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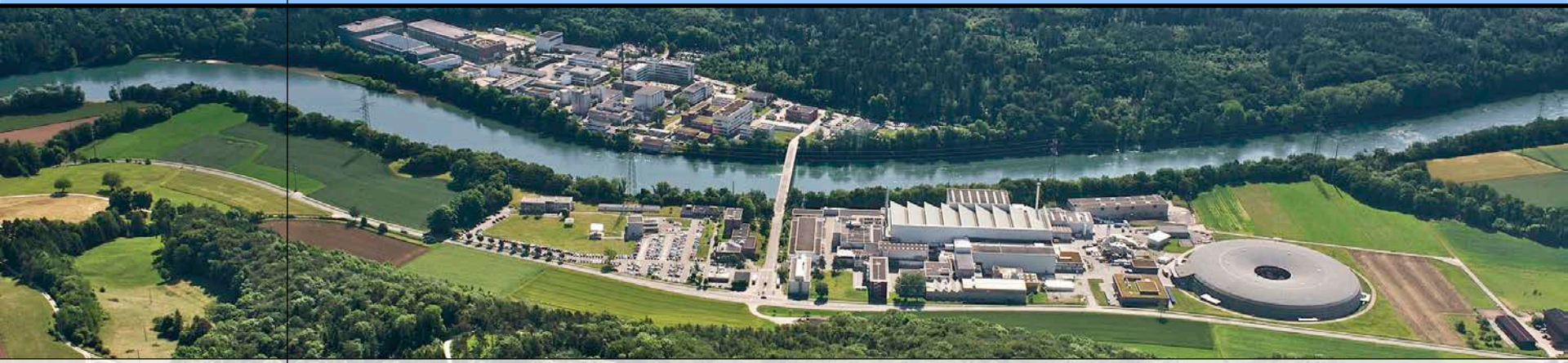
PSI



Wir schaffen Wissen – heute für morgen

Reconstruction of anthropogenic and biogenic carbonaceous aerosols emissions from an Alpine ice core

Fang Cao

Paul Scherrer Institut

Outline

- Introduction
  - Theoretical background
  - Goals
- Methods
  - Decontamination method for firn samples
  - Improvement of method on OC/EC separation
- Results
  - Comparisons with the old method
  - Historical OC/EC emissions from Fiescherhorn ice core : 1940-2002
- Conclusions

Ice cores as natural archives of past climate

… comprise invaluable records about past (climatic) conditions on earth

… help to analyse and understand coherencies and driving mechanisms in the climate system

… provide requisite data for climate models

Long-term ice core record

The records for greenhouse gases (CO_2, CH_4, and NO_2) and δD more positive values indicate warmer conditions) for the past 650'000 years from EPICA Dome C (Antarctica) and other ice cores.

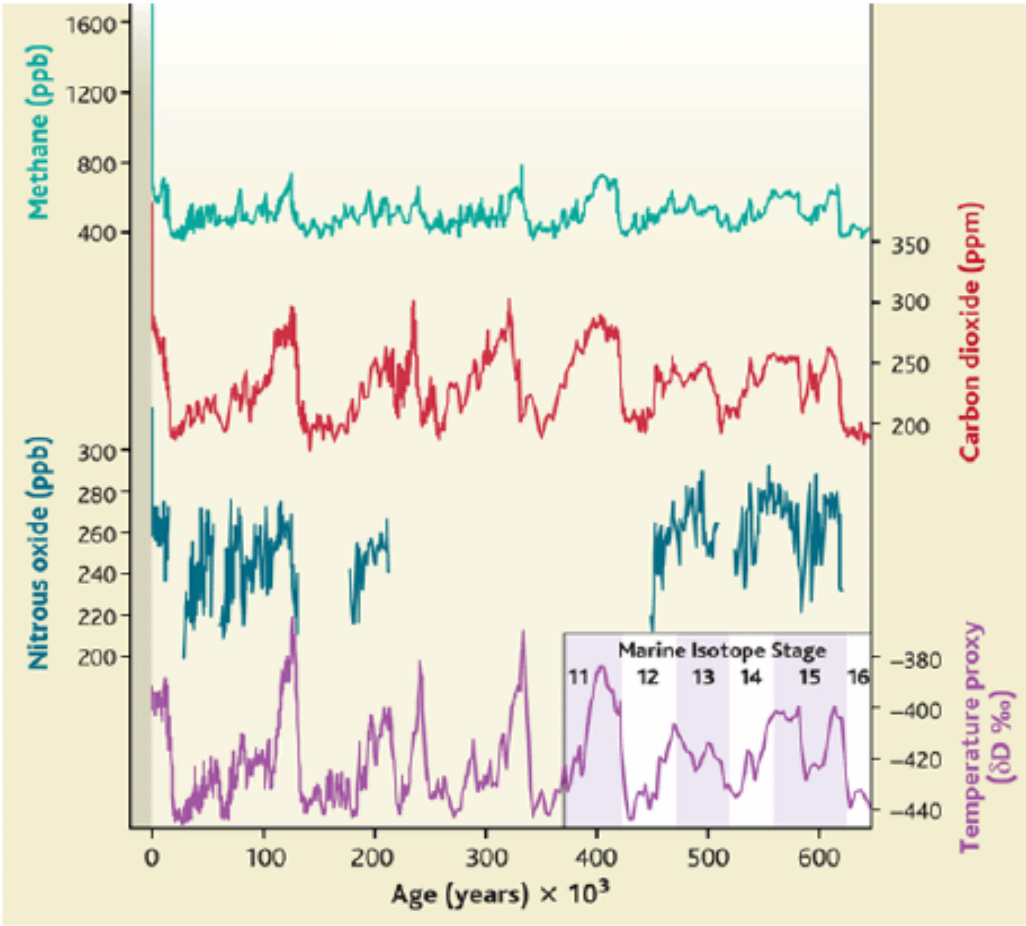
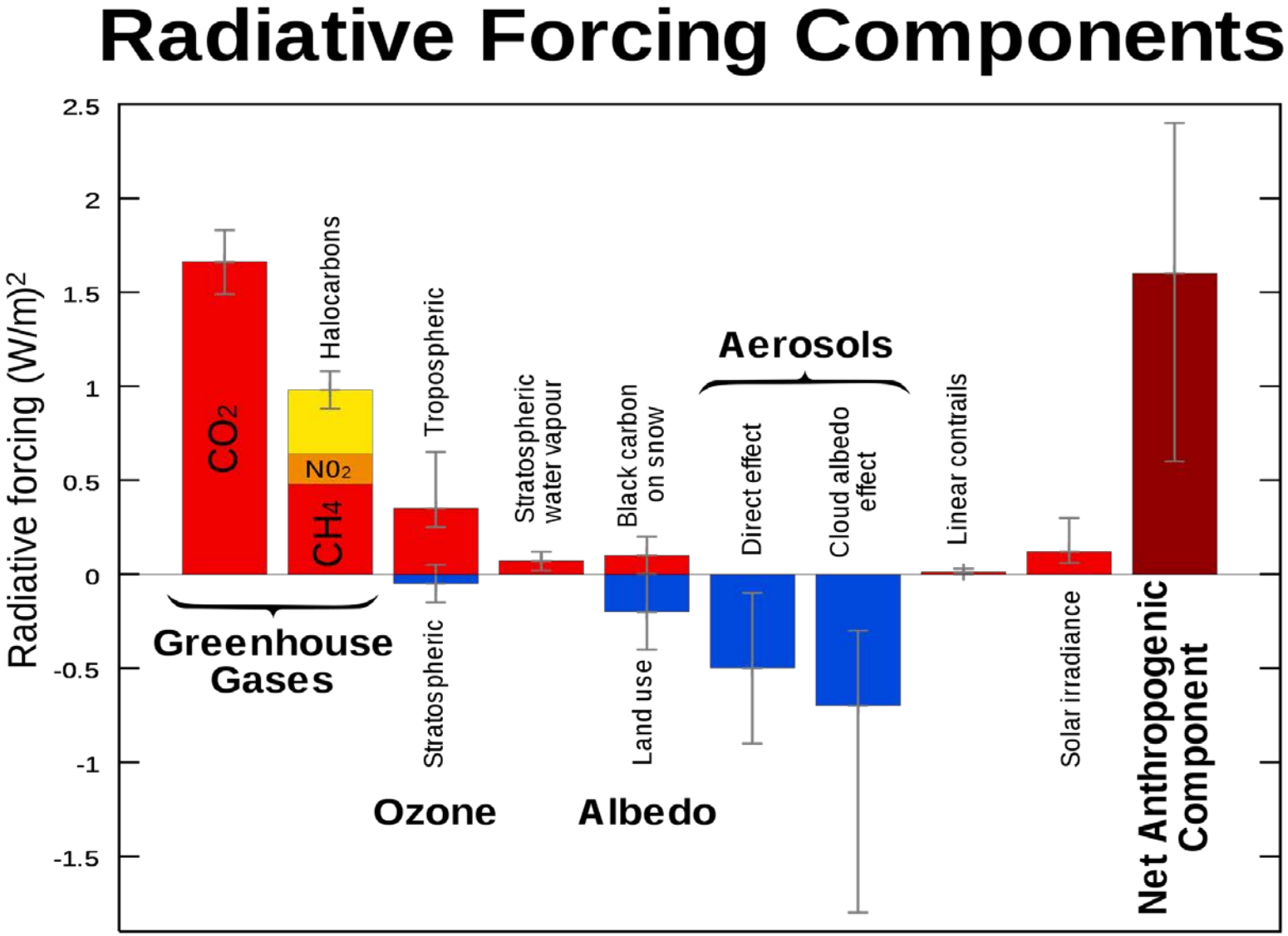


