Development and application of a Laserablation ICP-MS technique for multielement analysis of atmospheric deposition in ice cores

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Motivation and Goals

- Polar regions = Climate archive
- Ice core studies → Reconstruction of Earth climate history (~ 500,000 a)
- Deposition of atmospheric aerosols → Element sigantures
- **Up to now:** Element analysis in ice cores only with molten ice samples

  → High sample consumption → Low spatial and time resolution

  → Lost of valuable sample material
- **Aim of intention:** Multielement determination of element signatures in ice cores with high spatial resolution

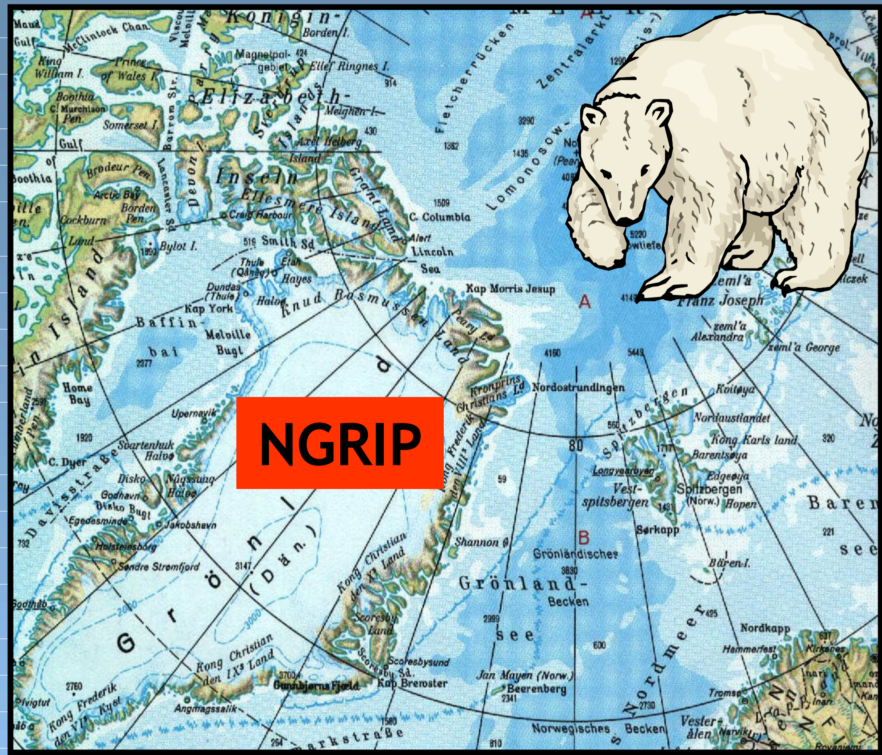
  New technique: Laserablation ICP-MS
- **Advantages of measurement system:**

  - Spatial resolution + detection limits - Low sample uptake

  - Analysis directly from solid sample

  → Minimum sample preparation → Low risk of contamination
- Analyses of real sample material from Greenland
  - signatures of: Sea salt, mineral dust, anthropogenic tracers

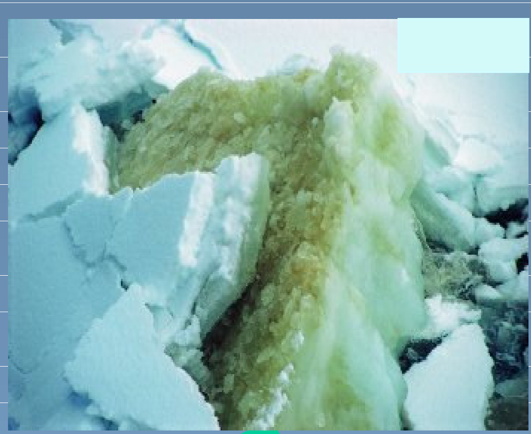
Recent deep-drilling efforts in polar regions

