Application of LA-ICP-MS in polar ice core studies

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Motivation and Goals

The direct determination of element signatures in polar ice core samples from Greenland by laser ablation ICP-MS has been investigated. Ice core studies enable a highly resolved reconstruction of Earth climate back to about 500,000 years. The analysis of trace element signatures and dust horizons along annual layers yields information about the strength of sources and transport mechanisms for aerosols in the paleoatmosphere as well as about the paleovolcanism. Annual layers and transitions from cold to warm periods are detectable due to changes in concentration of mineral dust and seasalt.

Up to now element analyses in ice cores are only possible with molten ice samples. Drawbacks are:

- High sample consumption
- Low spatial and temporal resolution
- Lost of valuable sample material

The aim of this work was to achieve a multielement determination of element signatures in ice cores with a higher spatial resolution especially in thin annual layers (< 0.5 cm) of old deep-ice. Laser ablation ICP-MS is the first analytical technique which fulfils the detection of elements at ultra trace level in thuch thin layers with the required resolution. Advantages are:

- Spatial resolution + detection limits
- Low sample uptake
- Analysis directly from solid sample
  - → Minimum sample preparation
  - → Low risk of contamination

In this study the element determination in real ice sample material is focused to following components:

Na, Mg = Sea salt tracer
Al, Fe, REE = Mineral dust tracer
Pb, Cd, Zn = Anthropogenic tracer

Experimental setup

The experimental setup is shown in fig. 1. To enable direct analysis of solid ice samples at a temperature of -45°C a cryogenic laserablation chamber (CRYOLAC™, German patent application) was constructed. The chamber has a large volume (table 1) to enable the measurement of ice core samples cut as discs or segments with one or more annual layers depending on the depth of the ice origin. The inner part of the chamber consists of high purity copper and contains a cooling canal for the cooling liquid (silicon oil). The outer shell consists of teflon and enables a good insulation against the copper block. A computer controls the sample stage of the laserablation chamber in xyz-orientation as well as the laser system.

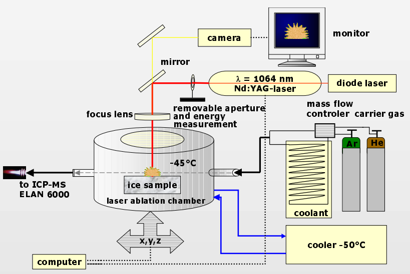

Fig. 1: Experimental setup.

By means of a laser beam at a wavelength of 1064 nm, which was found to be most suitable according to the absorption coefficient of ice, material from the surface is ablated. Argon is used as carrier gas. The gas is precooled to avoid droplets at the optical window of the cell. The ablated sample aerosol is introduced to an ICP-MS (ELAN 6000, PerkinElmer) for subsequent ion analysis.

Table 1: Cell parameter.

Tube length to ICP	50 cm
Cell volume	730 mL
∅ optical window	10 cm
Wash out time	7 min
Sample dimension	1 cm, 5 cm, 10 cm (h,w,d)

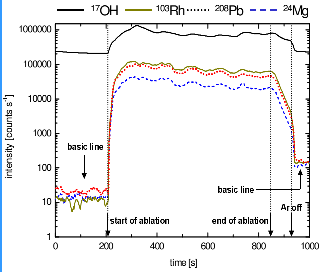

Fig. 2: Signal of 10 µgkg^{-1} "daily performance" ice standard at different masses. ^{17}OH is used as internal standard.

Table 2: Optimized operating conditions for the ICP-MS system in combination with the IR-laser for trace element analyses in frozen ice samples.

ICP-MS	PerkinElemer/Sciex ELAN 6000
RF power	1300 W
carrier gas	0.92 L min^{-1}
auto lens	on
isotopes measured for optimisation	^{17}OH, ^{23}Na, ^{24}Mg, ^{27}Al, ^{64}Zn, ^{103}Rh, ^{114}Cd, ^{208}Pb
laser	Nd:YAG, 1064 nm
pulse mode	Q-switched
frequency	10 Hz
laser energy	300 mJ
spot size	300 µm

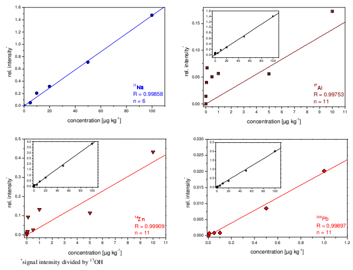

Fig. 3: Calibration studies with frozen standard solutions were performed with 6 to 11 standards ranging from 10 ngkg^{-1} to 100 µgkg^{-1}.

