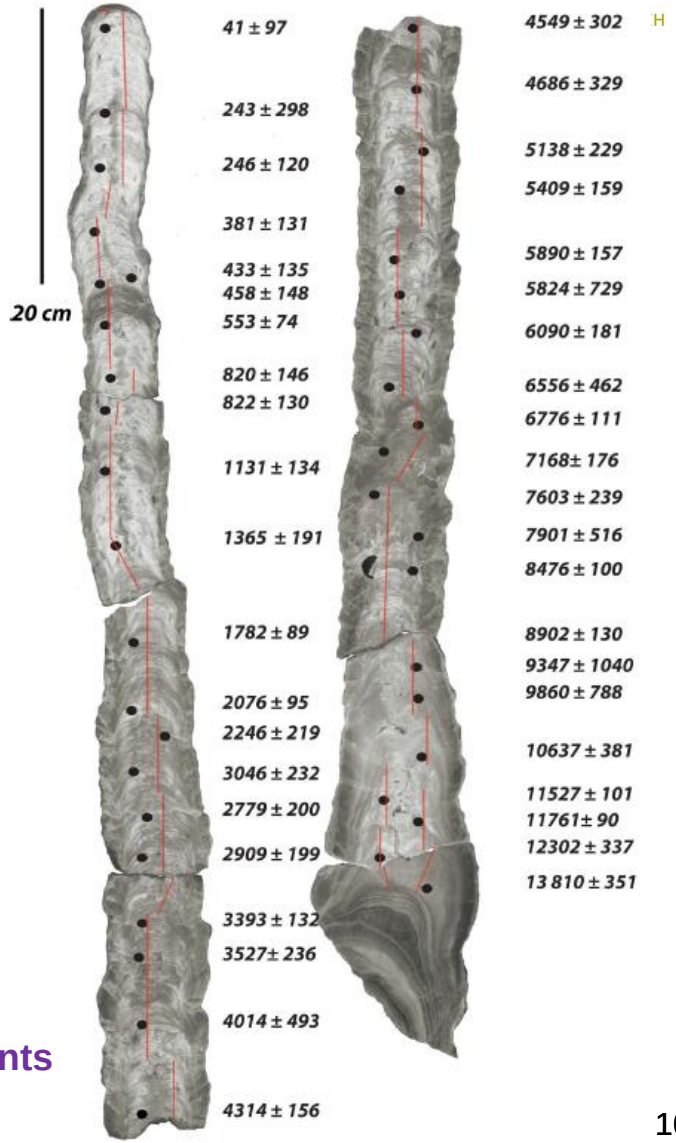
- Interval measured:
  14 ka– 9 ka B.P.
- 7 Th ages
- 15 FI measurements

M6 stalagmite

- Interval measured
  12 ka B.P. – recent
- 42 Th ages
- 269 FI measurements
- + ~30 samples replicated

- **Total of 314 samples**

+ ~3340 $\delta^{18}O_c$ measurements



Affolter et al., *Science Advances*, 2019

Fluid inclusions

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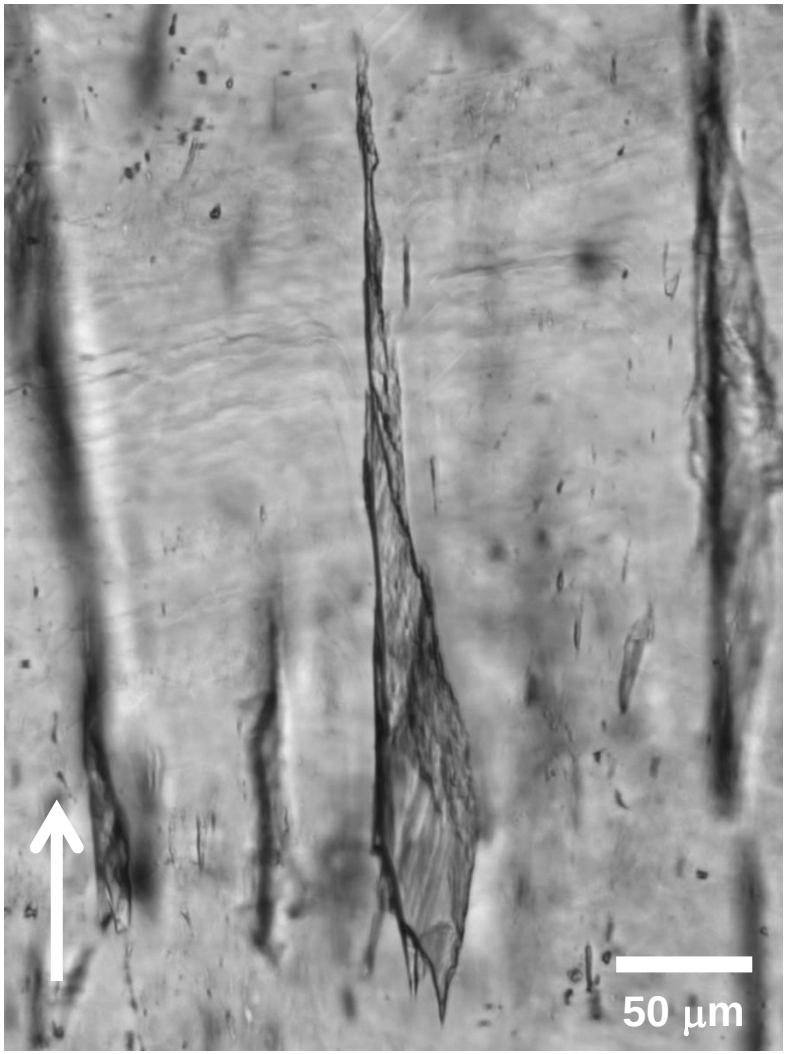
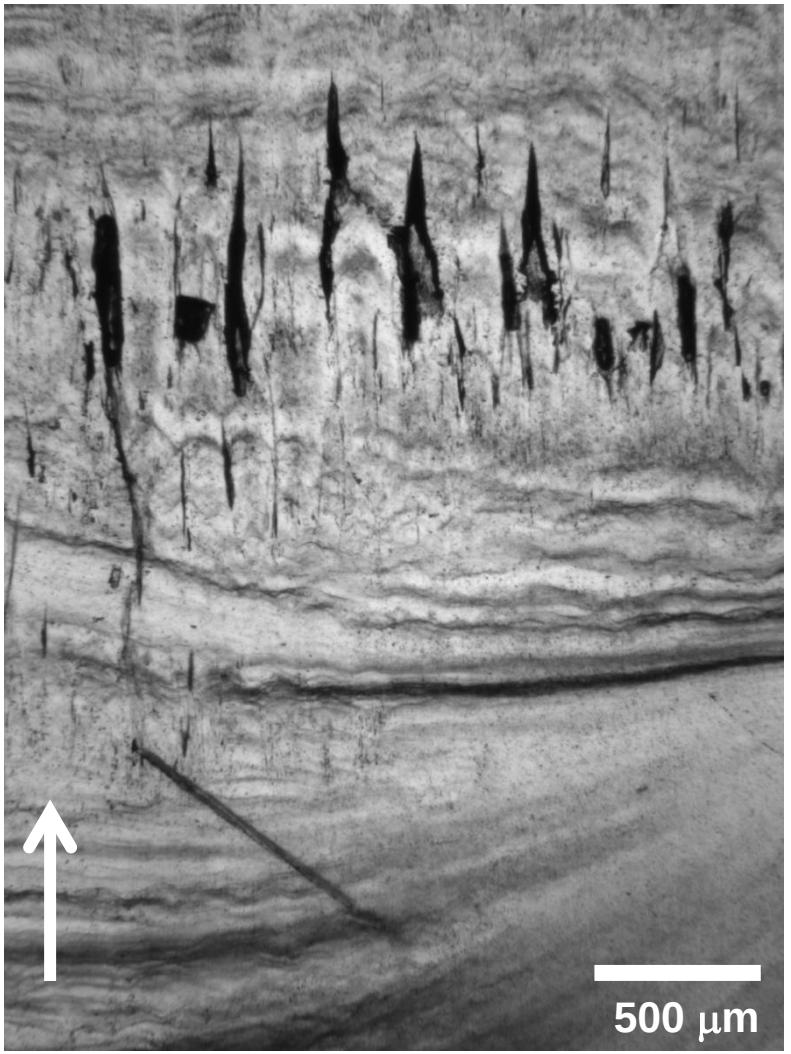
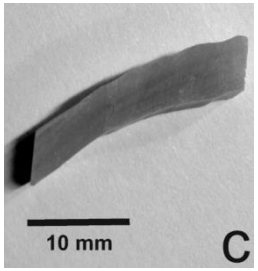