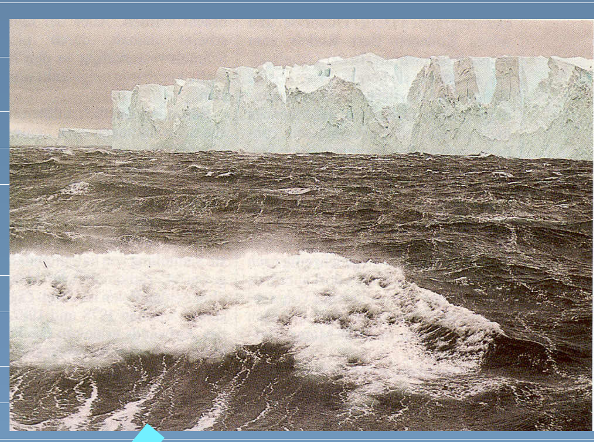


Antarktica:
EPICA 2001-2004
3300 m
~ 500,000 yr

Greenland
NGRIP 1998-2001
3080 m
~ 300,000 yr

Aerosol sources
- looking for tracers





SO_4^{2-}
Sulphate

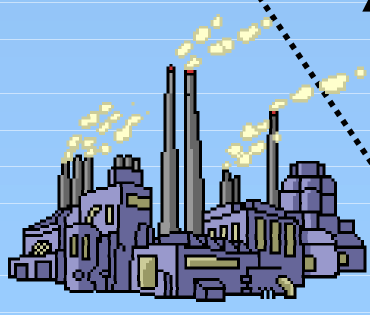
$CH_3SO_3^-$
MSA

Na^+, Cl^-, Mg^{2+}
Seasalt

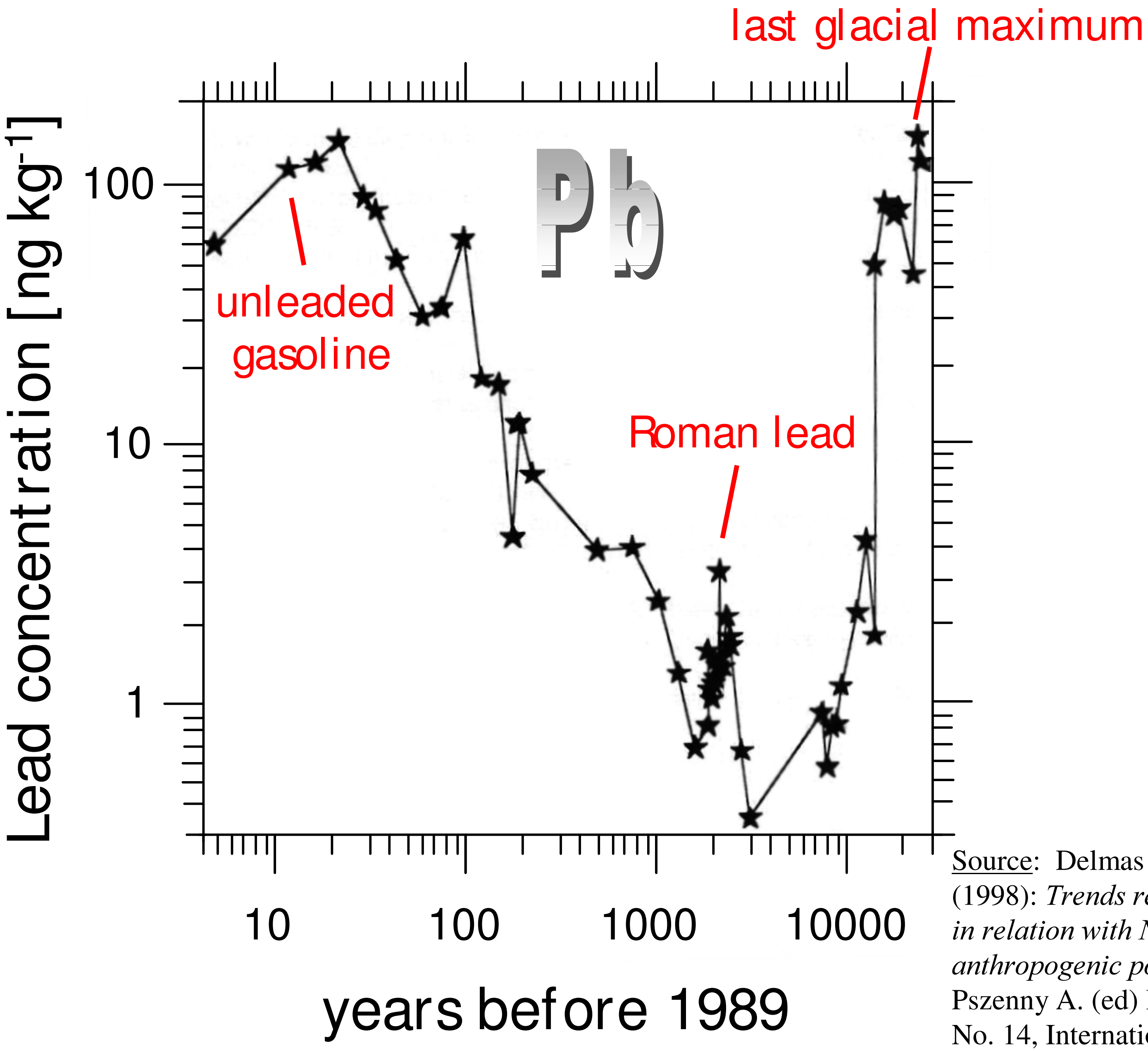
Al, Si, Ca, Fe, REE
Mineral dust

Pb, Cd, Zn
anthropogenic sources

NO_3^-
Nitrate

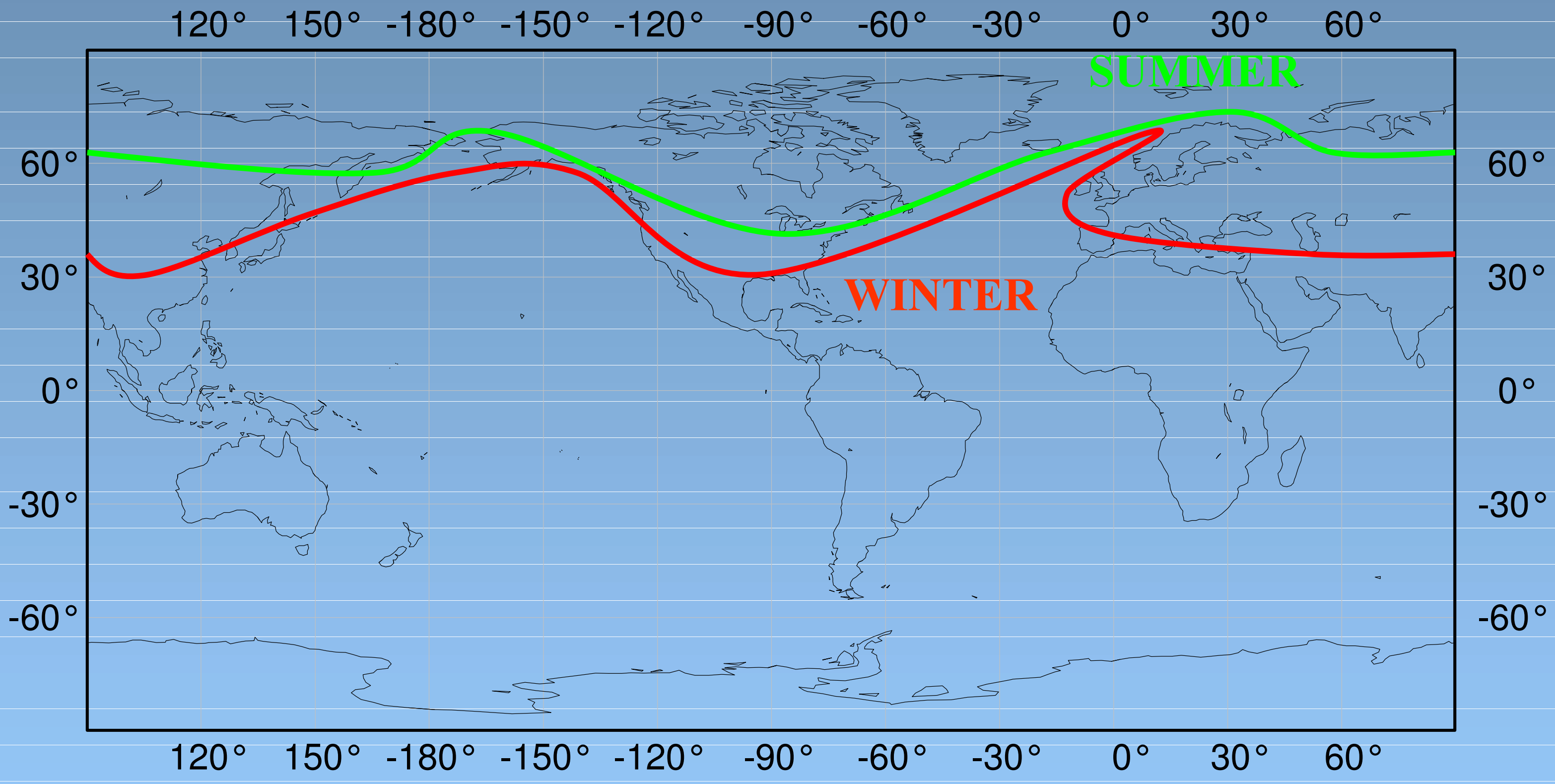


Lead concentration in ice cores at summit (Central-Greenland) for the last 30,000 years



Source: Delmas R. J., Legrand M. (1998): *Trends recorded in Greenland in relation with Northern Hemisphere anthropogenic pollution*, In: Pszenny A. (ed) IGACtivities-Newsletter, No. 14, International Global Atmospheric Chemistry, 14-17.

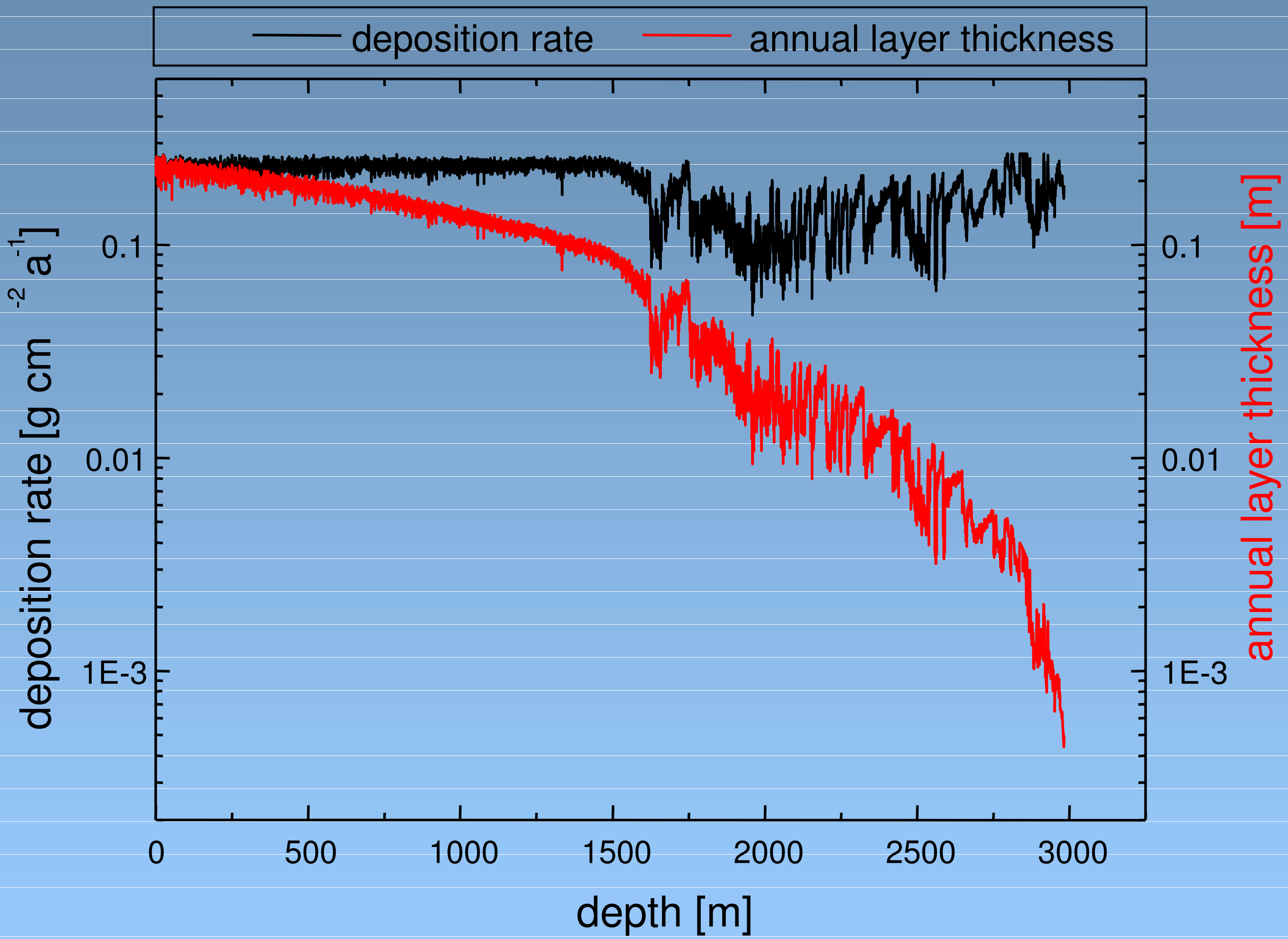
Geographical position of polar front in summer and winter time at sealevel



