Microparticles, soil derived chemical components and sea salt in the Hans Tausen Ice cap ice core from Peary Land, North Greenland

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Abstract

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Selected segments of the 344 m deep ice core from Hans Tausen ice cap in Peary Land, North Greenland have been stratigraphically analyzed for chemical impurities and insoluble microparticles (Dust). Two different components of the microparticles have been identified by their different sizedistributions: A component of small particles from remote sources, and a component of large particles from local sources. The abundance of large particles increases with depth (and age) in the ice core resulting in an increase in total dust mass. Very high dust mass in the lowest 100 m of the core are believed to be a result of melt water run-off. Compared to Central Greenland ice cores the Hans Tausen ice is strongly enriched in soluble crustal material from local sources manifested by high concentrations of Ca2+ and nss. Mg2+. In the bottom 100 m section our results indicate a loss of Ca2+ and Mg2+ relative to dust due to melt water runoff. Sea salt concentrations show little variation with depth, and our results indicate, that the sea salt in Hans Tausen ice is from remote sources. The North Polar Sea has not been a significant source of sea salt in the life time of the Hans Tausen ice cap. All our results are consistent with the hypothesis that the Hans Tausen ice cap was formed sometime during the Holocene: It started as a small ice cap of superimposed ice with heavy melting and strong influence of local dust sources. With time the ice cap grew, both horizontally and vertically, the surface got colder with less melting and the influence from local sources got weaker. Today the impurity content of Hans Tausen snow is comparable to that of the Central Greenland ice sheet with the exception of the influence of soluble crustal material from the ice free Peary Land area which remains.

Keywords: Ice core; microparticles; sizedistributions; sea salt; melting/ refreezing.

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Introduction

Stratigraphic analysis of ice cores from polar ice caps provide important palaeoclimatic information. In ice cores originating from sites where melting never occurs changes with depth in e.g. stable isotopic composition or concentrations of chemical impurities and insoluble microparticles (dust) reflect changes in past atmospheric composition and climate. Over large areas in the interior of the Greenland ice sheet, including ice core drilling sites such as GRIP (Johnsen et al. 1992), GISP2 (Grootes et al. 1993) and NGRIP (Dahl-Jensen et al. 1997), melting at the surface is very rare. However at sites where summer melting occurs, the ice core stratigraphy may be disturbed by melting and refreezing processes. At sites where this summer melting is limited, the melt water refreezes in the cold spring and winter snow below. In the firn this can be observed as blue layers of ice in the white firn. In ice cores, these layers show up as clear layers without gas bubbles. Although the chemical composition and the dust content may change due to melting/refreezing there is no loss of material and mixing between annual layers is limited. Ice cores from such sites still provide reliable palaeoclimatic information, but great care should be exercised in the interpretation of stratigraphical details since some features of the stratigraphical profiles may be due to melting and not a consequence of atmospheric changes. Ice core drilling sites such as Dye-3 (Dansgaard et al. 1982) and Renland (Johnsen et al. 1992) fall into this category. At sites where summer melting is heavy the snow below the surface melt layer may become saturated with melt water and material may be lost due to run-off. Here, the chemical composition, the dust content and even the stable isotopic composition may be altered over large sections of the stratigraphical profiles to

such degrees that these cores contain very little reliable palaeoclimatic information. A large number of ice cores from smaller ice caps in the north polar region originate from such sites (Koerner 1997).

In the Hans Tausen ice cap ice core layers of refrozen meltwater are found in abundance. The percentage of layers showing melting/refreezing increases with depth from about 10% close to the surface until it reaches 100% in the deepest 10% of the core (K. Nørregaard Madsen 2001). Here the ice core is completely clear without any bubbles from trapped atmospheric air. The stratigraphical profiles of stable isotopic composition, chemical compostion and the dust content from this core therefore have to be interpreted with great care in order to separate "real" climatic and atmospheric signals from the effects of melting/refreezing.