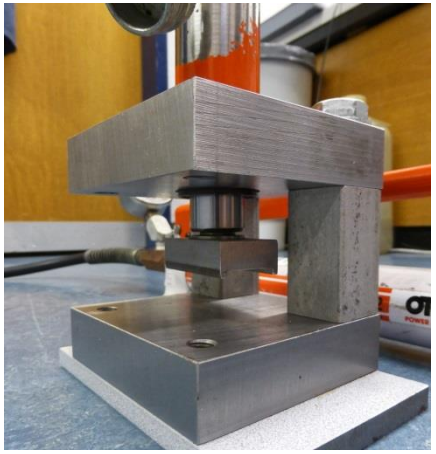
M8 stalagmite (photo: Y. Krüger)

METHOD

Laboratory work



~ 1 gram



Extraction line connected to a CRDS instrument

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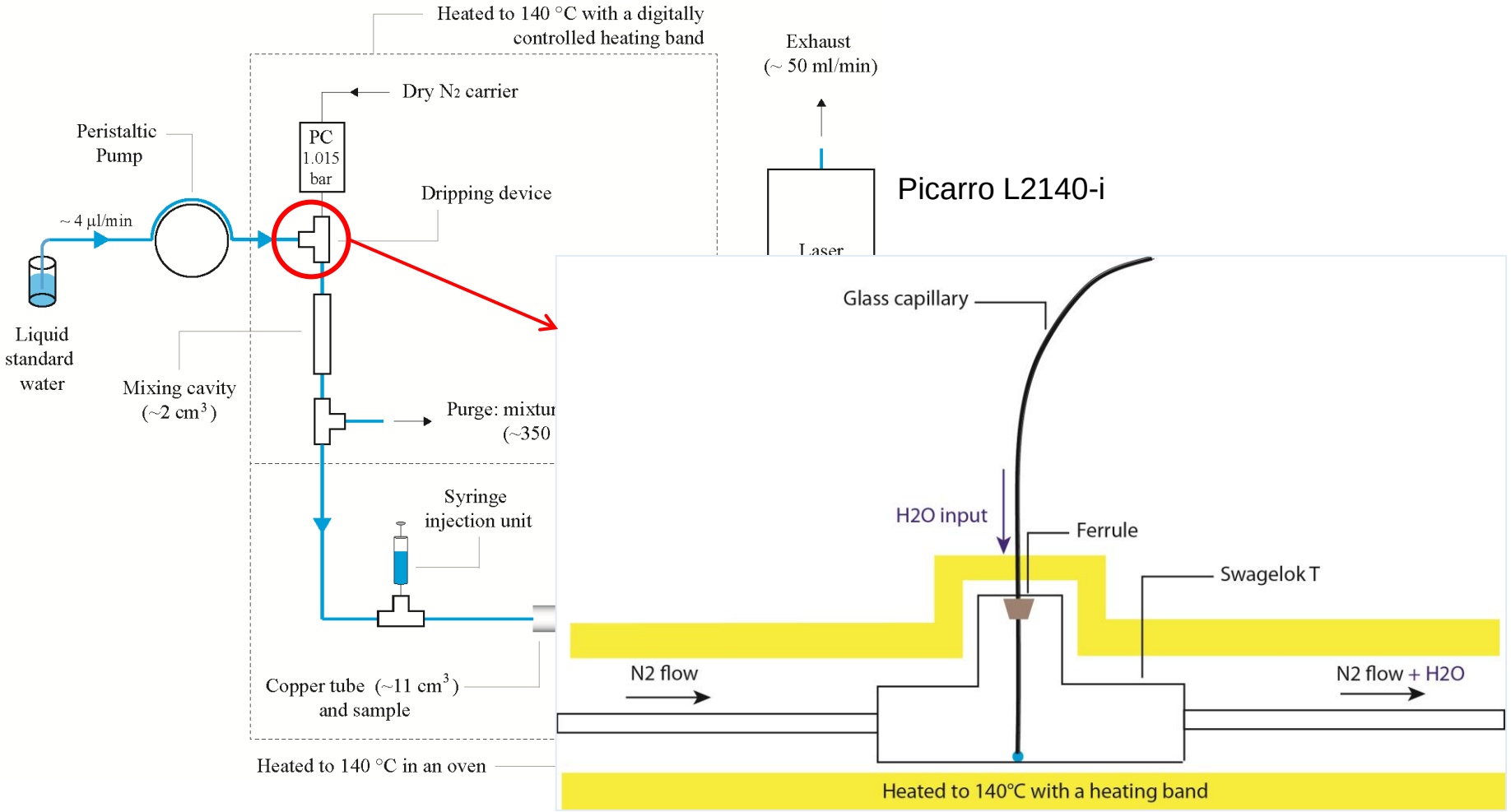