Scale: 1:249187266 at Latitude 0°

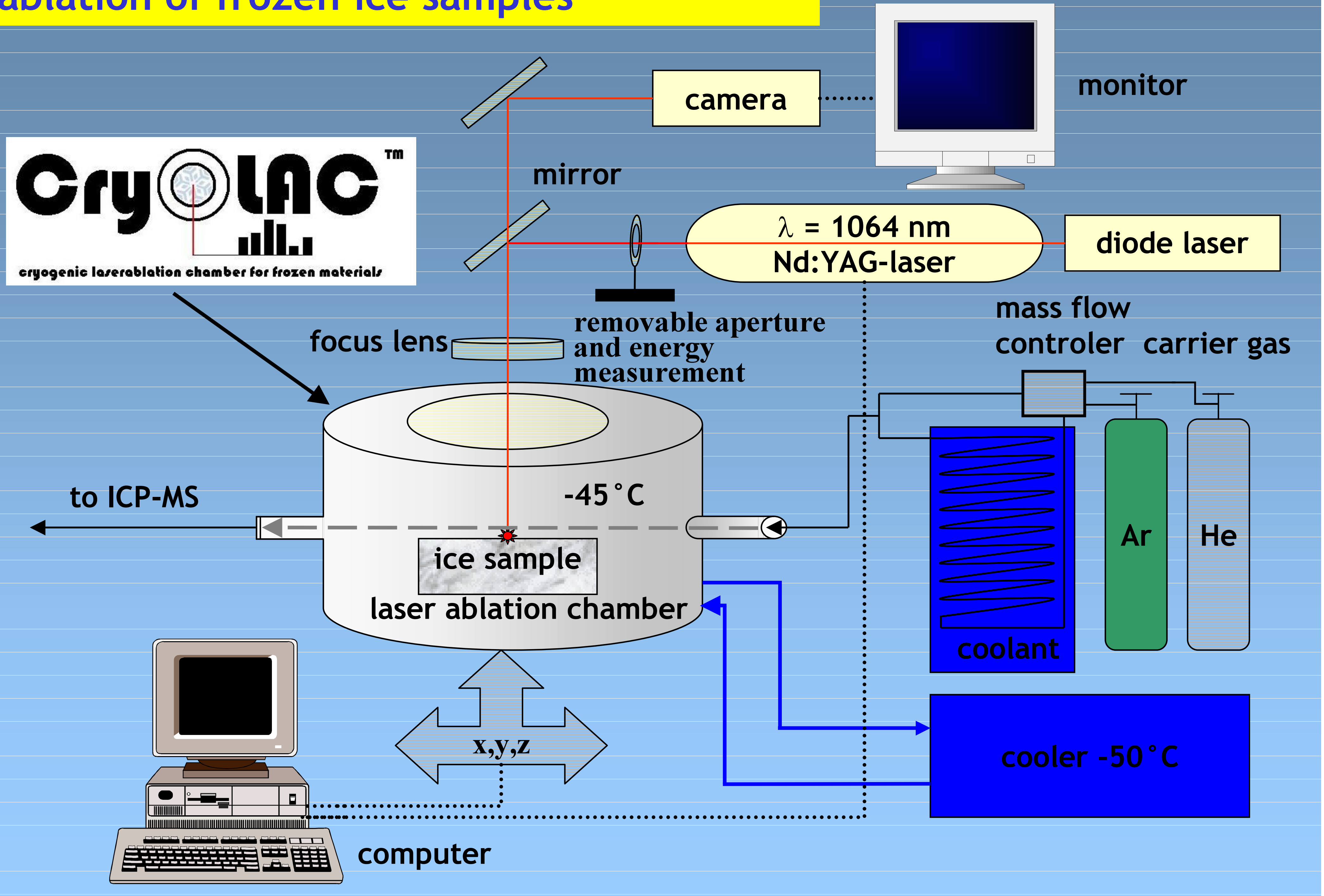
<u>Source:</u> Heidam NZ (1984) Atmos Environ, 18:243-329

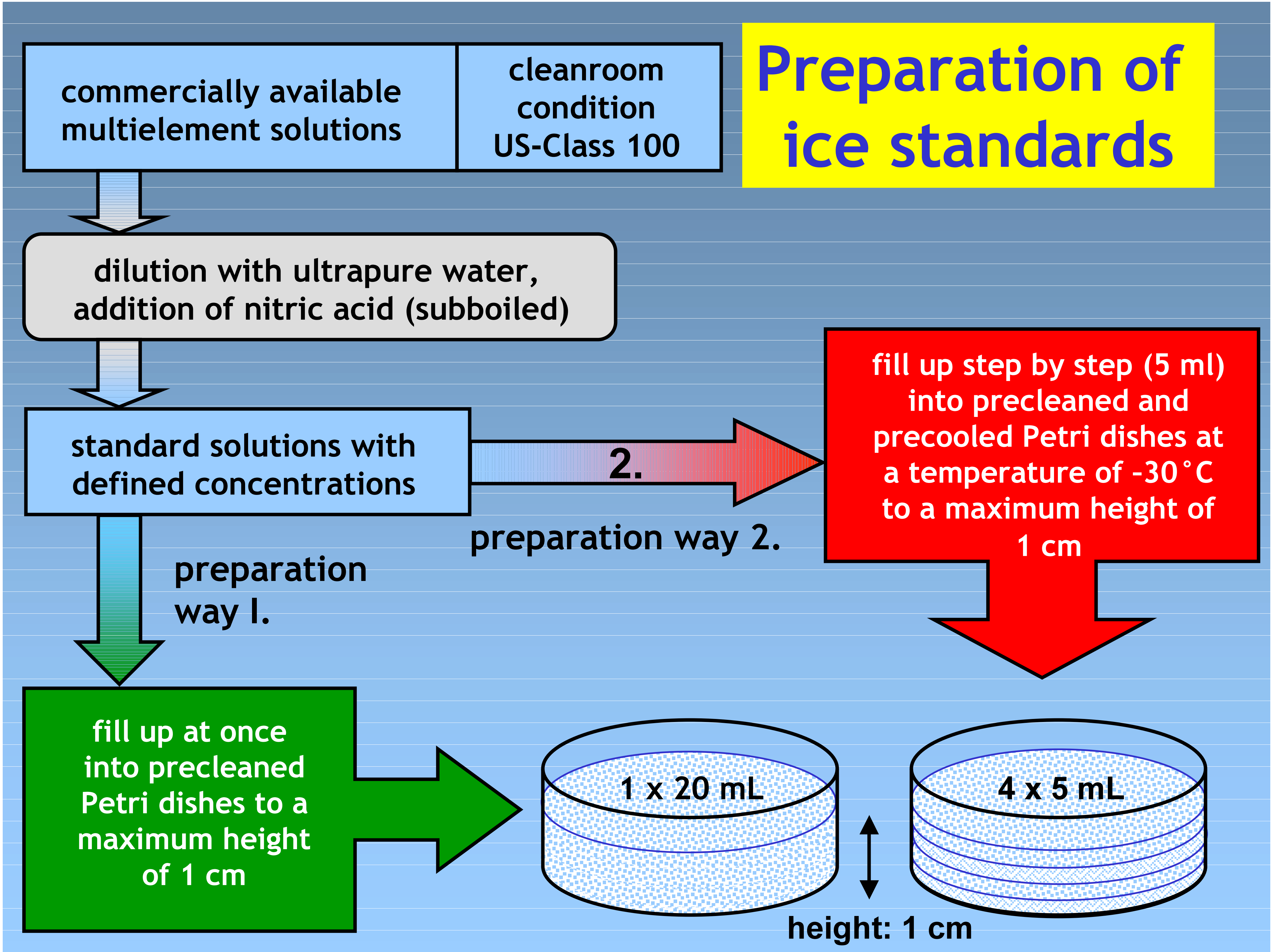
Deposition rate and annual layer thickness for the GRIP- ice core