Figure from Brook, 2005

Climate effects of aerosols



IPCC 2007

Glacial retreat

Rhône Glacier, Switzerland

M. Funk, ETH-VAW

Glacial retreat

Rhône Glacier, Switzerland

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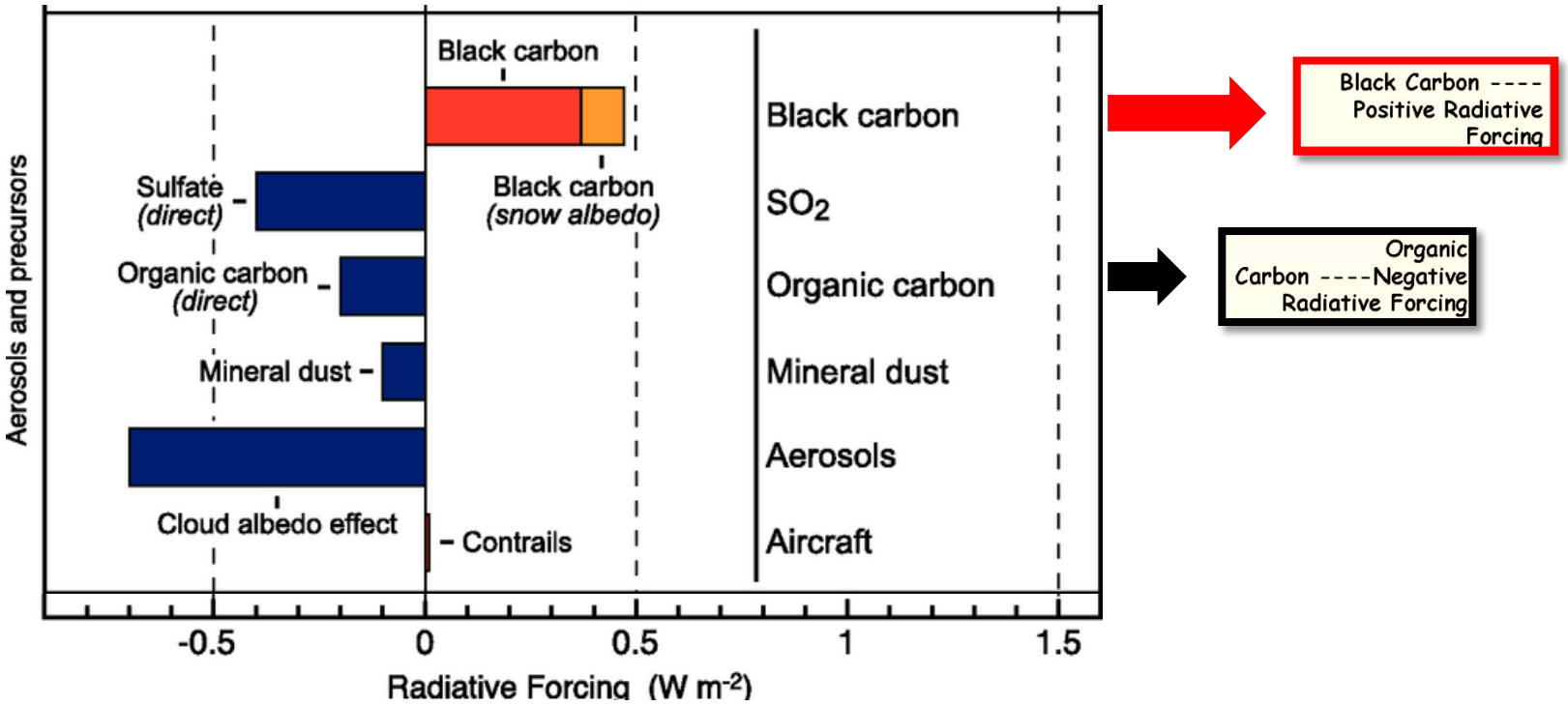
Glacial retreat