Affolter et al., *Climate of the Past*, 2014

Measurement sequence

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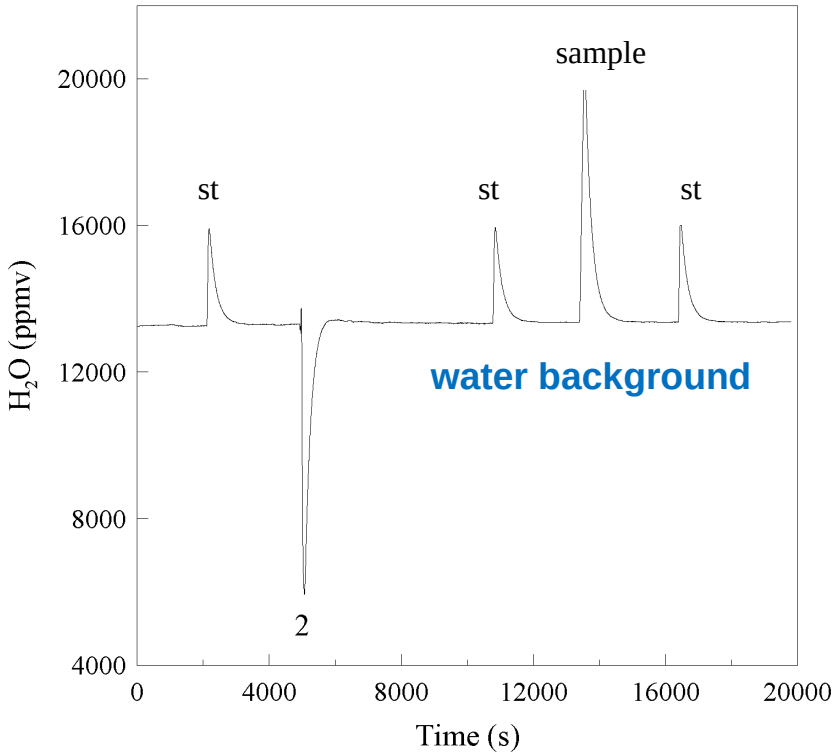