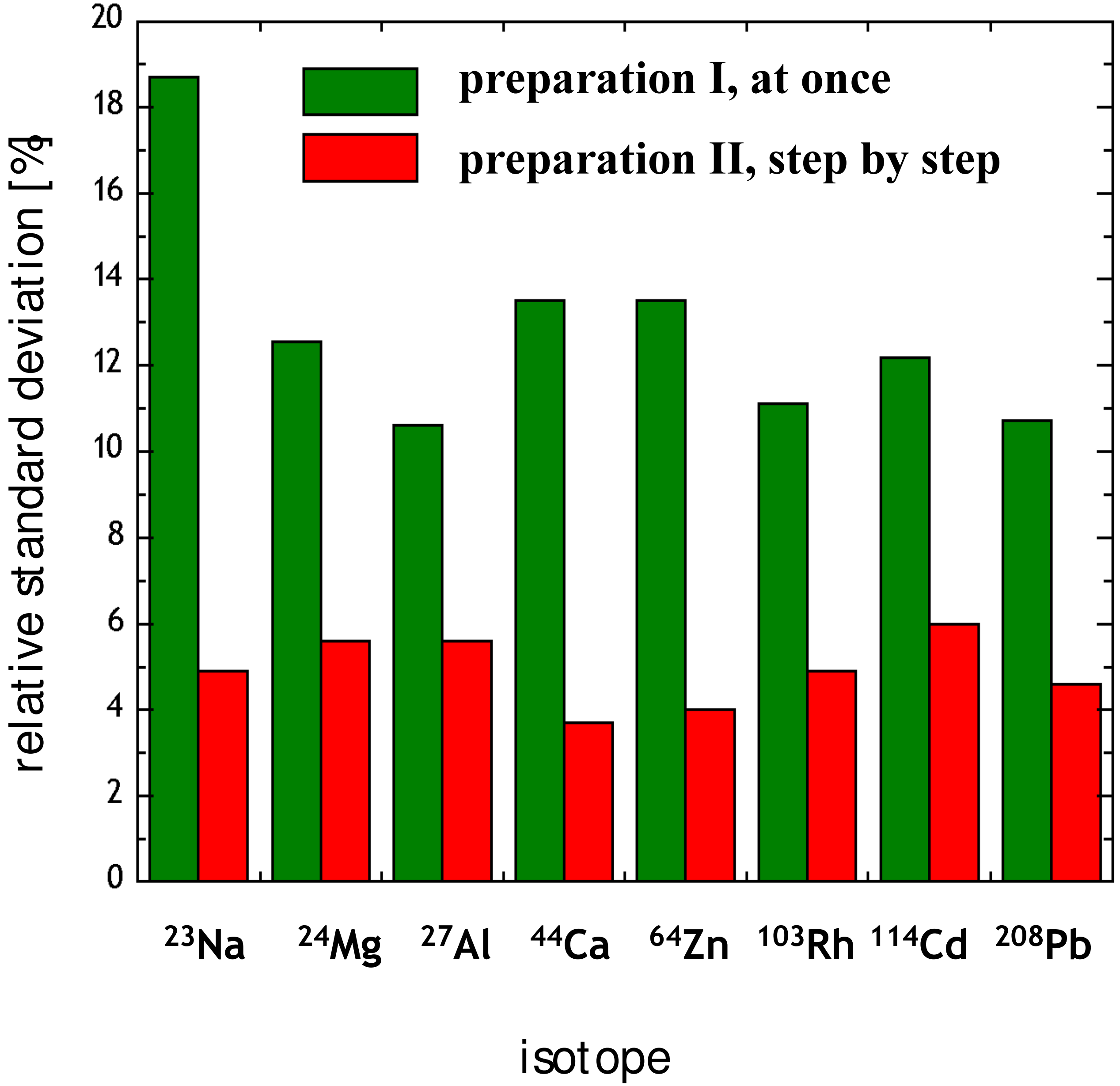
Source: The Greenland Summit ice cores CD-ROM (1997): Available from the National Snow And Ice Data Center, University of Colorado at Boulder, and the world data center-A for paleoclimatology, National Geophysical Data Center, Boulder, Colorado.

Patented experimental setup for the laser ablation of frozen ice samples

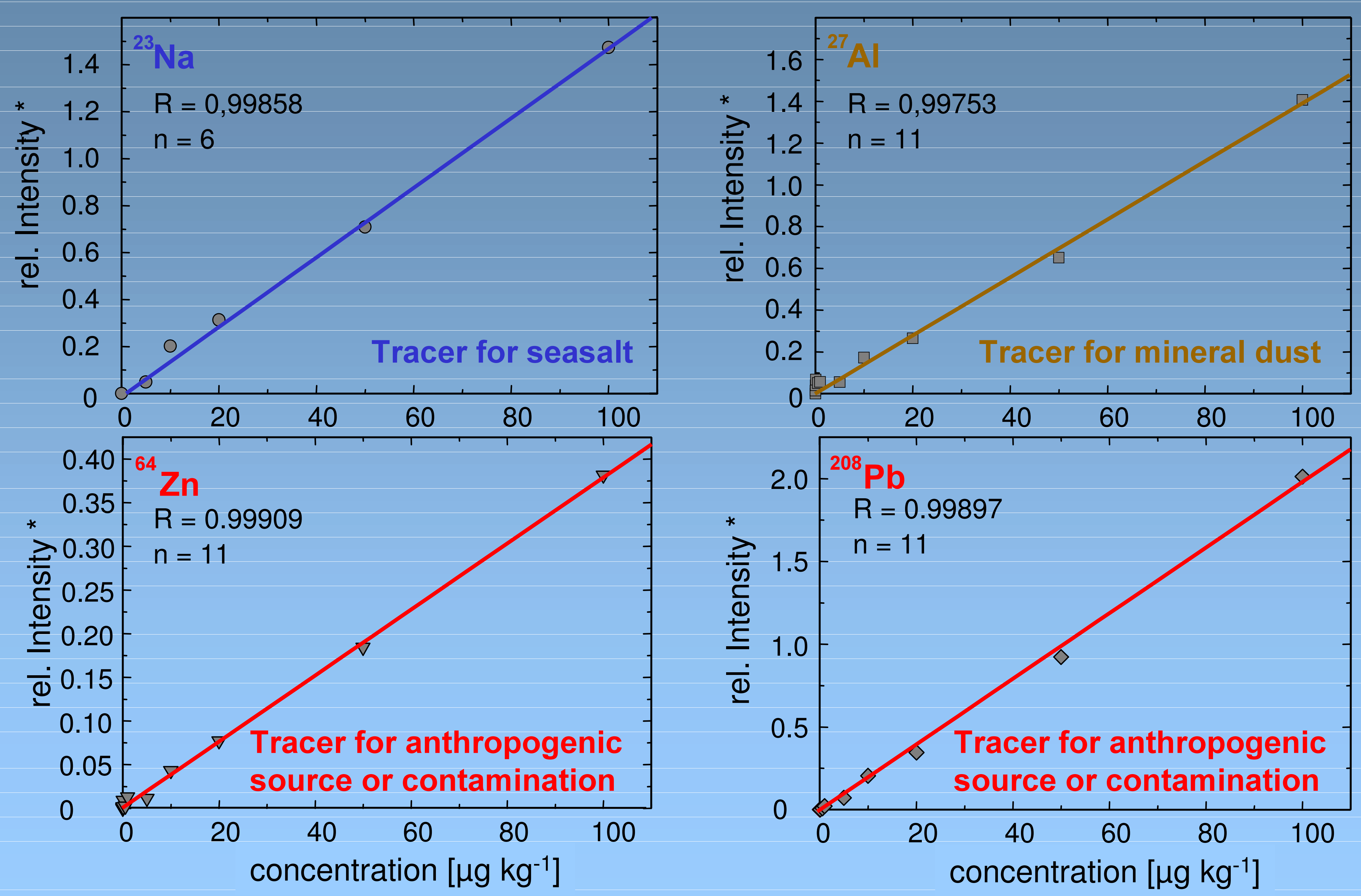



Preparation of ice standards
commercially available multielement solutions
cleanroom condition US-Class 100
dilution with ultrapure water, addition of nitric acid (subboiled)
standard solutions with defined concentrations
2.
preparation way 2.
fill up step by step (5 ml) into precleaned and precooled Petri dishes at a temperature of -30°C to a maximum height of 1 cm
preparation way I.
fill up at once into precleaned Petri dishes to a maximum height of 1 cm
1 x 20 mL
4 x 5 mL
height: 1 cm

Relative standard deviations of LA-ICP-MS signals for 10 ppb ice standards prepared by different ways