Rhône Glacier, Switzerland

M. Funk, ETH-VAW

Carbonaceous particles and their Climate effects

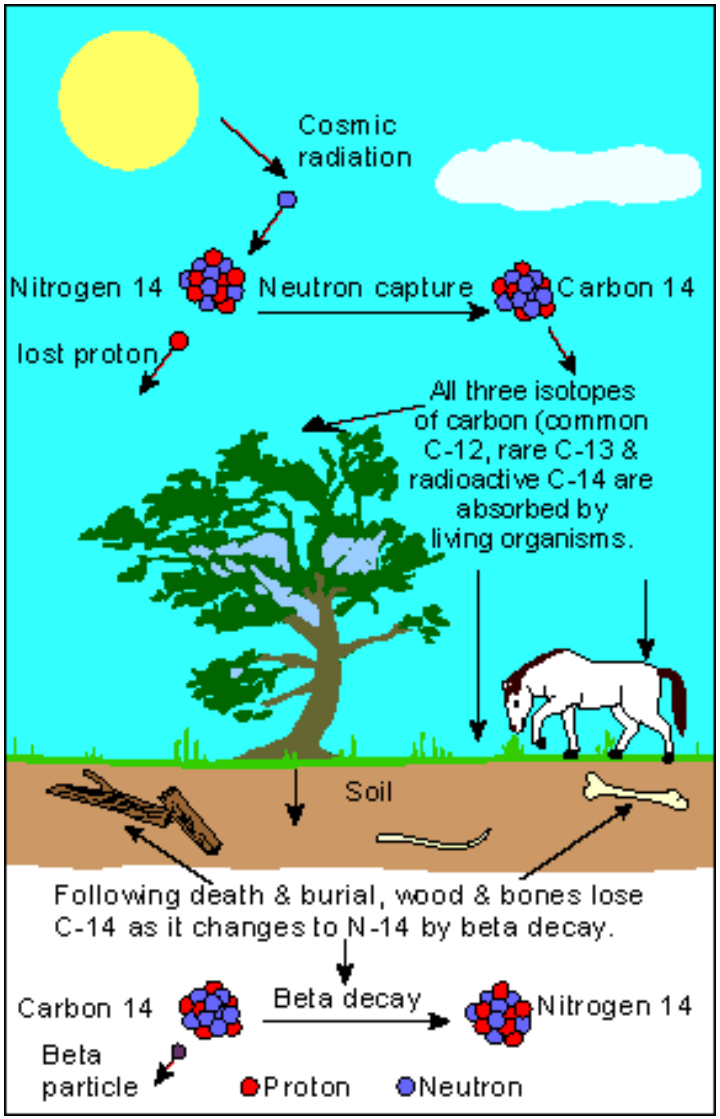
Carbonaceous particles (total carbon, TC) are a major fraction of the atmospheric aerosols, which contain carbon.



IPCC2007

What is radiocarbon?

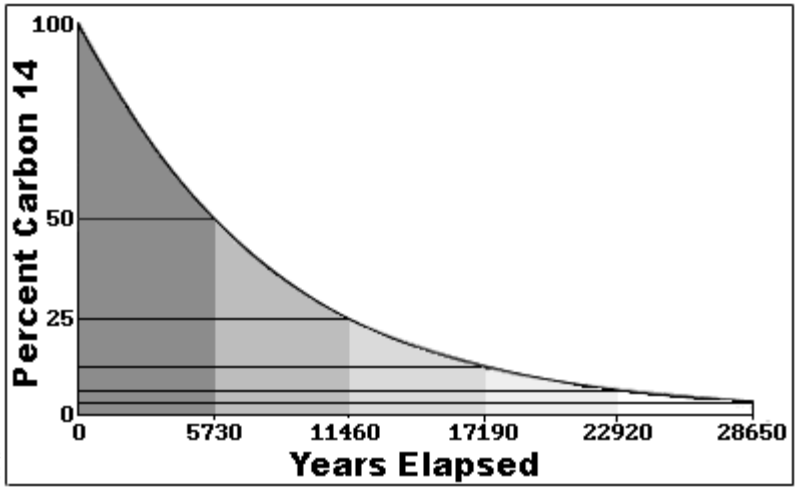
Radiocarbon is a radioactive isotope of carbon with 6 protons and 8 neutrons.



http://www.sciencecourseware.org/virtualdating/files/rc0/rc_0.html

bio organisms

Contemporary $^{14}C/^{12}C$; f_m (fraction of mordern)=~1



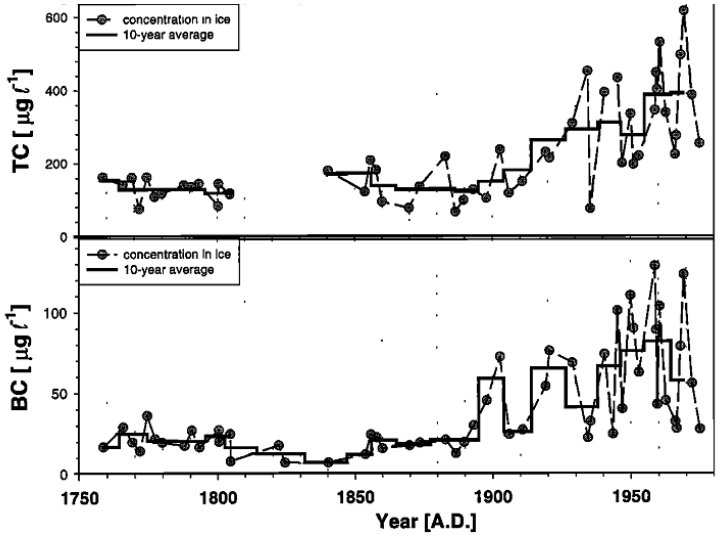
fossil fuel

14C-depleted; fm=0

Previous studies on CP in Alpine ice cores

Historical record of carbonaceous particle concentrations from a European high-alpine glacier (Colle Gnifetti, Switzerland)

V. M. H. Lavanchy[1] and H. W. Gäggeler[1]
Department of Chemistry and Biochemistry, University of Bern, Bern, Switzerland
U. Schotterer,[2] M. Schwikowski, and U. Baltensperger
Paul Scherrer Institute, Villigen, Switzerland

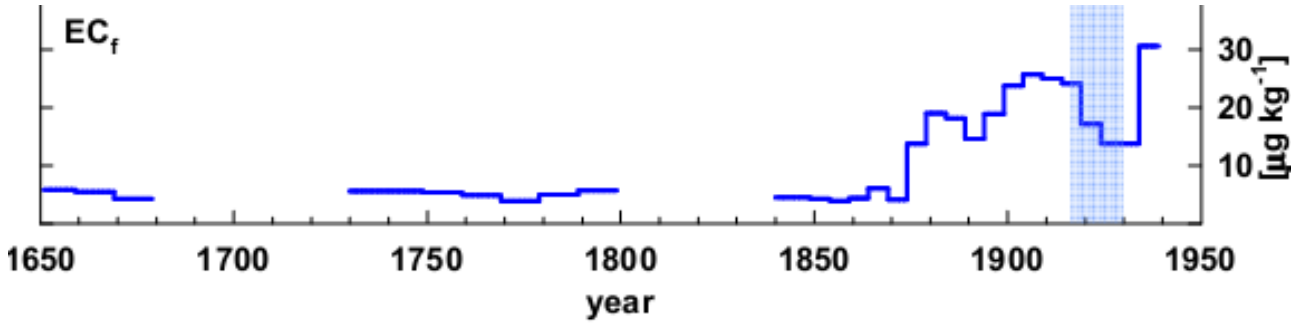


Fossil VS non-fossil???