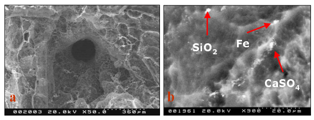

Fig. 4: Cryo-SEM pictures of ice samples. 4a: IR-laser crater, 4b: Particles in deep-ice (1102 m; 6209 years old) from Greenland are orientated at grain boundaries. Diameter of particles: 3-20 µm.

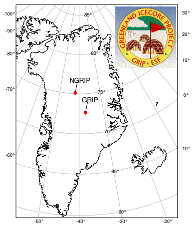

Fig. 5: Locations of ice coring in Greenland (NGRIP-North Greenland Ice Core Project).

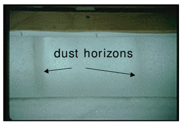

Fig. 7: Visible dust horizons in an ice core sample.

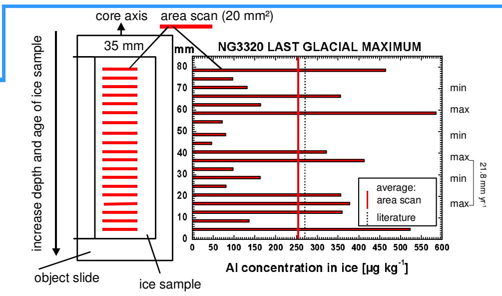

Fig. 6: Sampling pattern (left) for element analyses (area scans) in ice cores by laser ablation. The element signature of Al (right) is exemplarily shown by plotting concentration vs. sample length. The signature contains an undulated progression (min/max) which points to a seasonal variation (winter--> high Al conc., summer--> low Al conc.). The annual layer thickness (distance between two maxima/minima) is about 21.8 mm.

Table 3: Comparison of measurement values for sample NGRIP Last Glacial Maximum obtained by different analyse techniques (values in µgkg^{-1}).

Element	LA[1]	SN-ICP-MS HNO$_3$[2]	SN-ICP-MS tri-acid[3]	IC[4]	Literature[5]
Na	49.3 ± 24.5	77.649	175.005	88.280	84.030
Mg	63.5 ± 41.6	102.855	121.427	50.020	37.920
Al	253.8 ± 172.5	163.689	441.318	-	270.000
K	89.8 ± 60.4	16.746	122.272	10.560	17.050
Fe	196.0 ± 128.8	137.271	253.550	-	-
Zn	2.2 ± 1.7	16.282	20.196	-	0.563
Cd	0.054 ± 0.036	0.126	0.137	-	0.003
Pb	0.317 ± 0.217	0.946	1.170	-	0.151

[1] axial averaged concentrations obtained by laser ablation area scans

[2] fraction dissolved in HNO$_3$

[3] total content after tri-acid digestion HNO$_3$/HF/HClO$_4$

[4] obtained by ion chromatography

[5] comparable values from the GRIP ice core obtained by IC or GFAAS

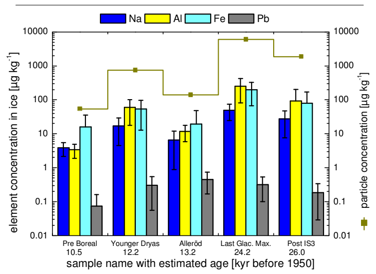

Fig. 8: Comparison of average values obtained by LA with the measured particular matter in the respective geological interval.

Calibration studies

- For calibration, ice standards were performed in a stepwise procedure from comercially available standard solutions.
- The signal of **^{17}OH** coming from the ice was found to be most suitable to use as an **internal standard**.
- A study of ^{17}OH, ^{24}Mg, ^{103}Rh and ^{208}Pb signal progressions (laser ablation line scan mode) is demonstrated in Fig. 2.
- Normalizing the analytic signal to ^{17}OH intensities, standard deviations could be reduced by a factor of 2. **RSDs of 3-6 %** could be achieved for all measured masses.
- **Calibration graphs** for Na (sea salt tracer), Al (mineral dust tracer) Zn and Pb (anthropogenic or contamination tracer) are exemplarily shown in Fig. 3. Linearity could be found for many elements over the whole calibration range.
- **Detection limits**: Pb ⇒ 0.001 µg kg^{-1}
  Na, Mg, Al, Zn ⇒ 0.1 – 1 µg kg^{-1}
  Fe, Ca ⇒ 1 – 10 µg kg^{-1}
- **Validation of method** by certified standard reference materials which were prepared as normal ice standards. Na, Mg, Al, Ca, Fe, Zn, Cd, Pb ⇒ **recovery approx.** ± **10 %**
- Optimized **operating conditions** are summarized in table 2.
- **Figure 4a** shows a cryogenic scanning electron microscopy picture of an ice surface (diameter 300 µm) with an **IR laser crater** (50 shots, 300 mJ, ∅ = 300 µm).
- Along an area scan the laser beam vaporizes small inclusions of particles together with the surrounding ice. Such particles are exemplarily shown in Fig. 4b.