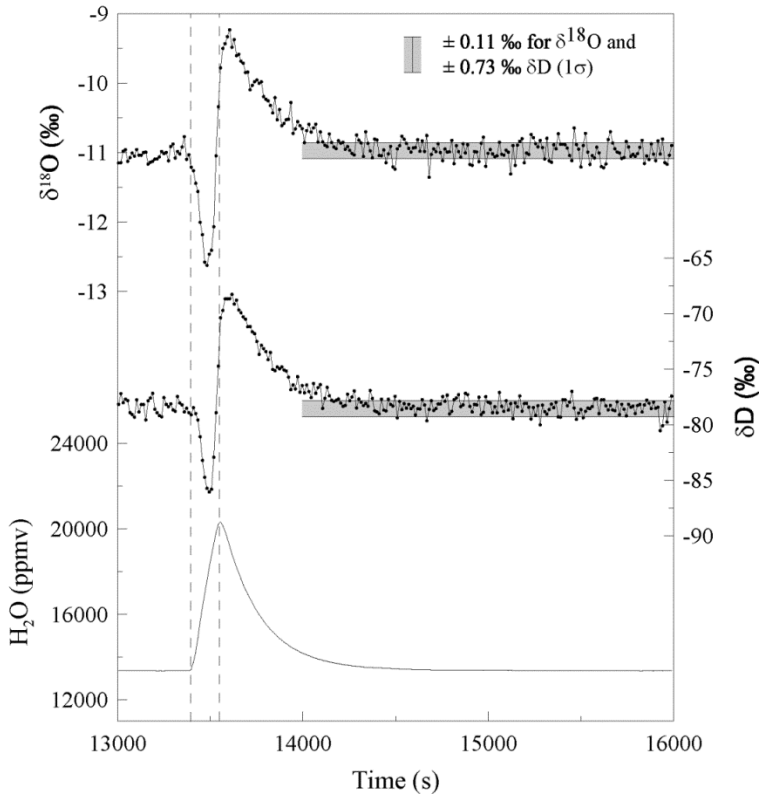

Affolter et al., *Climate of the Past*, 2014

Water content determination

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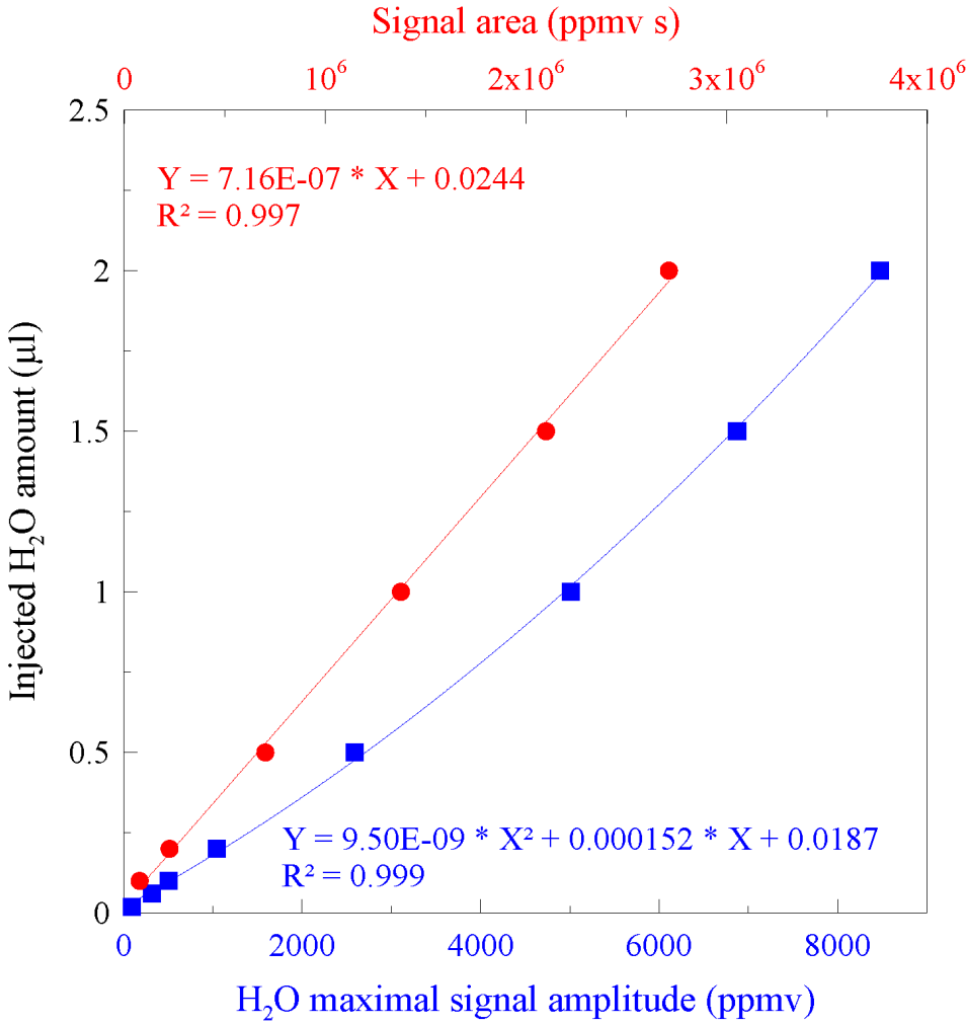

Affolter et al., *Climate of the Past*, 2014

Isotope values calculation

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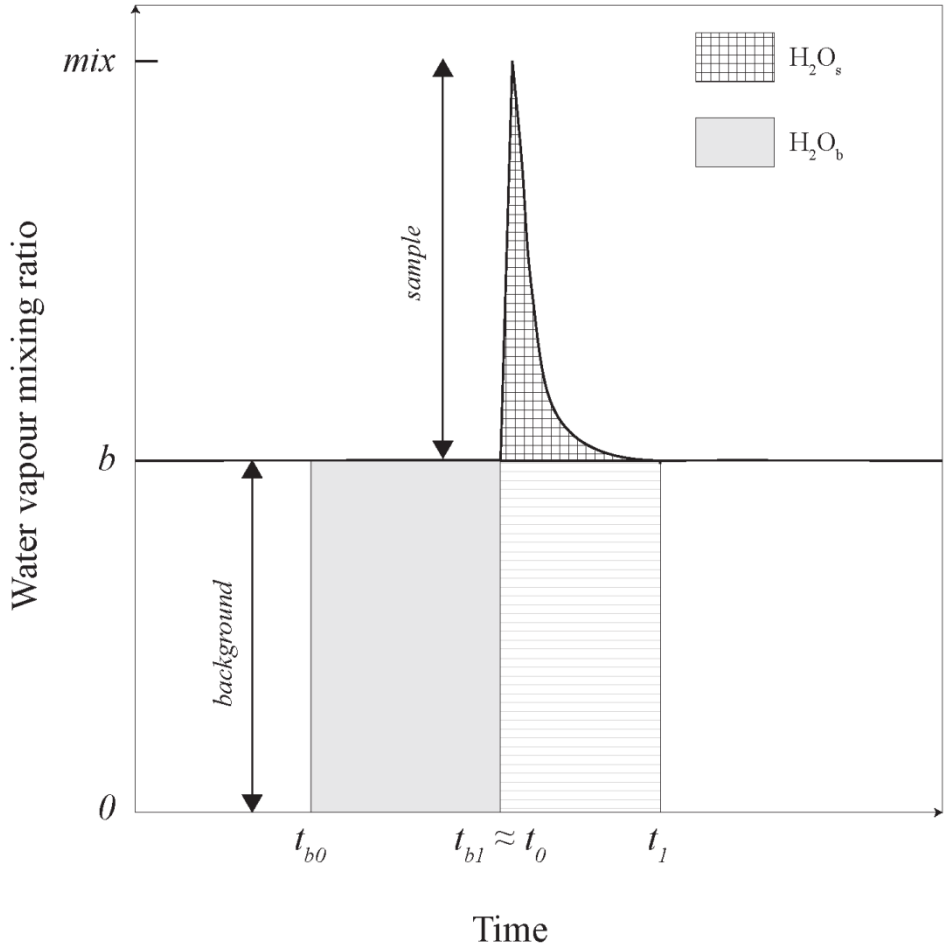

$$\overline{\delta^{18}O_j} = \frac{\int_{t_0}^{t_1} \delta^{18}O_j(t) \cdot H_2O_j(t)}{\int_{t_0}^{t_1} H_2O_j(t)}$$

$$\overline{H_2O_j} = \frac{\int_{t_o}^{t_1} H_2O_j(t)dt}{\int_{t_o}^{t_1} dt} = \frac{\int_{t_o}^{t_1} H_2O_j(t)dt}{t_1 - t_0}$$

where j is either the mixture, the background or the sample

$$\delta_s = \frac{\overline{\delta^{18}O_{mix}} \cdot \overline{H_2O_{mix}} - \overline{\delta^{18}O_b} \cdot \overline{H_2O_b}}{\overline{H_2O_{mix}} - \overline{H_2O_b}}$$