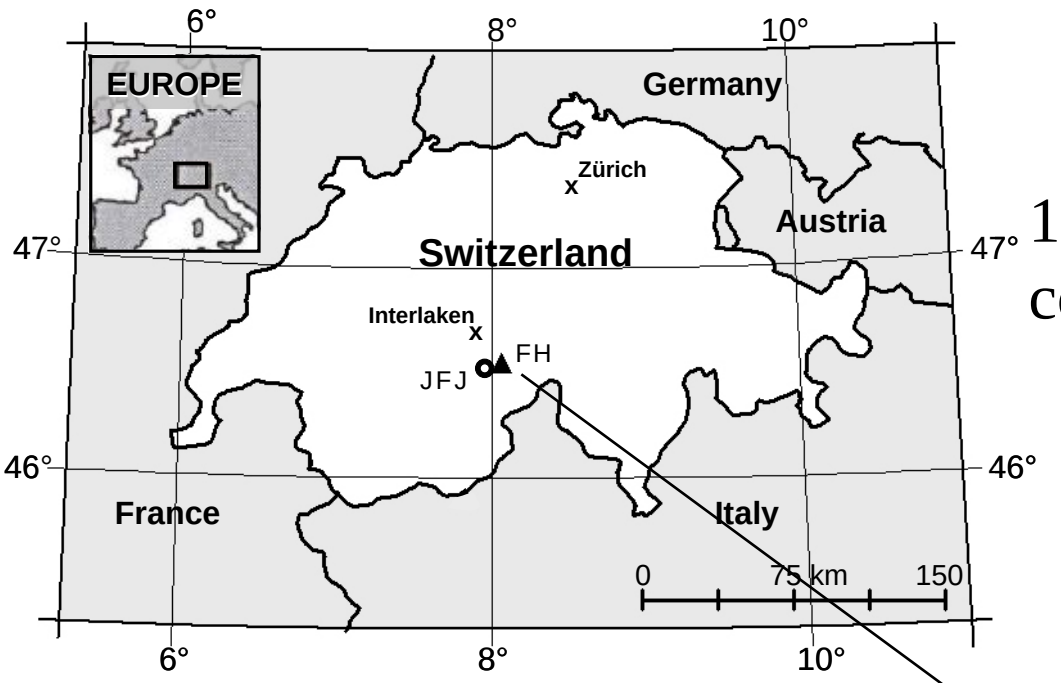
Radiocarbon analysis in an Alpine ice core: record of anthropogenic and biogenic contributions to carbonaceous aerosols in the past (1650–1940)

Not covering industrial period

T. M. Jenk[1,2], S. Szidat[1,2], M. Schwikowski[2], H. W. Gäggeler[1,2], S. Brütsch[2], L. Wacker[3], H.-A. Synal[4], and M. Saurer[2]



Sampling site

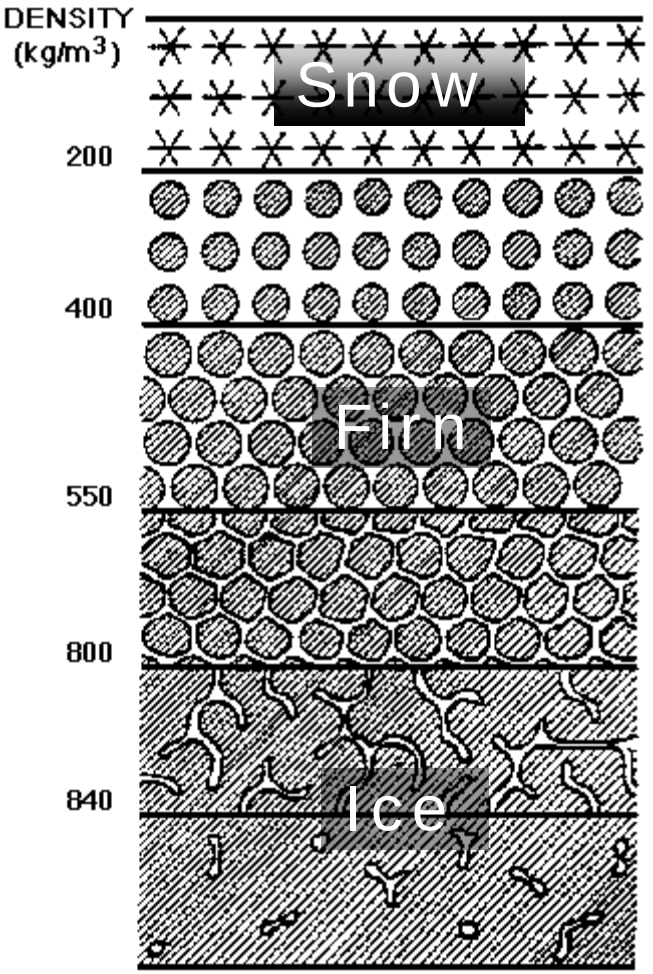


150.5 m long ice core with 246 consecutive sections

Fiescherhorn 2002

Structure of glacier archieve

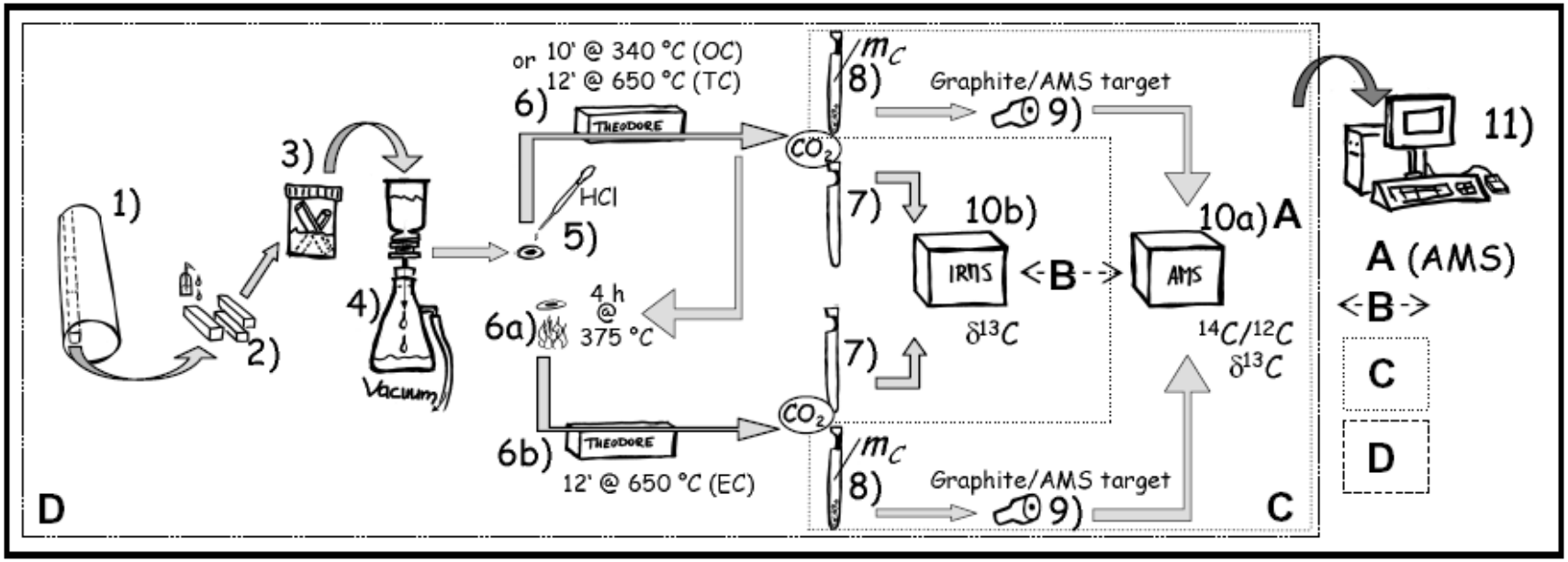
Approx density (g cm^{-3})	Depth range (m)	Time period
0.62	0-36	1990-2002
0.82	36-52	1980-1990
0.86	52-69	1970-1980
0.90	69-106	1940-1970
0.92	106-137	1850-1940
0.92	137-150	1650-1850



vertical section

Previous method

Sample preparation and analysis by
THEODORE and Accelerator Mass Spectrometry (AMS)



