Regional and seasonal variability of particle and element-concentrations from snowpits in Antarctica

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Introduction

Mineral dust measured in Antarctic ice cores is a unique tool to reconstruct palaeo climate variations, but even the knowledge about present day dust in Antarctic snow is still very poor. In this study we analyzed different proxies of mineral dust (particle concentration, size distribution, elemental composition) in snowpits from Berkner Island, a coastal influenced site, and from Kohnen Station located on the plateau, in order to investigate differences in the transport behaviour of dust from the source to its deposition site and how this might change during the year.

Results

Particle concentration

At Berkner Island the particle concentration is low (3.75 ng/ml without very pronounced particle peaks), we find not a clear seasonality, but a slightly increase of particle-concentration in winter. There are very prominent peaks at 122-136 cm depth (year 2001), as shown in fig.4. This event is also detected in elemental composition investigations.

At Kohnen the particle concentration is higher (6.7 ng/ml), we find a clear seasonality in the particle-concentration with a maximum in winter (Fig.5).

Chemical composition

Additional the concentration for Fe as a tracer for mostly insoluble mineral dust particles is shown in fig. 4 and 5. For Kohnen station there is a good agreement obvious in the depth range from 16-58 and 76-96 cm.

At Berkner Island are only some few peaks for Fe which reflect the particle distribution. The prominent peaks for particle concentrations at 122-136 cm correspond very well with the distribution for sea salt elements like Na, Mg, Ca (fig. 6). This finding could not be explained yet. It could be an effect of chemical reactions during atmospheric transport whereby insoluble particles are produced.

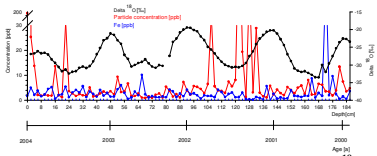


Fig. 4: Particle and Fe concentration as well as Delta ^{18}O (temperature proxy) at Berkner Island

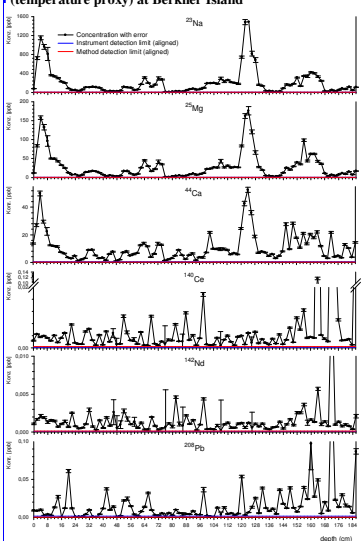
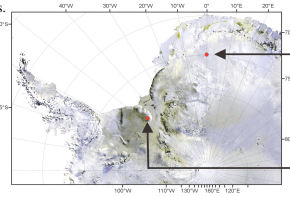


Fig. 6: Na, Mg, Ca (sea salt), Ce, Nd (mineral dust) and Pb (anthropogenic) concentration at Berkner Island

Experimental

Sampling

The samples were taken in polypropylen tubes, which were pressed into the snowpit walls. For the investigation of elemental composition the tubes were precleaned in 3 different acid baths (1:4 HCl, 1:4 HNO_3, 1:10 HNO_3) and rinsed with ultrapure water. After sampling, the tubes were packed into two polyethylene bags and kept frozen until analysis.



Snowpit Kohnen-Station
75°00'S, 0°04 E, 2890 m a.s.l.
2 m deep, 2 cm resolution
season 2003/2004
mean annual accumulation rate:
62 mm w.eq

Snowpit Berkner Island
79° 34' N, 45° 39' W, 880 m a.s.l.
2 m deep, 2 cm resolution
season 2003/2004
mean annual accumulation rate:
130 mm w.eq

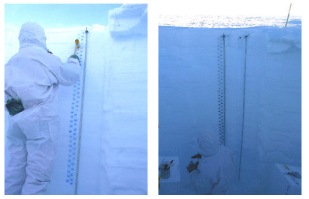


Fig. 1: Sampling in the snowpit at Kohnen-Station

Measurements of particle distribution

For the particle concentration and size distribution the samples were measured within 15 minutes after melting with a laser-sensor device (λ=670 nm). A cross-calibration with a Coulter-Counter was made by using samples from the EPICA deep-drilling-sites in Dronning Maud Land and on Dome C for particles <5 µm and samples from Greenland and spherical particles for particle >5 µm. To determine blank-levels ultrapure water was measured before and after the samples. The measuring range of the laser-sensor is between 1 and 10 µm. Each sample was measured at least three times using a sample volume of 4-10 ml.