Measurement precision with L1102-i

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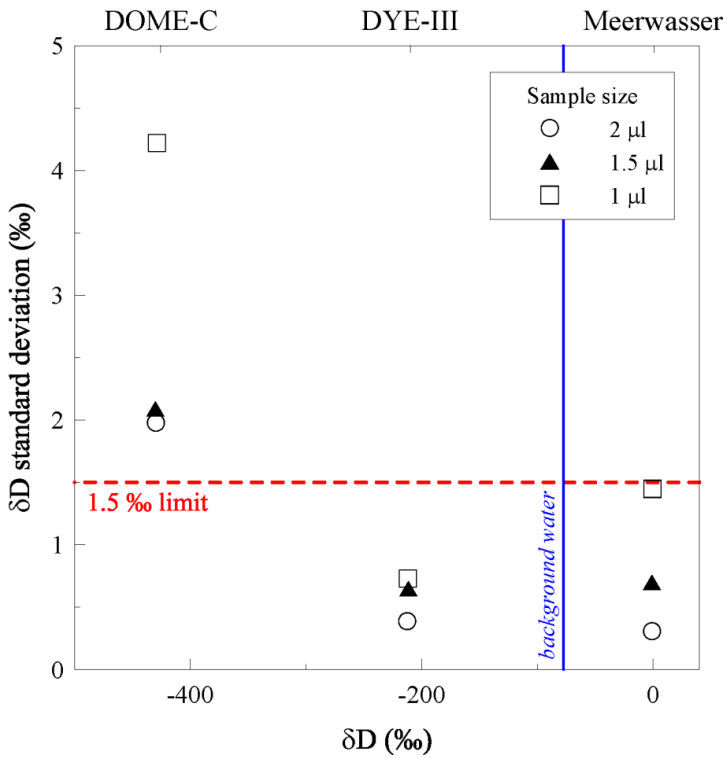
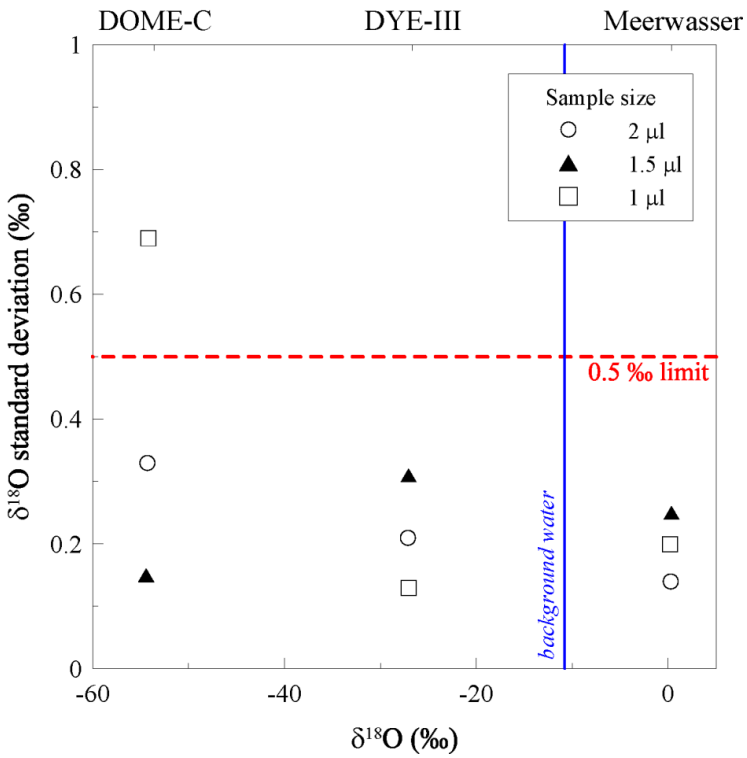
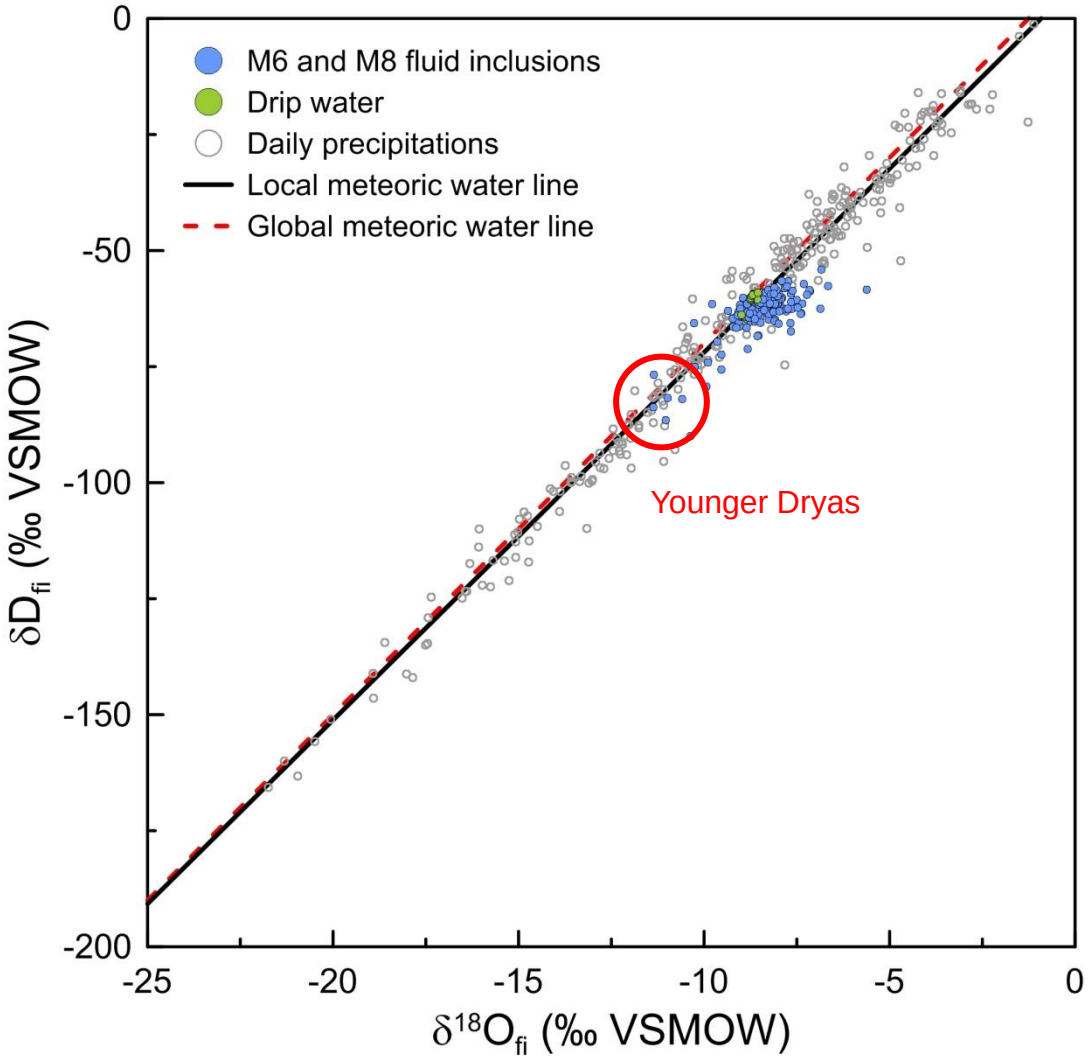