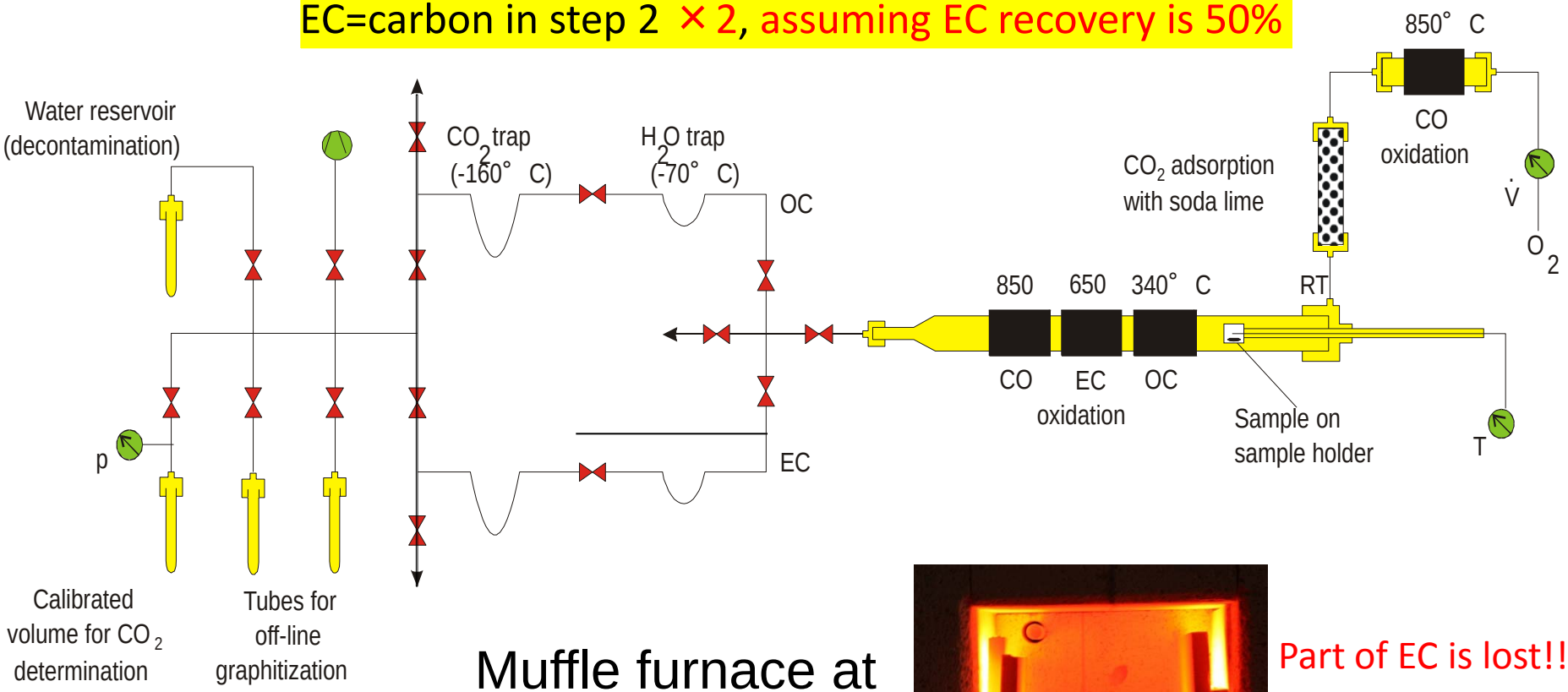
Jenk et al., 2007

Previous method - THEODORE

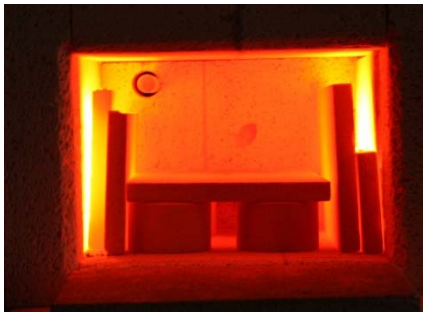
THEODORE: Two-step heating system for the EC/OC determination of radiocarbon in the environment **Szidat et al., 2004**

OC=carbon in step 1

EC=carbon in step 2 × 2, assuming EC recovery is 50%



Muffle furnace at 375 ºC for 4h



Part of EC is lost!!

Goals

1. Improve decontamination method for firn samples

✓ Quantify the procedural blank by ultra-pure water made blank ice

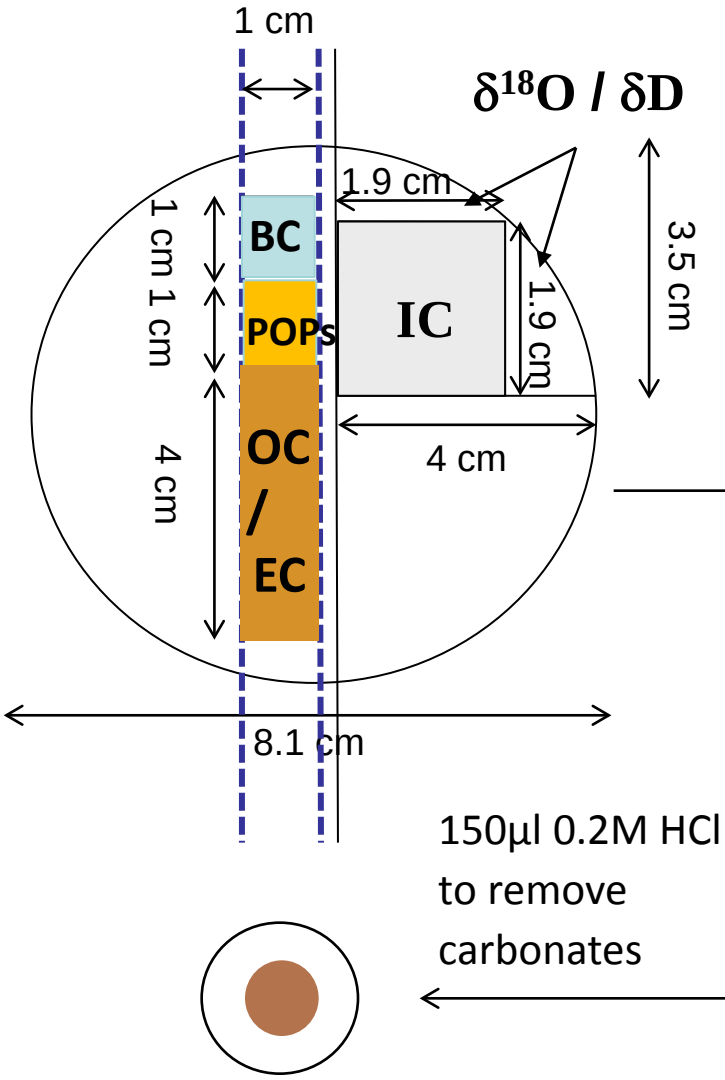
2. Apply a new separation method for OC/EC

✓ Validate the new method by analyzing FH old samples (Time period: 1912-1938; 1692-1773)