Fig. 2: Laser-sensor-setup, for particle size and -concentration measurements

Measurements of elemental composition

For determination of elemental composition the samples were processed and measured in cleanroom laboratories at AWI. After melting the initial sample volume was approximately 20 ml. The samples were treated under pressure with a full-acid digestion (HNO_3, HF, H_2O_2) and enriched by a factor of 10 (fig. 3). Trace and ultrace element analyses were carried out with an ICP-MS (ELAN 6000-Perkin-Elmer/Sciex) in combination with membran desolvatation system MCN 6000 (Cetac) and a 100 µl PFA nebulizer. The instruments setups are shown in table 1 and 2. As internal standard Rh was added to each sample. The method detection limits (MDL) of the measured elements are given in table 3. The MDL depence on the method of sample preparation and was calculated as three times the standard deviation of 91 blank treatments.

Fig. 3: Setup of full acid digestion under pressure for sample treatment and enrichment before ICP-MS analysis

Tab. 1: MCN 6000 parameters

Parameter	Setup
Argon flow	1,88 l/min
Nitrogen flow	18 ml/min
Sample uptake rate	~ 100 µl/min

Tab. 2: ELAN 6000 parameters

Parameter	Setup
Nebulizer gas	0,7 ml/min
Lens voltage ^{103}Rh	4,75 V
Plasma	1450 W
Autolens	on
Plasma gas	15 l/min
Auxillary gas	0,8 l/min
Peakhopping	on
Dwelltime	10 ms
Detector mode	Dual
Settlingtime	1500 µs

Tab. 3: Method detection limits (3 σ criteria, n = 91)

Element	MDL	Element	MDL	Element	MDL	Element	MDL
^{6}Li	2 ppt	^{60}Ni	52 ppt	^{111}Cd	1 ppt	^{160}Gd	1 ppt
^{9}Be	1 ppt	^{63}Cu	0,2 ppb	^{114}Cd	1 ppt	^{164}Dy	0,4 ppt
^{23}Na	8,0 ppb	^{64}Zn	2,6 ppb	^{115}In	0,3 ppt	^{165}Ho	0,2 ppt
^{24}Mg	1,8 ppb	^{65}Cu	0,2 ppb	^{138}Ba	88 ppt	^{166}Er	0,4 ppt
^{25}Mg	1,5 ppb	^{66}Zn	2,8 ppb	^{139}La	1 ppt	^{169}Tm	0,2 ppt
^{27}Al	21 ppb	^{69}Ga	13 ppt	^{140}Ce	2 ppt	^{174}Yb	0,4 ppt
^{39}K	2,8 ppb	^{75}As	11 ppt	^{141}Pr	0,4 ppt	^{175}Lu	0,2 ppt
^{43}Ca	3,6 ppb	^{78}Se	0,4 ppb	^{142}Nd	1 ppt	^{204}Pb	12 ppt
^{44}Ca	4,0 ppb	^{82}Se	38 ppt	^{143}Nd	1 ppt	^{205}Tl	6 ppt
^{51}V	15 ppt	^{85}Rb	4 ppt	^{144}Nd	0,8 ppt	^{206}Pb	12 ppt
^{52}Cr	0,1 ppb	^{86}Sr	39 ppt	^{147}Sm	1 ppt	^{207}Pb	11 ppt
^{55}Mn	0,1 ppb	^{88}Sr	33 ppt	^{149}Sm	1 ppt	^{208}Pb	13 ppt
^{56}Fe	1,4 ppb	^{89}Y	1 ppt	^{151}Eu	1 ppt	^{209}Bi	1 ppt
^{57}Fe	1,5 ppb	^{107}Ag	2 ppt	^{153}Eu	1 ppt	^{232}Th	1 ppt
^{58}Ni	58 ppt	^{109}Ag	2 ppt	^{159}Tb	0,3 ppt	^{238}U	0,4 ppt
^{59}Co	11 ppt						

From tab. 4 it is obvious that the mean concentrations for **sea salt elements** are higher at Berkner Island, while the **mineral dust tracer** show higher values at Kohnen. **Anthropogenic tracer elements** show slightly higher concentrations at Kohnen. All elements show a high variability.