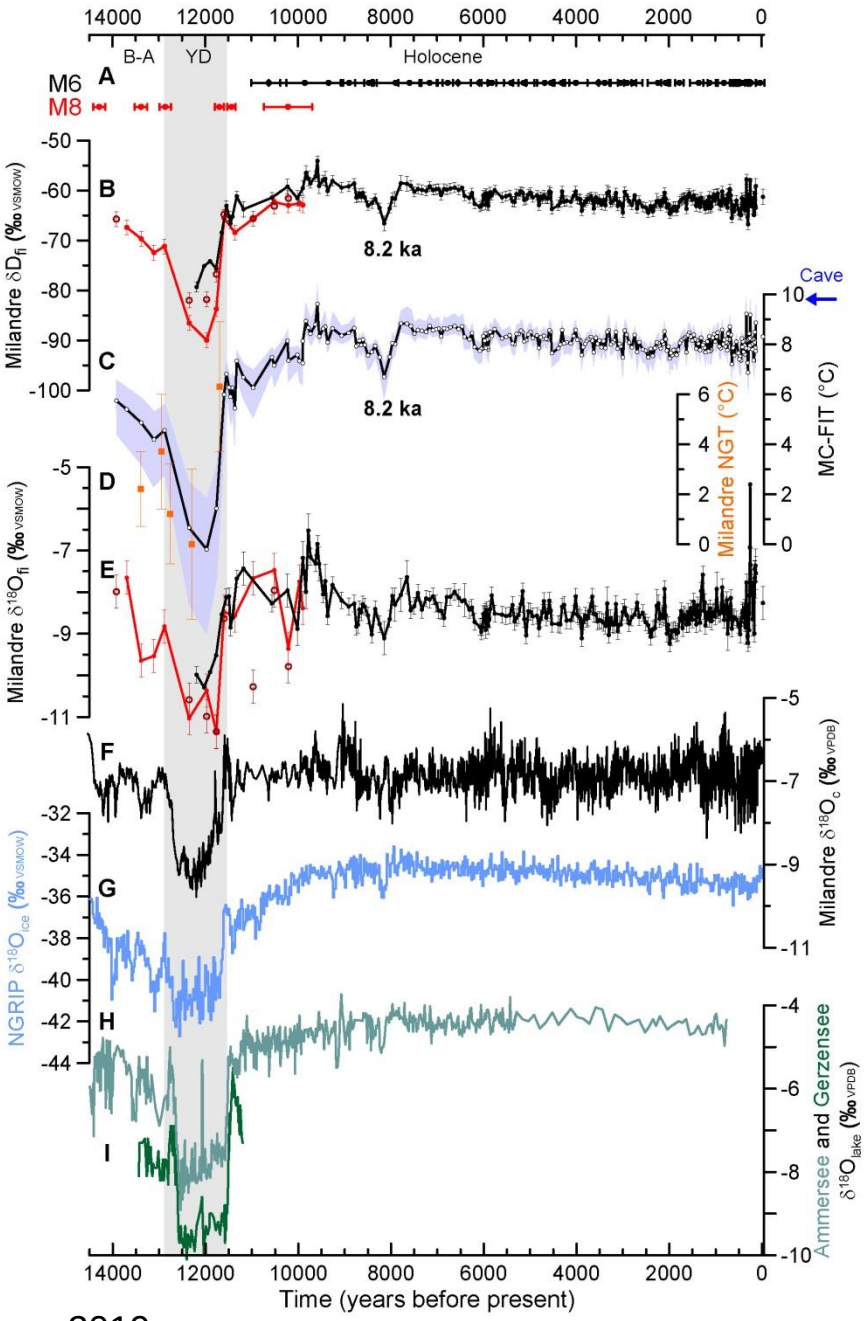
Affolter et al., *Climate of the Past*, 2014