Results and discussion

- Greenland ice core samples (position of NGRIP, Fig. 5) from different depths were analysed by LA-ICP-MS.
- Fig. 6 (left) shows the used sample pattern, a combination of area scans (20 mm², no. of replicates = 6) arranged vertically to the core axis.
- Fig. 6 (right) shows exemplarily the **element signature for Al** derived of sample material from the **last glacial maximum** (depth: 1,826 m; age: 24,200 yr before present. Al-concentration (on x-axis) is plotted versus sample length. Horizontal red bars give the concentrations originating from area scans.
- An undulated progression (min/max) is seen within the sample length which points to a seasonal variation with different deposition of particulate matter during summer and winter time. Maxima in element concentration could also originated from dust horizons due to volcanic eruptions (Fig. 7).
- The distance between two max/min - the annual layer thickness - is about 21.8 mm of sample length. This is in a good agreement with the value from the literature (21.2 mmyr^{-1}) measured by γ-spectroscopy.
- The vertical red line gives the average of area scans (253,8 ± 172.5 µgkg^{-1}). The value is in a good agreement with the black dotted line, the available Al-concentration (270.0 µgkg^{-1}; GRIP data) from the literature obtained by graphite furnace atomic absorption spectroscopy (GFAAS).
- Generally, a **comparison of local micro- with bulk analysis** is very difficult. However, to enable a comparison with conventional solution (bulk) analysis, average values for all measured samples were calculated. These average values were compared with data obtained by SN-ICP-MS, IC or literature data (Table 3).
- LA of ice samples enabled only a **2d-mapping microanalysis**. Nothing is known about particles and element concentration in the third dimension. However, it could be found that the element concentration obtained by LA were in the same order of magnitude as the values obtained from the solution after tri-acid digestion.
- Fig. 8: Sea salt and mineral dust tracer as well as REE in Greenland ice core samples have shown good correlation to particle content. It is assumed, that these elements are bonded to particulate matter. No correlation was obtained for Zn, Cd, Pb and Nd most probably due to contamination or other transport processes.
- Fractionation effects could not been observed during laser ablation. This could be related to the fact, that calibration was performed in the same matrix, however further studies will be carried out.

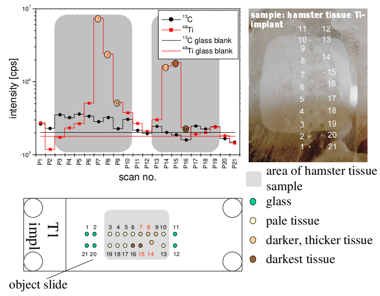

Fig. 9: **New applications for bioanalytical chemistry**. Analysis of **frozen soft tissue samples** by LA-ICP-MS. Here: 2-d mapping of Ti-implant abrasion in frozen hamster tissues.

Conclusions and outlook

- Development of a new method for **trace element analyses** directly from **frozen ice core samples** by **LA-ICP-MS**
- Successful preparation of ice standards and quantitative determination of trace elements in real ice samples
- Low sample consumption, quasi non-destructive, samples are available for other analytical techniques
- Reduced contamination risk, low detection limits
- **2-d mapping of Greenland deep-ice core** (depth: < 1000 m) samples with high spatial and hence temporal resolution has shown strong variations in sea salt and mineral dust concentration owing to changes in atmospheric transport processes in summer and winter time in the Arctic basin. Annual layers were detected also in deep-ice, which are impossible to resolve with conventional solution analysis.
- This application will be deployed for analysis of element signatures in **future Antarctic ice core studies**.

- **New field in bioanalytical chemistry:** The new developed cryogenic ablation chamber "CRYOLAC™" enables the **analysis of frozen soft tissue samples by LA-ICP-MS**. Fig. 9 shows an example for 2d-mapping of Titan (coming from implants abrasion) in frozen hamster tissues (-45°C).

Publication:

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