Calibration graphs for ice standards measured by LA-ICP-MS



*signal intensity normalized to ^{17}OH

Analysis of frozen standard reference materials by LA-ICP-MS

Element	TMRAIN-95 measured value [μg kg^{-1}]	TMRAIN-95 certified value [μg kg^{-1}]	SLRS-4 measured value [μg kg^{-1}]	SLRS-4 certified value [μg kg^{-1}]	NIST 1643d measured value [μg kg^{-1}]	NIST 1643d certified value [μg kg^{-1}]
Na	-	-	2,213 ± 108	2,400 ± 200	22,721± 1115	22,070 ± 640
Mg	-	-	1,555 ± 86	1,600 ± 100	7,267 ± 327	7,989 ± 35
Al	1.95 ± 0.064	1.70 ± 0.91	60 ± 3	54 ± 4	127 ± 8	127 ± 3.5
Ca	-	-	6,740 ± 606	6,200 ± 200	32,000 ± 3,200	31,040 ± 500
Fe	17.45 ± 1.65	24.20 ± 3.64	106 ± 5	103 ± 5	83 ± 7	91.2 ± 3.9
Zn	11.49 ± 0.57	11.10 ± 2.36	1.1 ± 0.06	0.93 ± 0.10	74 ± 5	72.48 ± 0.65
Cd	0.476 ± 0.023	0.480 ± 0.120	0.012 ± 0.002	0.012 ± 0.002	5 ± 0.3	6.47 ± 0.37
Pb	0.283 ± 0.010	0.290 ± 0.093	0.085 ± 0.007	0.086 ± 0.007	19 ± 0.9	18.15 ± 0.64

Detection limits (3σ) for ice samples (LA-ICP-MS) and solutions (Cross-Flow and MCN6000), values are given in μg kg^{-1}

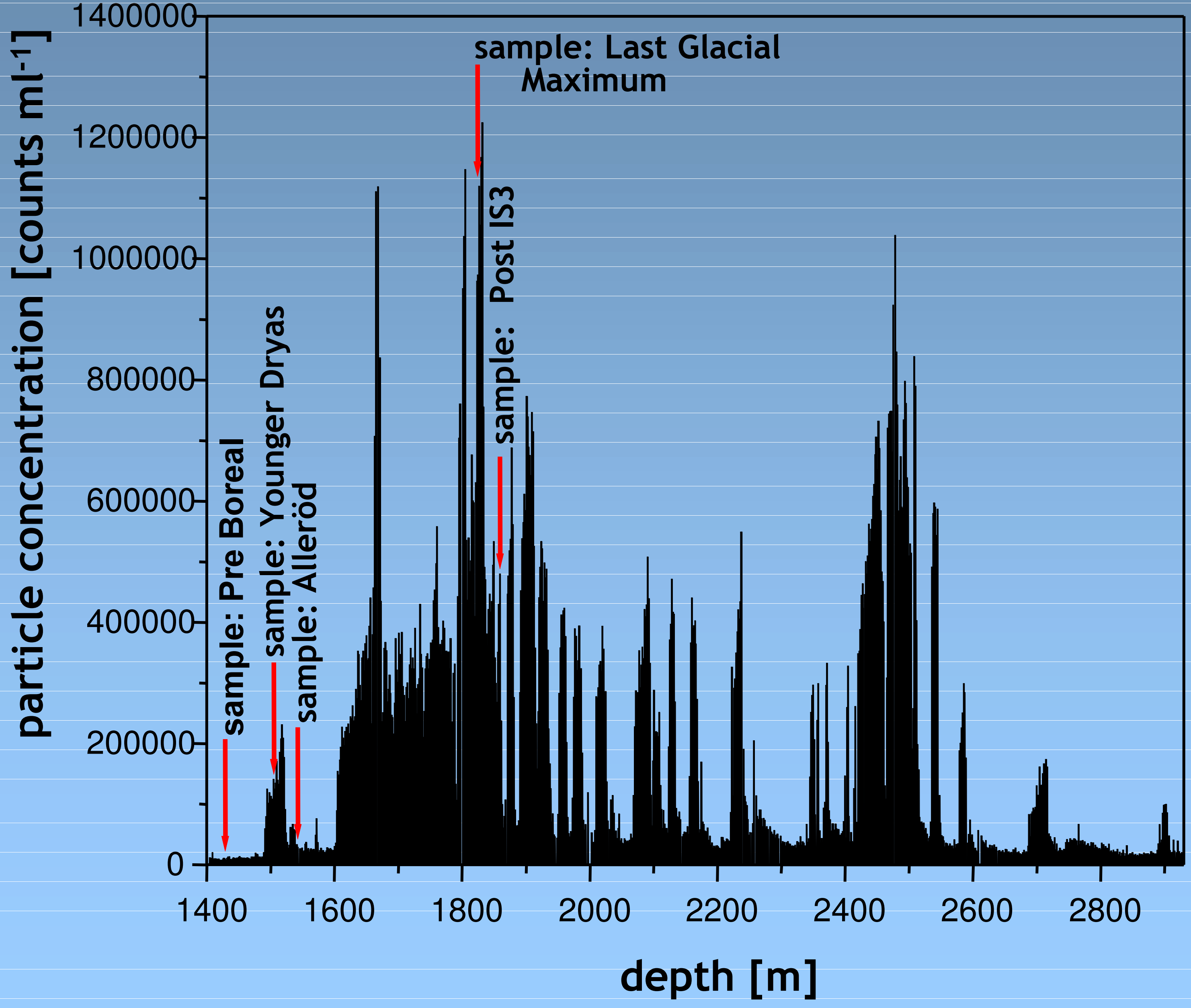
isotope	LA-ICP-MS	solution-ICP-MS	
		cross-flow[1]	MCN6000[2]
^{23}Na	0,46	1,63	0,02
^{24}Mg	0,05	0,04	0,01
^{25}Mg	0,43	0,05	0,02
^{27}Al	0,18	0,06	0,05
^{43}Ca	2,30	0,51	0,83
^{44}Ca	4,81	3,93	0,81
^{56}Fe	0,7	-	0,02
^{57}Fe	10,33	1,10	0,03
^{64}Zn	0,06	2,19	0,02
^{114}Cd	0,02	0,04	0,04
^{139}La[a]	2	0,5	0,9
^{140}Ce[a]	2	0,2	2
^{141}Pr[a]	1	0,2	1,4
^{142}Nd[a]	2	0,6	1,1
^{208}Pb	0,02	0,04	0,02
^{232}Th[a]	1	1,8	1,1
^{238}U[a]	1	0,3	1,1

[a] concentrations in ng kg^{-1}

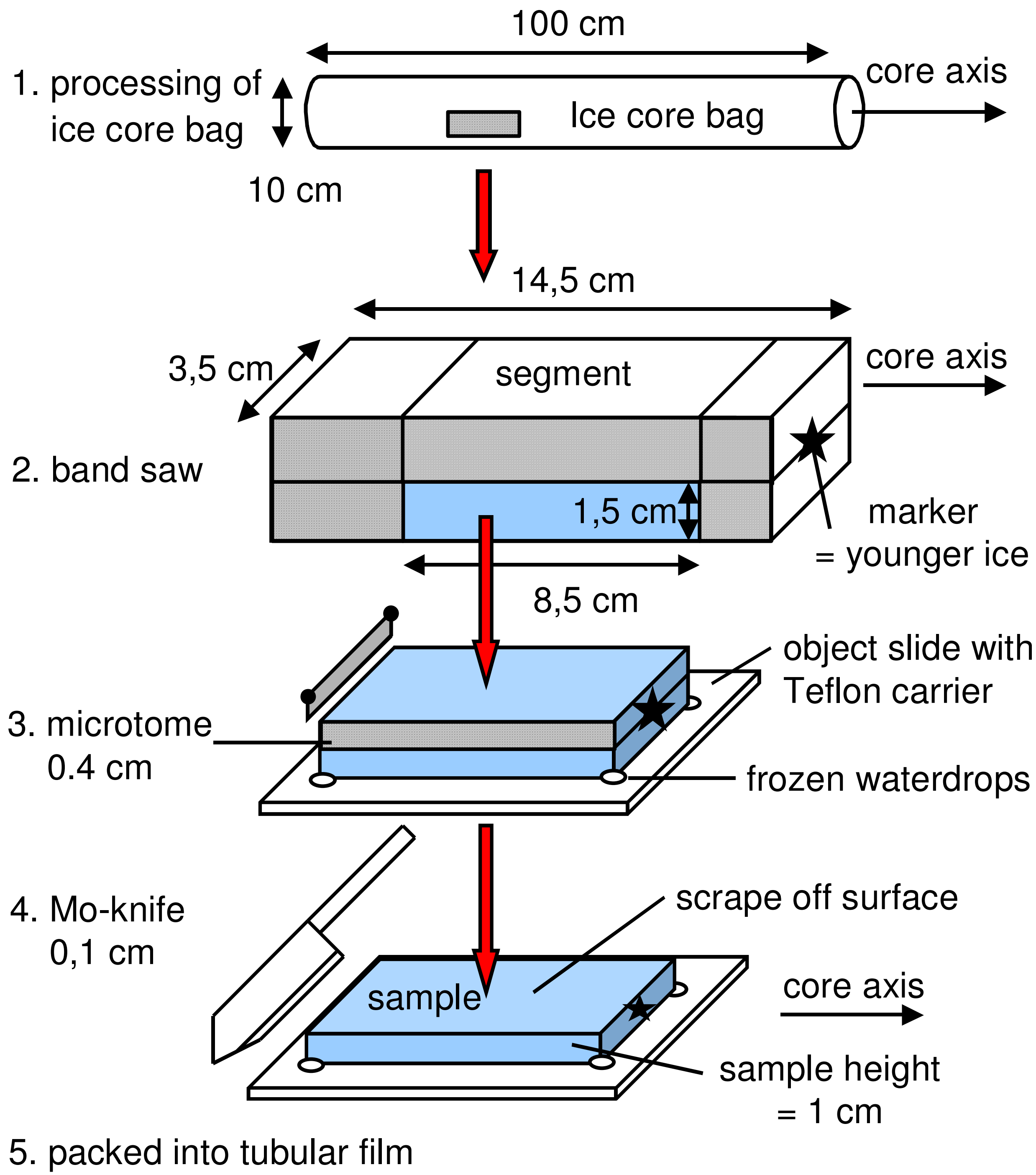
[1] Cross Flow Nebulizer: 1000 μl min^{-1}