RESULTS

$\delta^{18}O$ vs δD

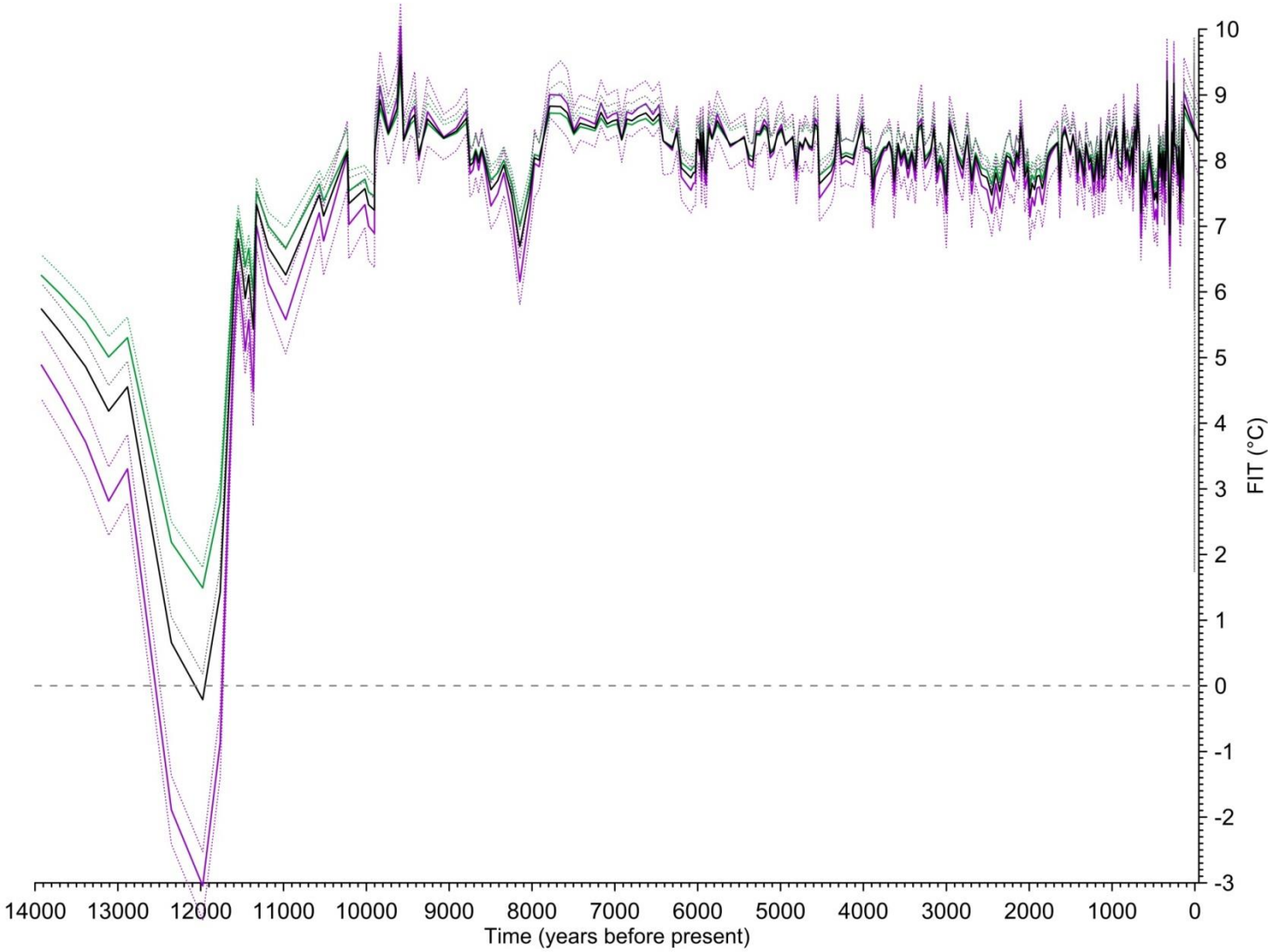


Results



Affolter et al., *Science Advances*, 2019

Fluid inclusion-based temperatures (FIT)



TF 2.88 ‰/°C
TF 3.84 ‰/°C
TF 4.80 ‰/°C

Affolter et al., *Science Advances*, 2019

Comparison with Greenland reconstruction

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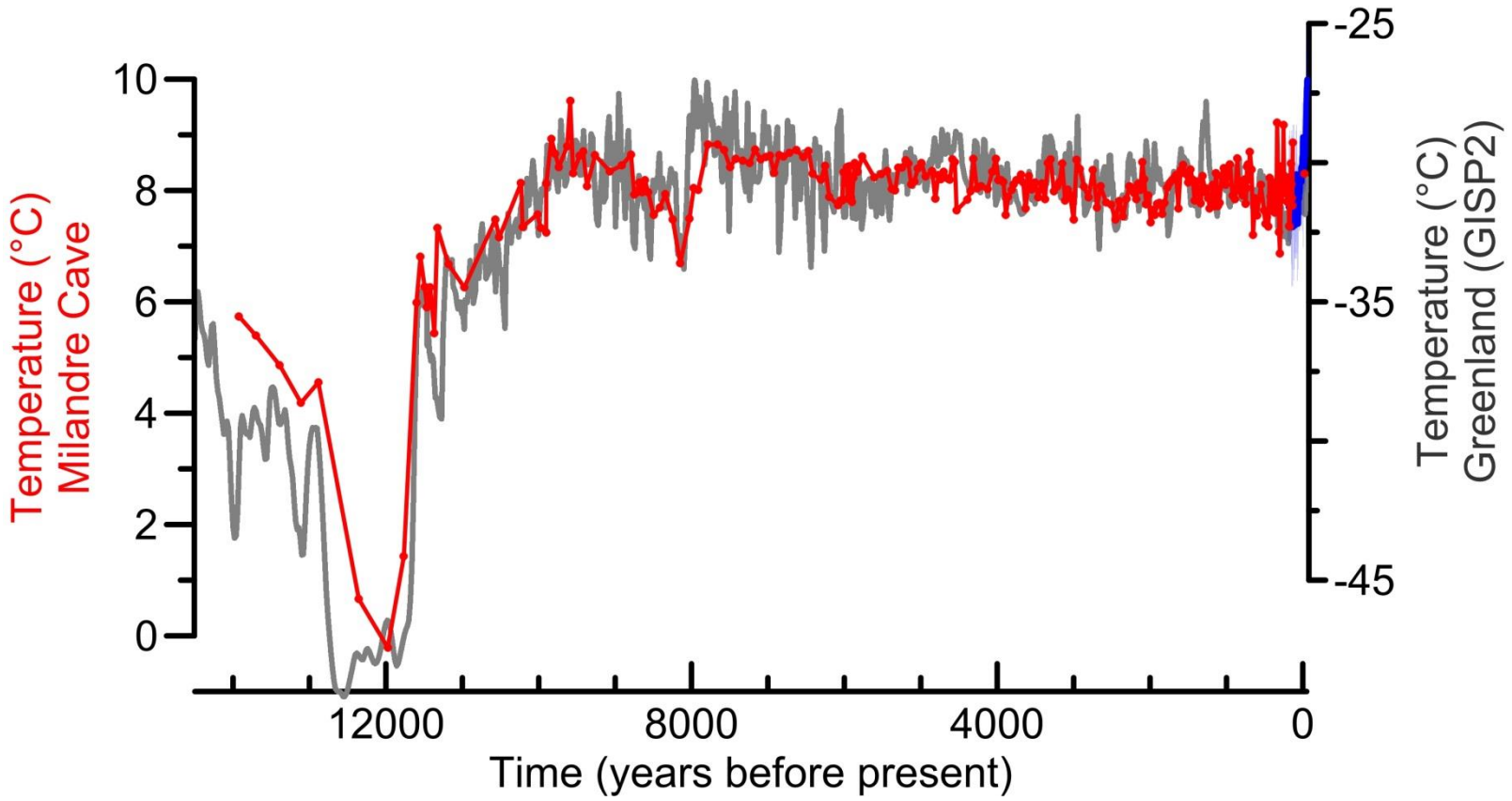
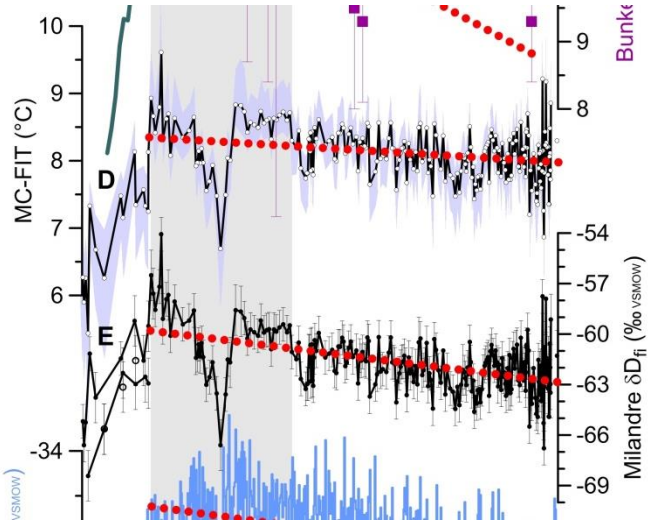
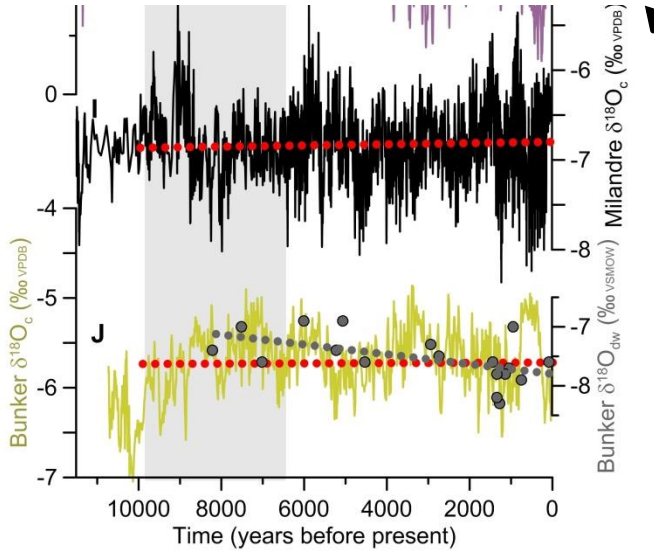
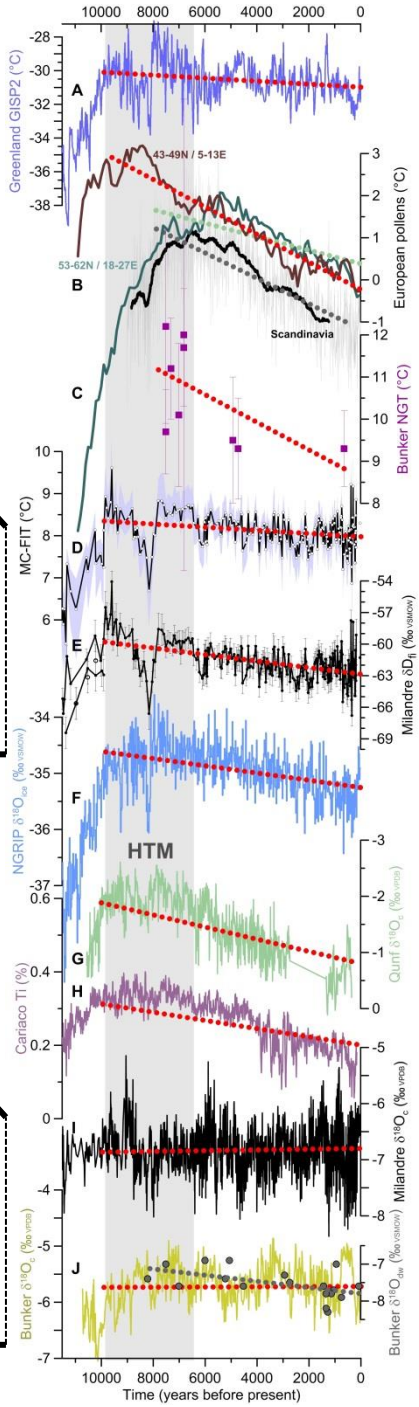