Tab. 4: Mean element concentrations with standard deviation as well as min. and max. values for snowpits as well as the deposition rate at Kohnen station and Berkner Island

	Kohnen					Berkner Island				
Element	Average	Min.	Max.	Std. dev.	Flux (µg m^{-2} a^{-1})	Average	Min.	Max.	Std. dev.	Flux (µg m^{-2} a^{-1})
^{6}Li	6,4 ppt	0,5 ppt	44 ppt	0,4 ppt	0.40	5,6 ppt	n.d.	63 ppt	0,5 ppt	0.73
^{9}Be	0,7 ppt	n.d.	18 ppt	0,2 ppt	0.043	0,25 ppt	n.d.	9,5 ppt	0,2 ppt	0.033
^{23}Na	27 ppb	68 ppt	327 ppb	0,7 ppb	1674	213 ppb	8,2 ppb	1491 ppb	7,6 ppb	27690
^{24}Mg	7,9 ppb	1,4 ppb	65 ppb	0,2 ppb	490	29 ppb	1,1 ppb	176 ppb	1,0 ppb	3770
^{27}Al	42 ppb	n.d.	1015 ppb	8,8 ppb	2604	5,7 ppb	n.d.	459 ppb	0,2 ppb	741
^{39}K	2,8 ppb	n.d.	10 ppb	70 ppt	174	11 ppb	0,6 ppb	66 ppb	0,3 ppb	1430
^{44}Ca	7,8 ppb	0,7 ppb	94 ppb	0,2 ppb	484	11 ppb	1,0 ppb	53 ppb	0,3 ppb	1430
^{51}V	41 ppt	n.d.	0,8 ppb	2,8 ppt	2.5	25 ppt	n.d.	0,9 ppb	3,9 ppt	3.3
^{52}Cr	0,2 ppb	n.d.	1,9 ppb	8,2 ppt	12.4	65 ppt	n.d.	0,8 ppb	4,5 ppt	8.5
^{55}Mn	0,1 ppb	n.d.	1,7 ppb	4,3 ppt	6.2	26 ppt	n.d.	0,4 ppb	1,8 ppt	3.4
^{56}Fe	4,1 ppb	0,6 ppb	52 ppb	0,1 ppb	254	2,9 ppb	n.d.	50 ppb	57 ppt	377
^{59}Ni	0,1 ppb	2,8 ppt	1,4 ppb	2,5 ppt	6.2	63 ppt	n.d.	0,8 ppb	1,6 ppt	8.2
^{59}Co	14 ppt	n.d.	0,1 ppb	0,3 ppt	0.87	7,3 ppt	n.d.	85 ppt	0,5 ppt	0.95
^{64}Zn	14 ppb	2,7 ppb	105 ppb	10 ppb	868	4,1 ppb	1,2 ppb	12 ppb	0,1 ppb	533
^{65}Cu	0,1 ppb	n.d.	1,4 ppb	5,4 ppt	6.2	52 ppt	n.d.	1,3 ppb	4,3 ppt	6.8
^{69}Ga	37 ppt	n.d.	1,2 ppb	0,6 ppt	2.3	19 ppt	n.d.	0,5 ppb	0,7 ppt	2.5
^{85}Rb	84 ppt	1,3 ppt	48 ppt	0,3 ppt	5.2	9,1 ppt	1,8 ppt	35 ppt	0,7 ppt	1.2
^{88}Sr	50 ppt	0,4 ppt	0,3 ppb	1,2 ppt	3.1	0,2 ppb	14 ppt	1,3 ppb	5,4 ppt	26
^{89}Y	2,9 ppt	0,05 ppt	29 ppt	0,1 ppt	0.18	1,6 ppt	0,1 ppt	25 ppt	0,2 ppt	0.21