[2] MCN6000: 65 μl min^{-1}

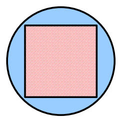
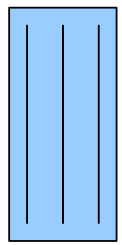
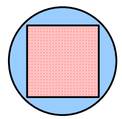
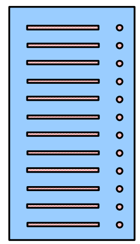
Particle concentration in the NGRIP ice core



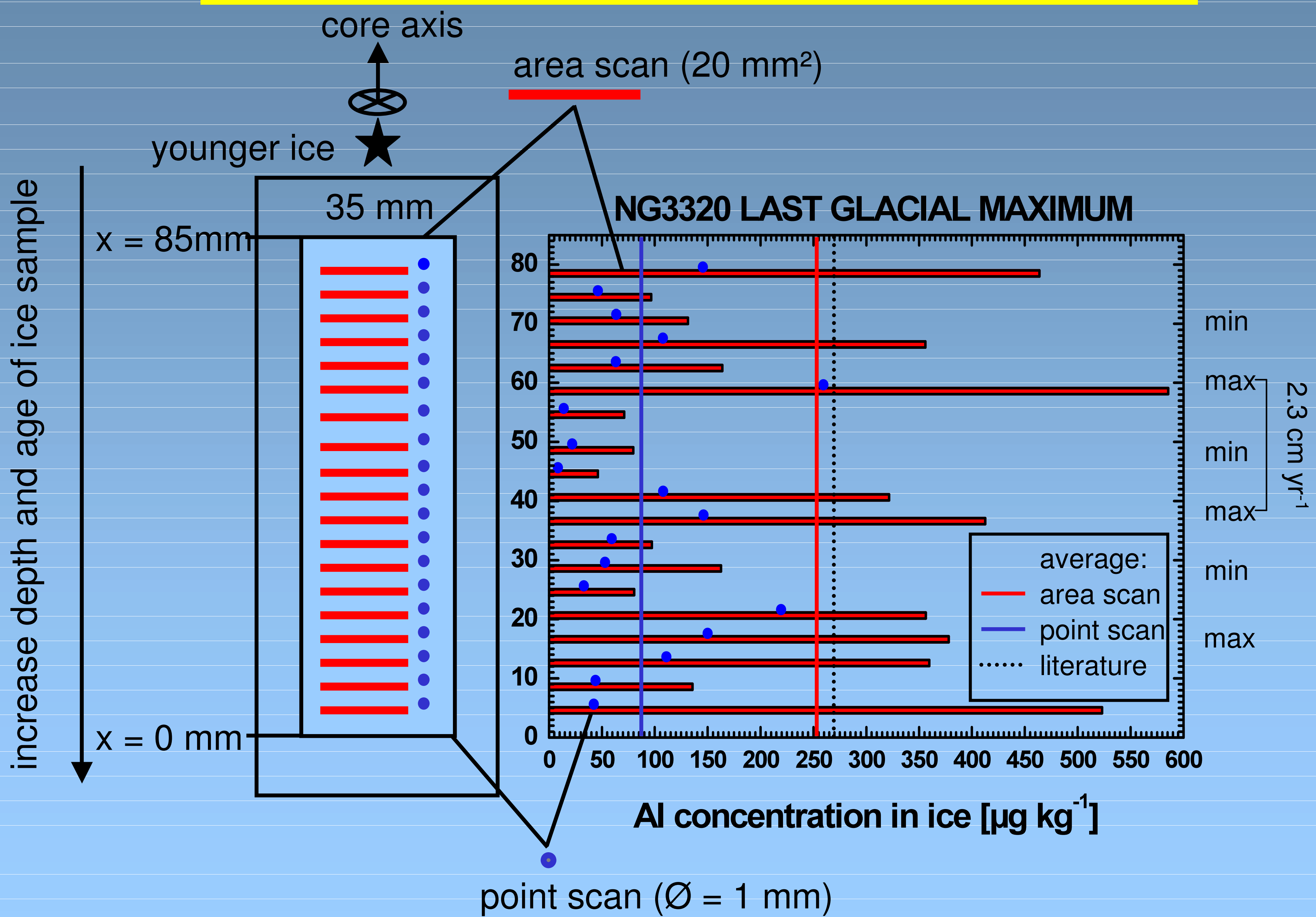
Ice core sample preparation for element analysis by LA-ICP-MS



Comparison of 2 different measurement strategies for calibration and analysis of real ice samples

	method A: line scan		method B: combination of area- and point scans	
no. of measured isotopes	12		69	
no. of analytic elements	8		39	
Isotope	12: ^{17}OH, ^{23}Na, ^{24}Mg, ^{27}Al, ^{43}Ca, ^{44}Ca, ^{56}Fe, ^{57}Fe, ^{64}Zn, ^{103}Rh, ^{114}Cd, ^{208}Pb.		62: ^{17}OH, ^{19}OH, ^{7}Li, ^{9}Be, ^{13}C, ^{23}, ^{24}Mg, ^{25}Mg, ^{27}Al, ^{34}S, ^{37}Cl, ^{39}K, ^{43}Ca, ^{44}Ca, ^{51}V, ^{52}Cr, ^{53}Cr, ^{55}Mn, ^{56}Fe, ^{57}Fe, ^{58}Ni, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{64}Zn, ^{65}Cu, ^{66}Zn, ^{85}Rb, ^{86}Sr, ^{88}Sr, ^{89}Y, ^{103}Rh, ^{111}Cd, ^{114}Cd, ^{138}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{142}Nd, ^{143}Nd, ^{144}Nd, ^{147}Sm, ^{149}Sm, ^{151}Eu, ^{153}Eu, ^{158}Gd, ^{159}Tb, ^{164}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{174}Yb, ^{175}Lu, ^{204}Pb, ^{205}Tl, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{209}Bi, ^{220}Bkgd, ^{232}Th, ^{238}U	
timing:	standard	sample	standard	sample
dwell time [ms]	10	10	10	10
sweeps	20	10	20	20
readings	1	1000	1	1
replicates	10	1	5	5
measurement time per standard or sample [s]	47	manual start / stop, 160 per line	80	manual start / stop, 80 per area or point
read delay [s]	40	0	40	40
sample pattern	area 	3 to 4 lines per sample 	area 	approx. 19 areas and point scans per sample 
spatial resolution [mm]	-	2,7	-	4