Holocene trends







Affolter et al., *Science Advances*, 2019

Comparison with proxies and model simulations

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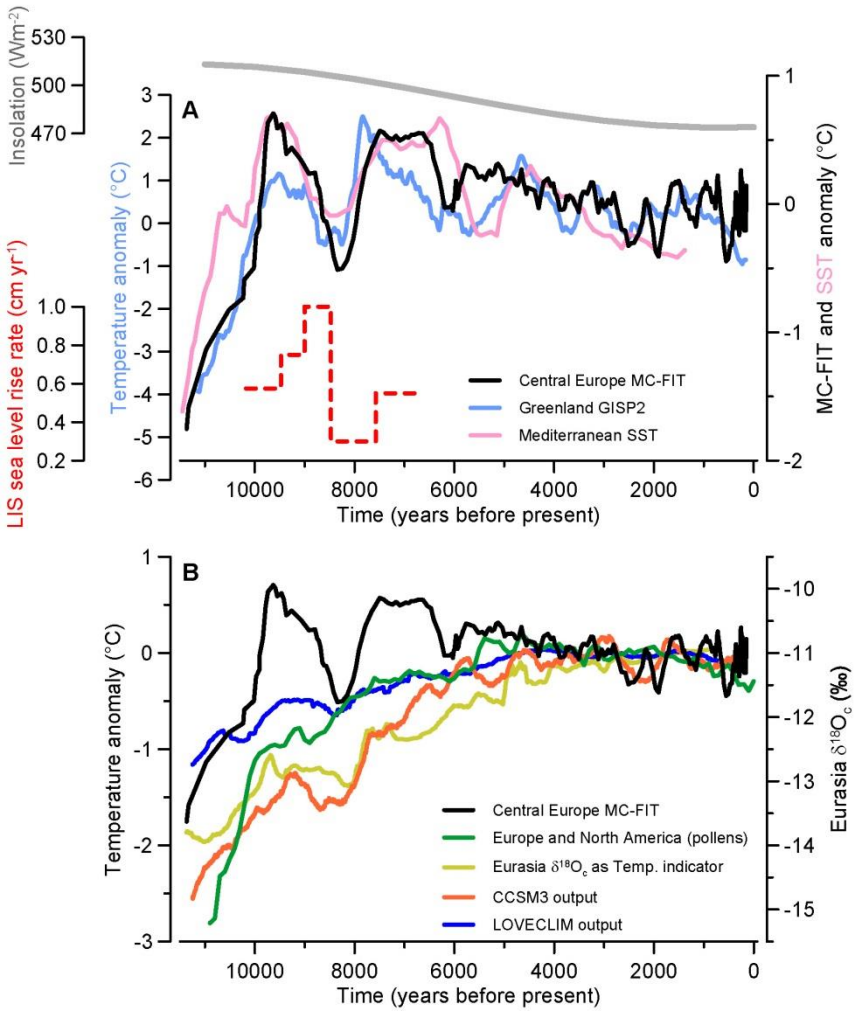

Affolter et al., *Science Advances*, 2019