^{109}Ag	8,2 ppt	0,5 ppt	0,1 ppb	0,2 ppt	0.51	2,8 ppt	n.d.	13 ppt	0,2 ppt	0.36
^{114}Cd	13 ppt	n.d.	0,1 ppb	1,8 ppt	0.81	4,0 ppt	n.d.	20 ppt	0,6 ppt	0.52
^{115}In	0,8 ppt	n.d.	17 ppt	0,1 ppt	0.050	0,3 ppt	n.d.	15 ppt	0,2 ppt	0.039
^{138}Ba	0,4 ppb	3,7 ppt	14 ppb	6,6 ppt	24.8	0,2 ppb	n.d.	5,8 ppb	4,8 ppt	26.0
^{139}La	6,8 ppt	0,2 ppt	0,3 ppb	0,2 ppt	0.42	3,0 ppt	0,2 ppt	63 ppt	0,3 ppt	0.39
^{140}Ce	15 ppt	0,5 ppt	0,6 ppb	0,3 ppt	0.93	6,4 ppt	0,6 ppt	0,1 ppb	0,3 ppt	0.83
^{141}Pr	1,3 ppt	n.d.	20 ppt	0,1 ppt	0.081	0,5 ppt	0,02 ppt	5,5 ppt	0,2 ppt	0.065
^{143}Nd	2,9 ppt	0,1 ppt	39 ppt	0,2 ppt	0.18	1,4 ppt	0,2 ppt	18 ppt	0,3 ppt	0.18
^{147}Sm	0,9 ppt	n.d.	18 ppt	0,2 ppt	0.056	0,5 ppt	n.d.	3,2 ppt	0,2 ppt	0.065
^{151}Eu	0,6 ppt	n.d.	17 ppt	0,1 ppt	0.037	0,3 ppt	n.d.	3,1 ppt	0,2 ppt	0.039
^{159}Tb	0,6 ppt	n.d.	17 ppt	0,1 ppt	0.037	0,2 ppt	n.d.	2,9 ppt	0,2 ppt	0.026
^{160}Gd	0,9 ppt	n.d.	19 ppt	0,1 ppt	0.056	0,3 ppt	n.d.	3,1 ppt	0,2 ppt	0.039
^{164}Dy	0,9 ppt	n.d.	20 ppt	0,1 ppt	0.056	0,3 ppt	n.d.	3,6 ppt	0,2 ppt	0.039
^{165}Ho	0,7 ppt	n.d.	17 ppt	0,1 ppt	0.043	0,2 ppt	n.d.	2,8 ppt	0,2 ppt	0.026
^{166}Er	0,9 ppt	n.d.	19 ppt	0,1 ppt	0.056	0,3 ppt	n.d.	2,9 ppt	0,2 ppt	0.039
^{169}Tm	0,6 ppt	n.d.	17 ppt	0,1 ppt	0.037	0,2 ppt	n.d.	2,8 ppt	0,2 ppt	0.026
^{174}Yb	0,9 ppt	n.d.	19 ppt	0,2 ppt	0.056	0,3 ppt	0,04 ppt	2,9 ppt	0,2 ppt	0.039
^{175}Lu	0,7 ppt	n.d.	18 ppt	0,1 ppt	0.043	0,2 ppt	n.d.	2,8 ppt	0,2 ppt	0.026
^{205}Tl	7,1 ppt	n.d.	30 ppt	0,8 ppt	0.44	2,2 ppt	n.d.	10 ppt	0,3 ppt	0.29
^{208}Pb	51 ppt	n.d.	0,6 ppb	1,2 ppt	3.2	16 ppt	0,1 ppt	0,2 ppb	0,9 ppt	2.1
^{209}Bi	2,1 ppt	n.d.	27 ppt	0,3 ppt	0.13	0,2 ppt	n.d.	11 ppt	0,2 ppt	0.026
^{232}Th	1,3 ppt	n.d.	27 ppt	0,2 ppt	0.081	1,6 ppt	0,09 ppt	15 ppt	0,2 ppt	0.21
^{238}U	0,8 ppt	n.d.	19 ppt	0,2 ppt	0.050	0,6 ppt	0,01 ppt	15 ppt	0,2 ppt	0.078