Sampling pattern for element analyses by point- and area scan for NGRIP samples

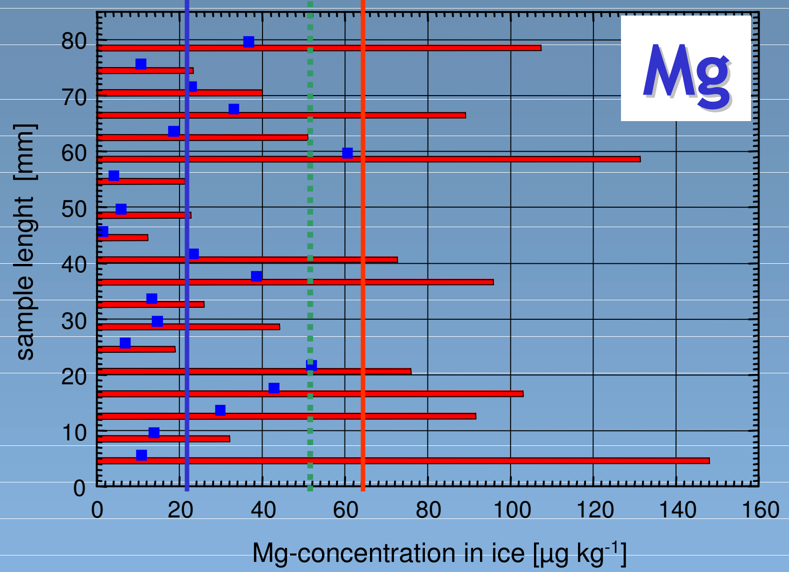


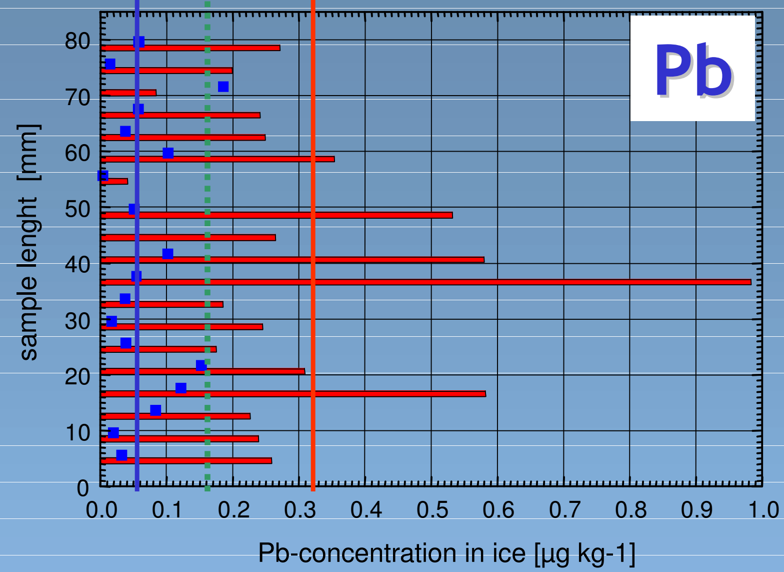
High resolution element signatures in a Greenland ice core