3. Reconstruct historical fossil and non-fossil emissions (Time period: 1940-2002)

✓ Analyze upper cores with the above methods

Sample preparation

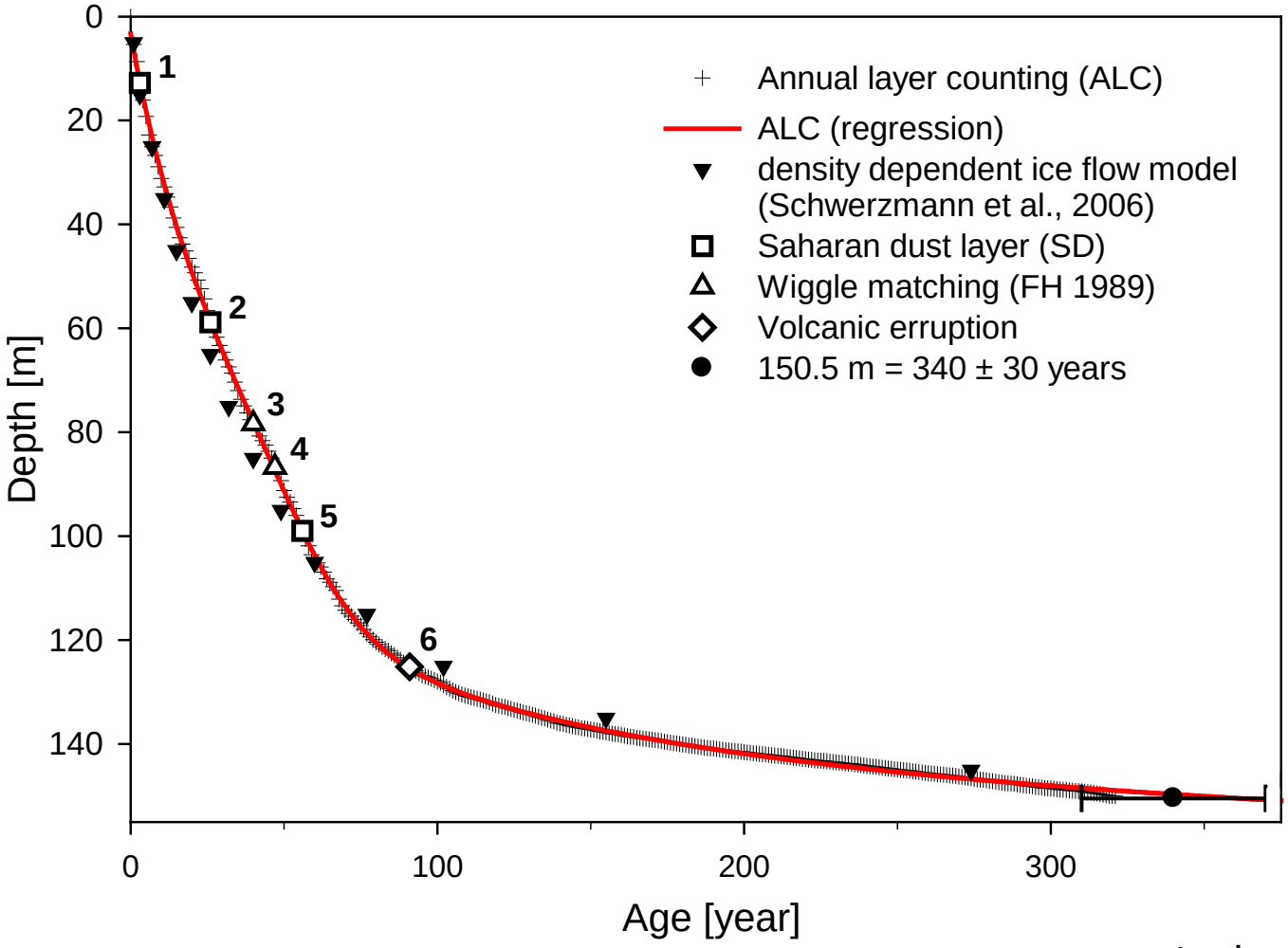


removing saw dust
with pre-cleaned
stainless steel scalpel

filtrate particles
onto a pre-heated
quartz filter

150µl 0.2M HCl
to remove
carbonates

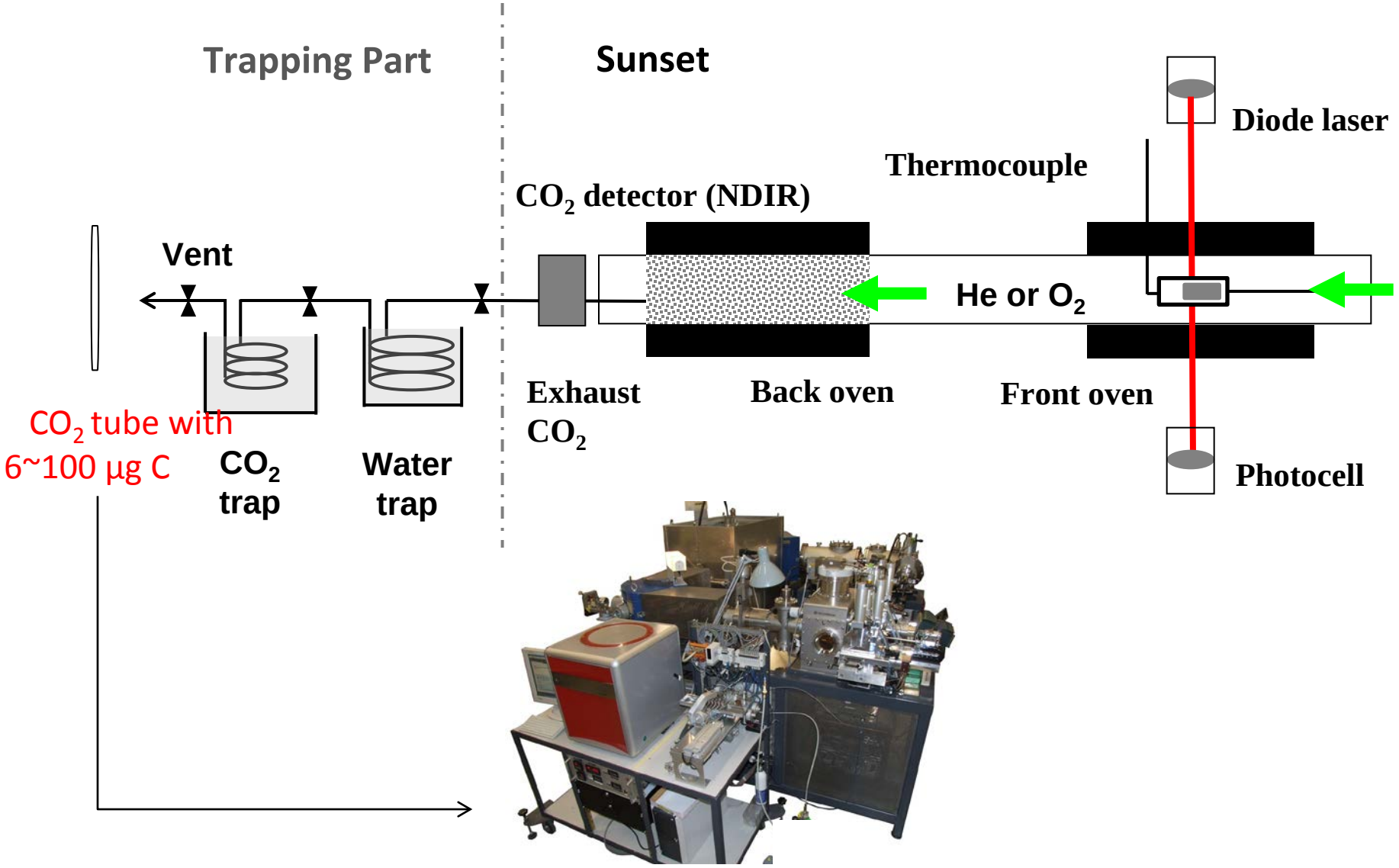
Ice core dating



Jenk et al., 2006

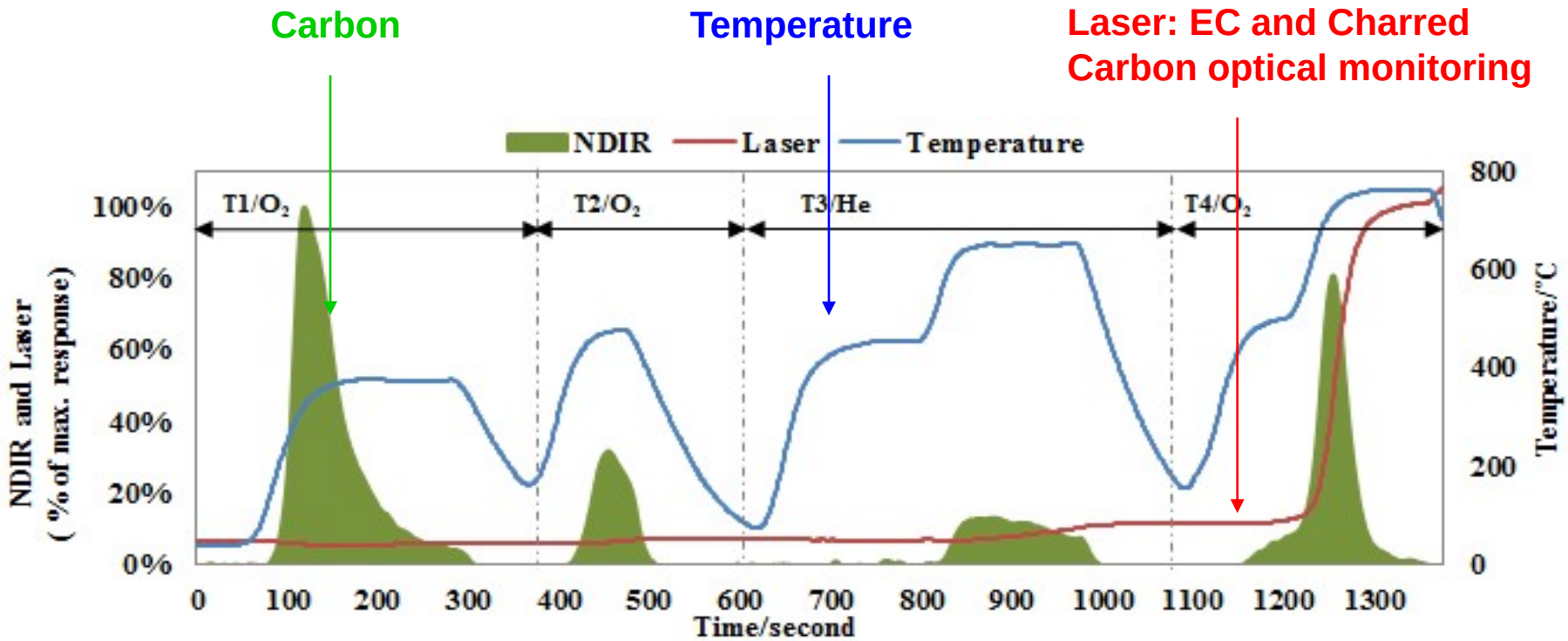
Thermal-Optical analyzer—— Sunset

OC/EC separations and 14C measurment



AMS@ETH

Four-step thermal-optical protocol for Sunset:Swiss_4S



S1/O_2 | S2/O_2 | S3/He | S4/O_2

Pure OC	Mixture of OC and EC	Pure EC

Aims at recovering OC for ^{14}C measurement

Aims at recovering EC for ^{14}C measurement

Method comparisons

	This study	Jenk et al., 2006
Time period	1692-1773 1912-2002	1650-1940
Decontamination	Chiseled	Rinsed
OC/EC separation and qualification	Sunset	Theodore
Graphitization	No	Yes
AMS measurement	MICADAS 250 KV AMS	TANDY: 500 kV AMS
Detection limit of AMS	~3ug	~10ug

Cao et al., 2014

Quantifying the procedural blank

The procedural blank : Ultra-pure water made blank ice

Blank	Mass (µg C)	f_M
OC	2.7±0.7 (n=9)	0.87±0.11 (n=4)
EC	0.3±0.3 (n=9)	-

Cao et al., 2014

Blank	Mass (µg C)	f_M
OC	1.3±0.6	0.6±0.1
EC	0.3±0.1	0.30 ± 0.30

Jenk et al., 2006

$$f_{m_{corrected}} = \frac{m_C \cdot f_{m_{initial}} - m_{procedblk} \cdot f_{m_{procedblk}}}{m_C - m_{procedblk}}$$