This strong variabilty is also shown for some selected elements in fig. 4-7. There is a clear seasonality in the sea-salt elements at Berkner Island.

At Kohnen sea salt-aerosol is not the dominating source, but shows also a seasonality with maxima in winter.

Mineral dust aerosol is the dominat source at Kohnen and shows a clear seasonality with maxima in winter.

Taking into account the yearly accumulation rate it can be seen from tab. 4 that the flux for sea salt aerosol is by a factor of 8-15 higher at Berkner Island than on the plateau at Kohnen. For mineral dust as well as for anthropogenic elements the deposition rate at both stations is nearly similar whereas there is a slightly higher amount at Kohnen.

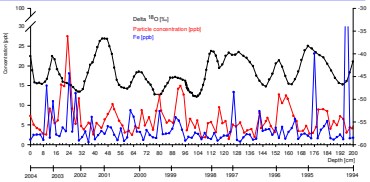


Fig. 5: Particle and Fe concentration as well as Delta ^{18}O (temperature proxy) at Kohnen station

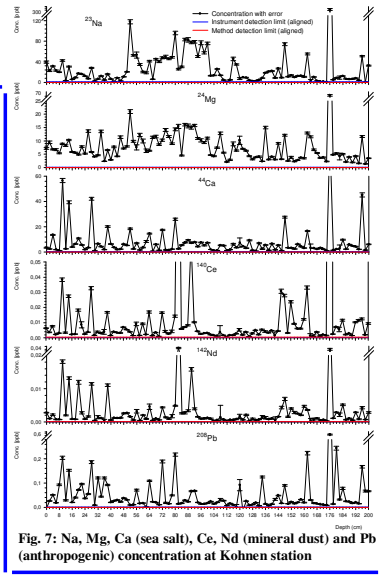


Fig. 7: Na, Mg, Ca (sea salt), Ce, Nd (mineral dust) and Pb (anthropogenic) concentration at Kohnen station

Conclusions and Outlook

The plateau position at Kohnen Station has a clear seasonality in dust concentration. The chemical composition shows that mineral dust is dominating. At Berkner Island the particle concentration and size distribution is dominated by single events, that might have a local source. A strong influence from the ocean could be observed when looking to typical sea salt tracer elements.

For future investigations of deep ice cores it is necessary to take into account at which position the drilling will be carried out. In ice core studies up to now Ca is used as a tracer for mineral dust in contnious flow analyses. This contribution shows that depending on the sampling location Ca has at least two different sources.

In further steps analyses will be carried out for samples from potential sources in the southern hemisphere to identify sources and possible changes during the year. For this analyses the Rare earth element distribution patterns will be used.

From fig. 6 it can bee seen that at Berkner Island is a good agreement in the depth profile for the sea salt elements Na, Mg and Ca. At Kohnen station (fig. 7) the profile for Ca is often different. In fig. 8 a and b the Na concentration is plotted versus typical other sea salt elements (Mg, Sr, Ca). For Berkner Island it can be seen that there is a good correlation between these elements and Na and the element ratios (marked by a red cross) in open ocean water agree very well.

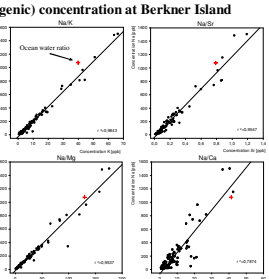


Fig. 8a: Correlation of Na versus , Mg, Ca, Sr at Berkner Island

In contrast to Berkner Island we found at Kohnen only a good correlation for Na and Mg. For all shown elements the seawater ratio could not be found. The reason might be fractionation effects during atmospheric transport or there are other sources.

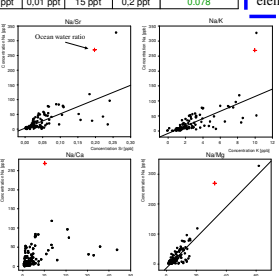


Fig. 8b: Correlation of Na versus Mg, Ca, Sr at Kohnen station

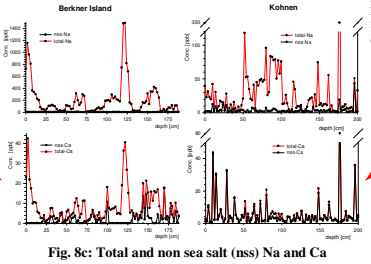


Fig. 8c: Total and non sea salt (nss) Na and Ca

To identify possible other sources e.g. for Na and Ca the non sea salt Na and Ca-concentration (nss-Na, Ca) was calculated. Fig. 8 c shows the results. At Kohnen most of the Ca is not from a marine source, while for Na except some few depths more than 90% is from sea salt. At Berkner Island except some few depths more than 90% of the total Ca and nearly 100% of Na is from an oceanic source.

Acknowledgement

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