Experimental

The Hans Tausen ice cap ice core was drilled in the summer of 1995 on a local dome at 82° 30' N, 37° 28' W, 1271 m a.s.l. on the Hans Tausen ice cap in Peary Land in North Greenland. The core reaches to bedrock at 344.85 m depth. Immediately after drilling the core was logged and the visible stratigraphy, such as melt layers, recorded. Electric Conductivity Measurement (ECM) was performed as well as the cutting of samples for stable isotopic composition before the core was cut into 55 cm core segments. The core segments are called "bags" in reference to the numbered plastic bags they are packed into. The bags were packed in insulated boxes for shipment in frozen condition to the cold storage in Copenhagen. 30 selected segments of the core were sampled in Copenhagen for chemical and dust analysis. The segments were cleaned and sampled under laminar flow by cutting away the outer surface using a steel microtome knife in the cold room. The samples were stored in Coulter Accuvettes and kept frozen until analysis. Measurement of the concentrations of ionic components, such as Na⁺, Cl⁻, Mg²⁺ and Ca²⁺ was done on a Dionex 4000i ionchromatography system capable of measuring both anions and cations on the same aliquot. Measurement of the sizedistribution of microparticles between radii 0.4 µm and 6.5 µm was done on a Coulter Multisizer II. A total of more than 700 samples each of them 5 cm long were measured this way. 55 cm averages of the sizedistribution data were made and the results fitted to a lognormal distribution (Steffensen 1997).

The log-normal distribution:

$$\frac{dV}{d\log r} = \frac{V_{\rm T}}{\sqrt{2\pi}\log\sigma} \exp\left(-\frac{1}{2}\left(\frac{\log r - \log\mu}{\log\sigma}\right)^2\right)$$

V(r) is the volume concentration of particles larger than r. r is particle radius in µm. In this distribution the volume is normal (or Gaussian) distributed as a function of log r. log µ plays the role of the mode, thus µ is called the log-normal mode and log σ plays the role of the standard deviation, thus σ is called the log-normal standard deviation. V_T is the total volume concentration of particles. In this distribution 70% and 95% of the total volume is inside the radius intervals:

$$\begin{split} & [\exp(\log\mu - \log\sigma) \ ; \ \exp(\log\mu + \log\sigma)] \quad (70\% \text{ of } V_T) \\ & [\exp(\log\mu - 2\log\sigma) \ ; \ \exp(\log\mu + 2\log\sigma)] \quad (95\% \text{ of } V_T) \end{split}$$

Logarithms to base "e" was used.

Also, the total dust mass (in $\mu g/kg$) and the mass fraction of large particles (2.5 μ m < r < 6.5 μ m) to the total particle mass was calculated.

Results

Mean concentrations in 55 cm ice core segments ("bags") of ionic components and dust data are presented in Table 1. The total dust mass for individual sam-

ples is presented in Fig. 1. Although there are large variations in dust mass between individual samples there is an increase in dust mass with depth. Below 300 m the dust mass is more than 10 times higher than at 100 m. Six 55 cm mean dust sizedistributions are shown in Fig. 2, including the fit of the data to log-normal distributions. For comparison, a sizedistribution from GRIP has been included. With increasing depth the sizedistributions are shifted towards larger particles. This is reflected by the mode parameter, µ, of the log-normal fit that shifts from 0.8 µm to around 2.6 µm and the increasing mass fraction of large particles, that shifts from 5% to around 50%.

> In the two ice cores from GRIP and Dye-3 there was a clear correlation between to-

tal dust mass and the concentration of Ca^{2+} which is believed to be due to the common continental origin and shared atmospheric transport of these species (Steffensen 1997). In Fig. 3 the Hans Tausen results are presented. As can be seen there is very little correlation between Ca^{2+} and dust mass in the Hans Tausen core. And compared to GRIP and Dye-3, the Hans Tausen ice is strongly enriched in Ca^{2+} . Five outliers are marked with their corresponding depths. Four of them are from great depth.

Also, at GRIP and Dye-3 the concentrations of non sea salt (nss.) Mg²⁺ and Ca²⁺

correlated. This correlation also is believed to be due to a common origin and shared transport (Steffensen 1997). A significant amount of Mg^{2+} in the ice may originate from sea salt. So the sea salt fraction of Mg^{2+} has to be calculated to obtain nss. Mg^{2+} . The Hans Tausen nss. Mg^{2+} concentrations are plotted as a function of Ca^{2+} concentrations in Fig. 4. In the Hans Tausen ice nss. Mg^{2+} and Ca^{2+} do correlate; but the molar ratio of nss. Mg^{2+} to Ca^{2+} is 0.43 which is 3.5