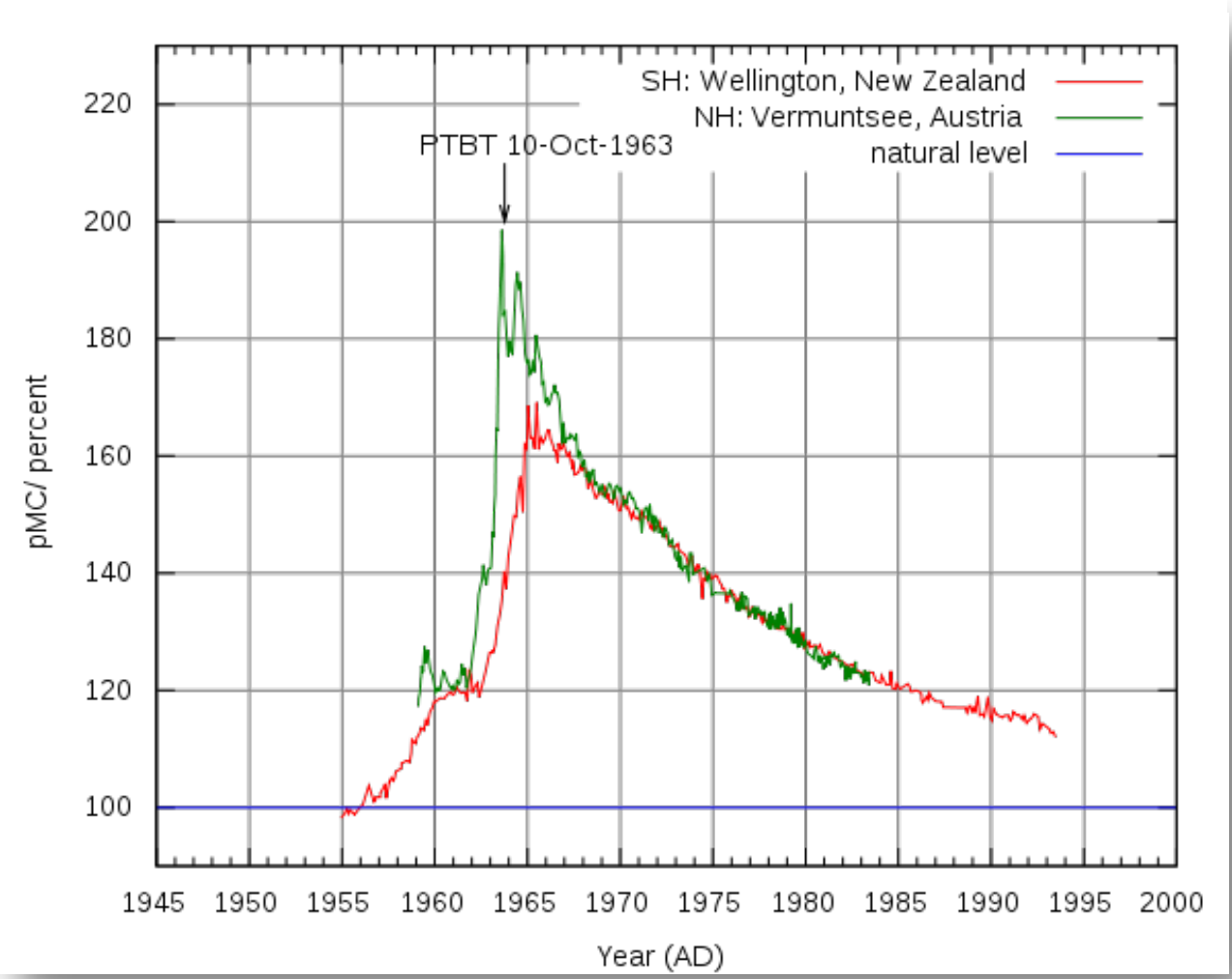
Validation: comparisons of two methods

	This study				Jenk et al., 2006			
Sample	OC (µg /kg)	f_M	EC (µg /kg)	f_M	OC (µg /kg)	f_M	EC(µg/kg) *2	f_M
FH_1937-1938	63.3±3.7	-	14.2±1.3	0.26±0.01	74.0±1.2	0.54±0.01	60.1±0.3	0.19 ±0.02
FH_1934-1936	43.9±2.1	0.83±0.04	14.1±0.6	0.38±0.01	38.6±0.8	0.61±0.01	21.8±0.1	0.31±0.03
FH_1928-1933	49.6±2.8	0.78 ±0.01	23. 5±1.4	0.31±0.01	40.5±0.8	0.77±0.02	25.1±0.1	0.31±0.03
FH_1925-1927	42.2±2.7	-	22.4±1.5	0.33±0.01	30.2±0.8	-	22.2±0.1	0.39±0.08
FH_1915-1917	29.7±0.8	0.83±0.01	16.2±0.5	0.33±0.04	19.3±1.5	0.82±0.07	51.8±0.5	0.29±0.02
FH_1912-1914	32.2±0.3	0.83±0.01	12.6±0.3	0.28±0.03	29.1±1.3	0.82±0.04	38.9±0.4	0.31±0.02
FH_1773-1722	46.3±2.3	1.01±0.01	8.3±0.3	0.97±0.04	29.2±0.7	-	12.0±0.2	0.42±0.10
FH_1721-1692	64.1±1.8	1.04±0.02	12.3±0.3	0.94±0.02	44.9±0.9	0.94±0.02	13.2±0.2	-

Cao et al., 2014

Bomb test and radiocarbon

Radiocarbon bomb peak



"Radiocarbon dating". University of Utrecht. http://www1.phys.uu.nl/ams/Radiocarbon.htm.

Conclusions

1. **An alternative decontamination method for firn samples consisting of chiselling off the outer parts instead of rinsing them was developed and verified.**

2. **For separation of OC and EC for subsequent ^{14}C analysis, a thermal-optical method instead of the purely thermal method was applied for the first time to firn and ice samples, resulting in a reduced uncertainty of both the mass and ^{14}C determination.**

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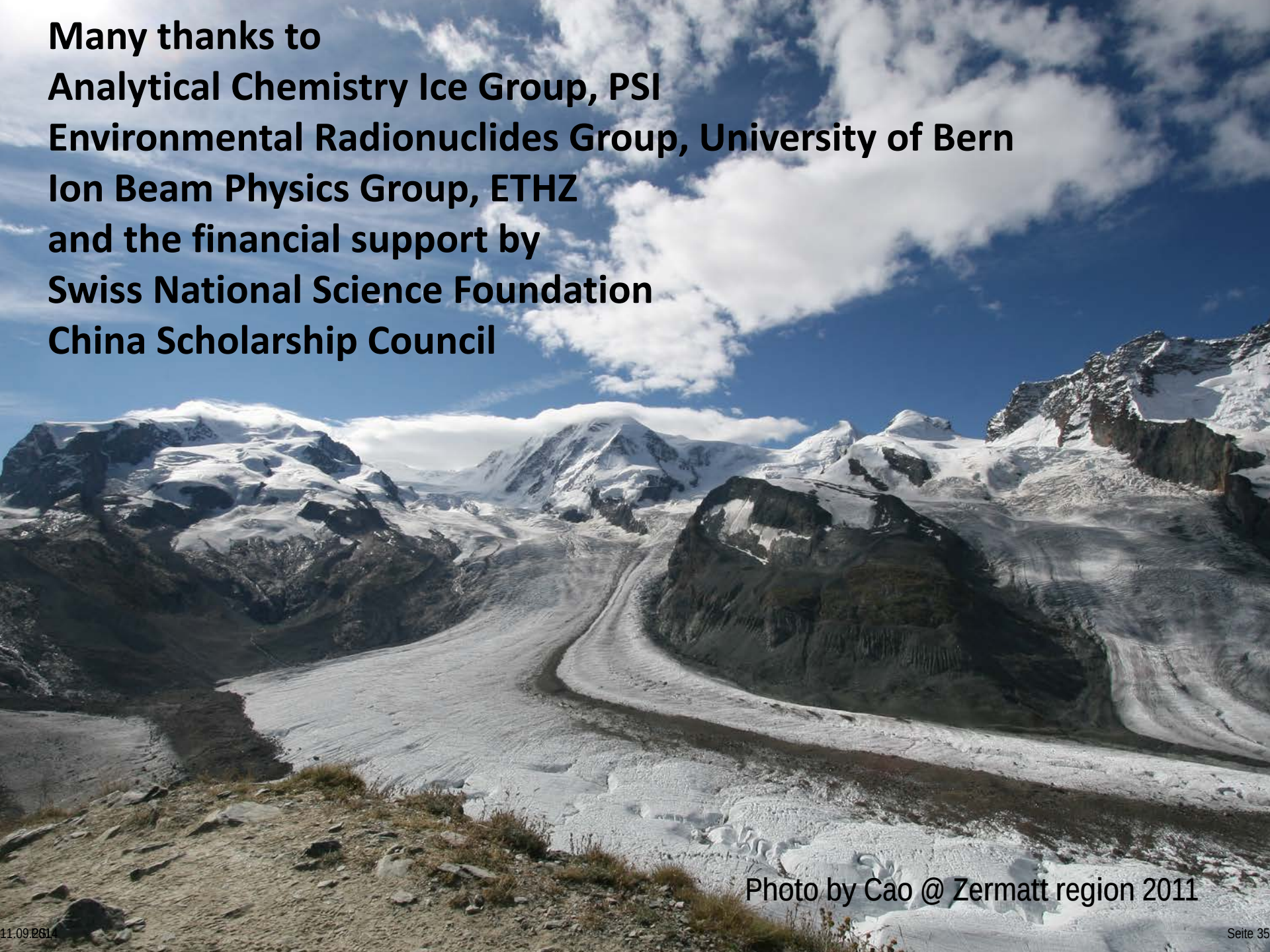

Photo by Cao @ Zermatt region 2011