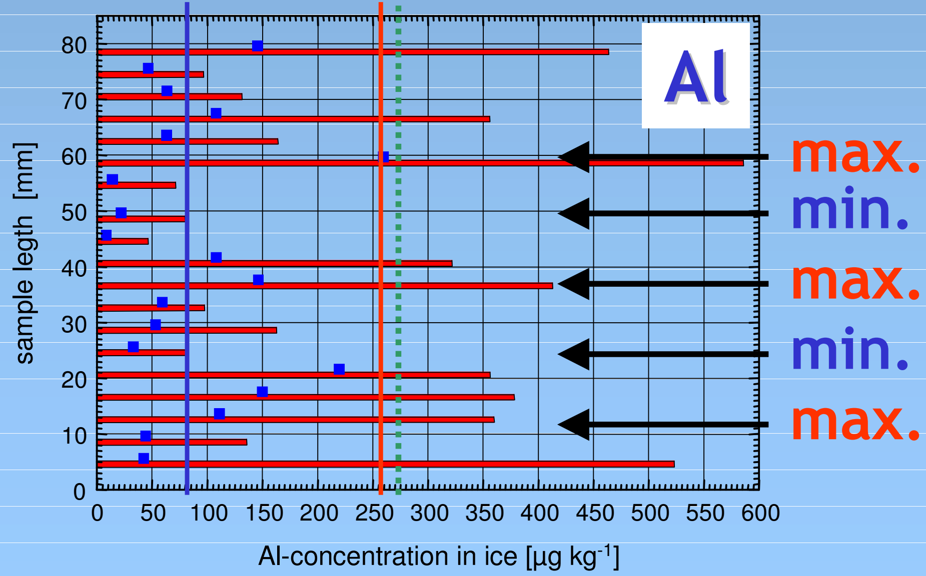
NGRIP, period: Last Glacial Maximum

younger ice

older ice



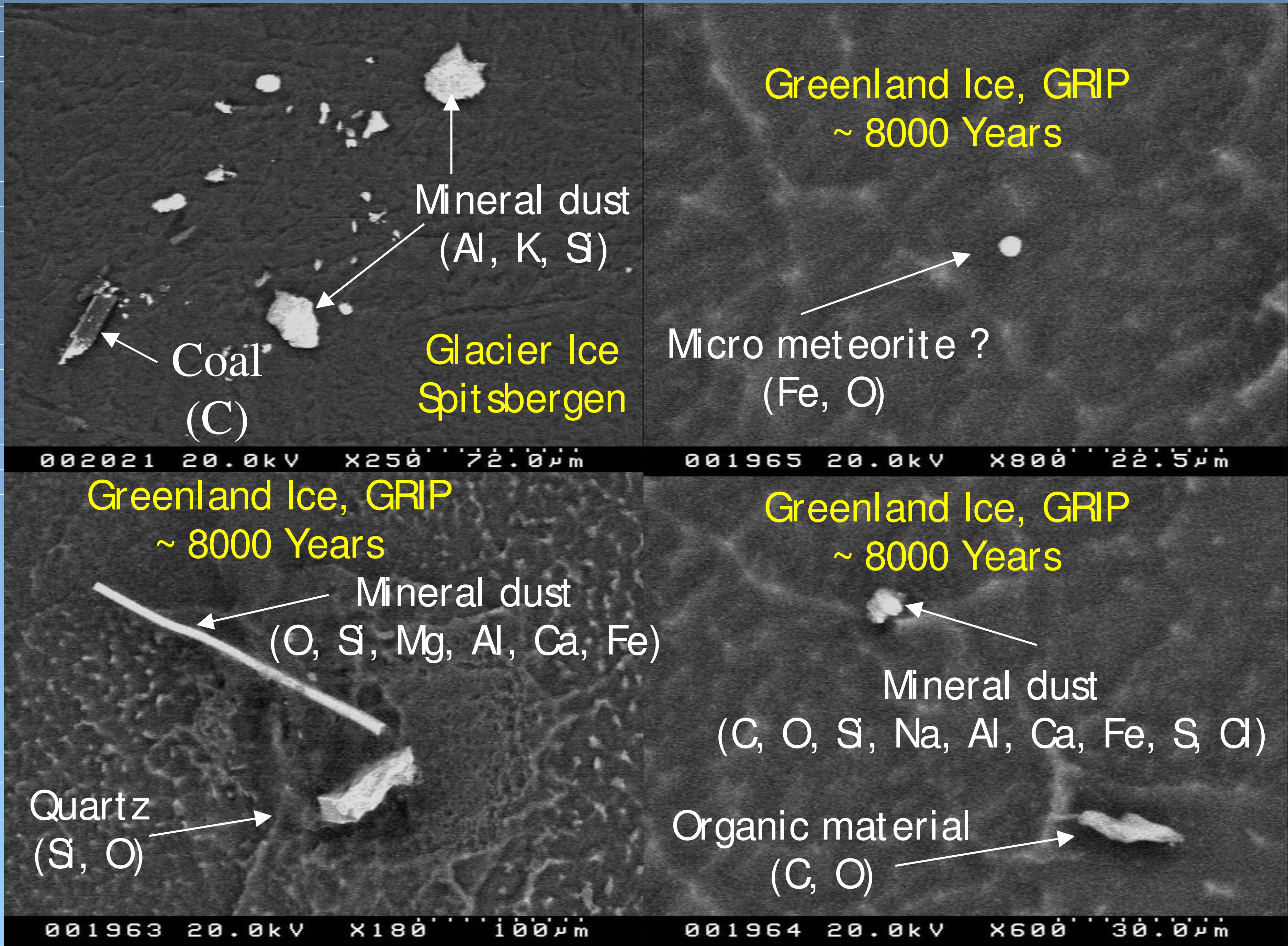




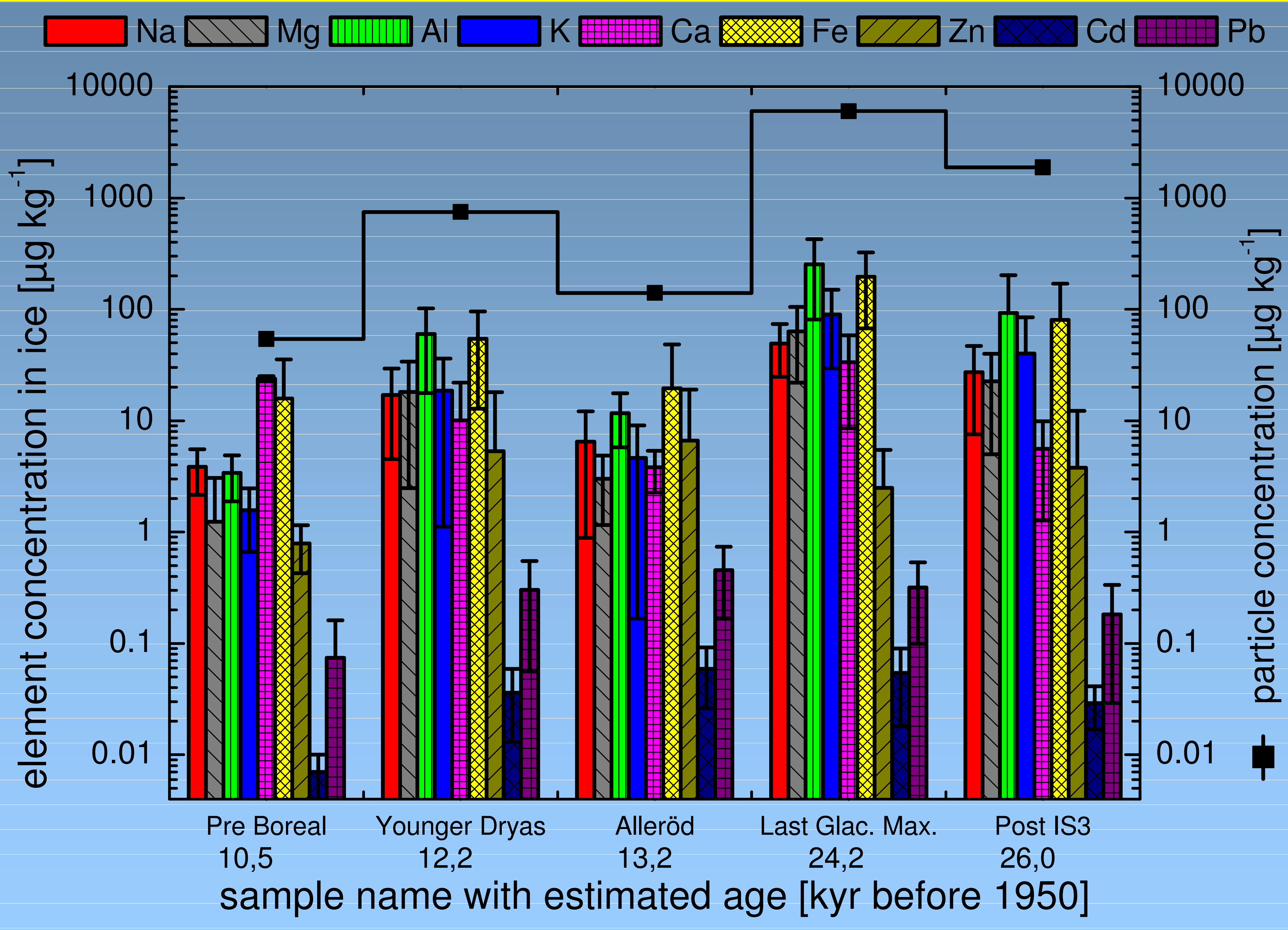
depth: 1826 m
age: 24200 years
thickness ~ 2-3 cm yr^{-1}

average: point scan
average: area scan
average: solution-literature

Cryo-SEM pictures of real ice samples



Element concentrations measured by LA-ICP-MS in comparison to particle concentrations for the NGRIP-ice core samples



Conclusions and Outlook

-development of a new method
for trace element analyses directly from
frozen ice core samples by LA-ICP-MS

-successfull preparation of ice standards
and quantitative determination of
trace elements in real ice samples

-low sample uptake rate and good
counting rates for the ablated material
as well as good relative standard deviations

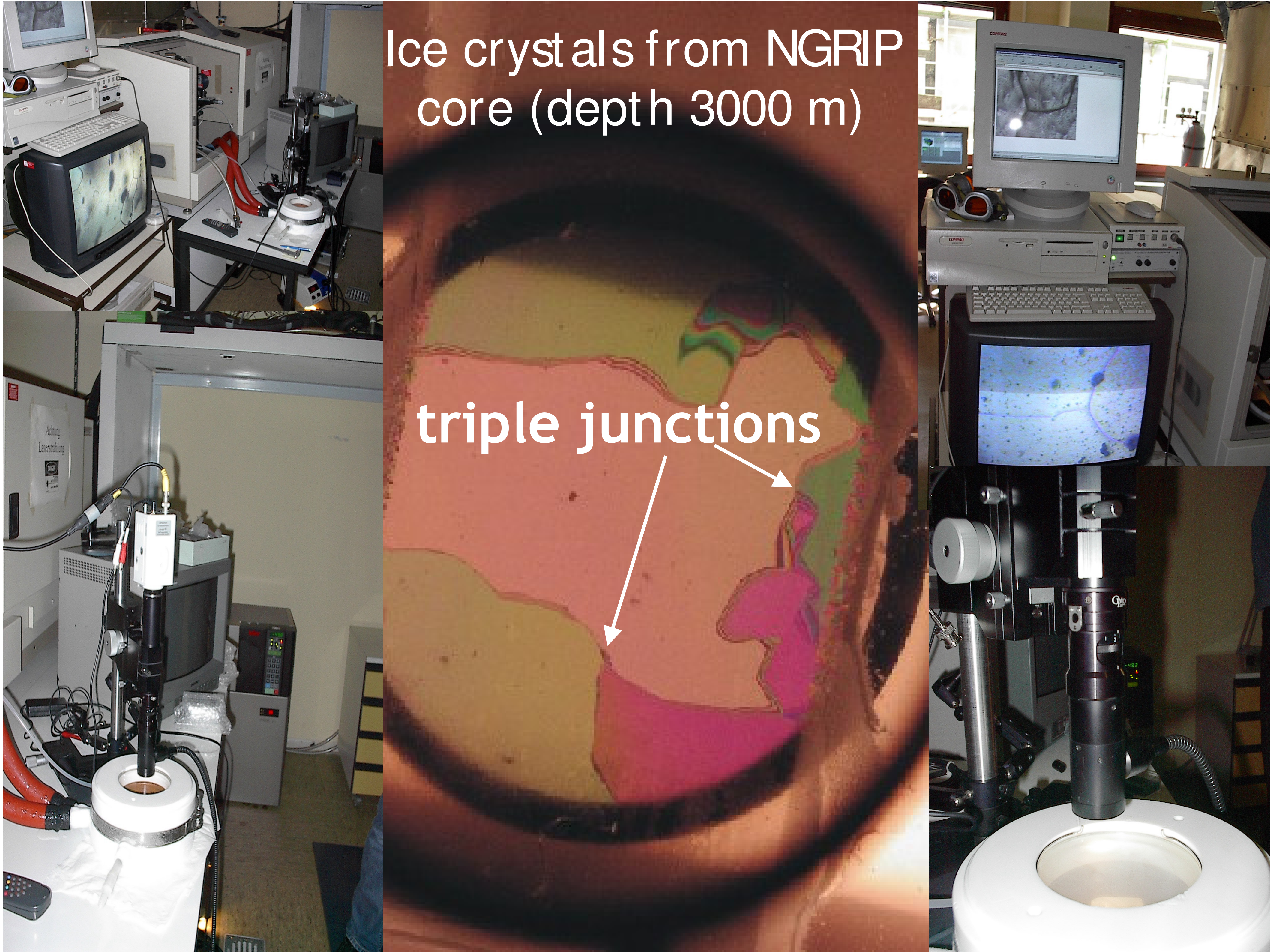
-high spatial and hence time resolution,
reduced contamination risk,
low detection limits

-coupling the laser system
to a ICP-TOFMS,
reduction of RSDs
and better spatial resolution

-optical modification to
reduce the spot size

-combination with a
microscope system for the
determination of impurities in
ice at triple junctions

-laserablation of frozen tissue
samples, applications with
pharmaceutical and medical
interest


Ice crystals from NGRIP core (depth 3000 m)
triple junctions