Depth	Bag #	Na⁺	Cl⁻	Mg ²⁺	Non sea salt	Ca ²⁺	Dust mass	Dust mass	Mass fraction	Relative amount
					Mg ²⁺		0.4 <r<6.0< th=""><th>0.4<r<2.5< th=""><th>of 2.5<r<6.0< th=""><th>of melt layers</th></r<6.0<></th></r<2.5<></th></r<6.0<>	0.4 <r<2.5< th=""><th>of 2.5<r<6.0< th=""><th>of melt layers</th></r<6.0<></th></r<2.5<>	of 2.5 <r<6.0< th=""><th>of melt layers</th></r<6.0<>	of melt layers
[m]	μ	[µequiv/kg]	[µequiv/kg]	[µequiv/kg]	[µequiv/kg]	[µequiv/kg]	[µg/kg]	[µg/kg]	[%]	[%]
0.55	1	0.90	1.22	1.87	1.68	4.09				2
1.1	2	1.78	1.82	1.04	0.65	1.91				4
18.15	33			1.90		3.54	114	108	5	1
18.7	34			2.81		5.57	47	43	10	2
19.25	35			1.39		2.14	55	51	7	0
30.8	56			1.95		3.64	76	73	4	5
31.35	57			0.82		1.74	49	47	4	1
31.9	58			1.93		4.07	108	105	3	9
32.45	59			0.82		1.74	86	81	5	6
35.2	64	2.14	1.89	2.86	2.38	4.28	76	72	6	1
35.75	65	1.26	1.23	0.88	0.61	1.85	51	49	5	0
69.85	127	0.78	1.07	1.25	1.08	2.38	88	85	4	0
70.4	128	0.54	0.69	0.88	0.76	1.50	36	34	4	2
94.05	171	0.67	0.95	0.97	0.82	2.57	60	53	12	40
94.6	172	1.38	1.53	2.31	2.01	5.25	26	25	2	26
96.8	176	0.69	0.85	1.82	1.67	4.51	34	31	9	7
97.35	177	0.67	0.80	1.79	1.64	3.24	101	81	20	1
100.1	182	0.51	0.56	2.02	1.91	3.71	91	84	7	3
100.7	183	1.16	1.68	2.05	1.79	5.01	103	100	3	9
101.2	184	0.78	0.99	1.10	0.93	2.53	80	75	6	12
105.6	192	1.01	1.60	2.72	2.50	7.99	228	168	26	2
107.8	196	0.65	0.83	1.65	1.51	3.40	86	80	7	0
108.4	197	1.44	1.41	1.45	1.13	4.36	153	125	18	1
120.5	219	1.13	1.59	1.18	0.94	2.79	303	189	38	0
131.4	239	1.07	1.72	1.47	1.23	3.24	88	85	3	4
132	240	0.46	0.64	0.77	0.67	2.62	92	85	7	1
135.9	247	0.99	1.23	1.54	1.32	3.30	126	102	19	2
150.2	273	0.99	1.63	3.94	3.72	8.48	190	127	33	22
165	300	1.08	1.39	4.69	4.46	9.09	477	250	48	27
180.4	328	0.96	1.16	4.41	4.20	7.21	182	109	40	69
194.7	354	1.16	1.68	2.46	2.20	5.94	37	33	10	67
210.1	382	0.95	1.31	4.13	3.92	6.20	284	241	15	29
226.1	411	1.41	1.66	4.92	4.61	12.82	133	90	32	44
226.6	412	1.43	1.35	1.20	0.89	1.95				91
240.9	438	1.09	1.94	3.16	2.92	9.57	88	81	7	24
244.8	445	1.08	1.21	2.10	1.86	5.72				20
245.3	446	1.24	1.40	1.64	1.37	5.11				86
255.2	464	0.51	1.31	2.94	2.83	5.53	78	72	7	100
270	491	1.53	2.30	6.30	5.97	15.28	192	165	14	76
286	520	0.88	1.36	8.41	8.22	14.78	71	67	7	100
300.3	546	1.04	1.48	2.60	2.37	7.04	2009	1078	46	100
315.2	573	1.09	1.74	3.28	3.04	5.24	543	310	43	100
330	600	1.28	1.97	4.39	4.11	12.99	1986	1421	28	100
344.8	627	1.33	2.00	5.30	5.01	12.82	487	467	4	100

Table 1. Note: All values represent 55 cm mean values of between 11 and 22 individual samples.

times higher than the ratio at GRIP of 0.12. No significant changes in the ratio of magnesium and calcium with increasing depth is observed.

The sea salt correction on the concentrations of Mg²⁺ appear to be reasonable because all Na⁺ and most of Cl⁻ in Hans Tausen ice is believed to be from sea salt. In Fig. 5 the Cl⁻ concentrations are plotted versus Na⁺. Chloride and sodium are correlated, and the molar ratio of chloride and sodium is close to the ratio in sea salt: $[Cl^-]/[Na^+] = 1.17$. There are several points that show an excess of chloride, but chloride has other sources than sea salt. In particular, volcanic eruptions may contribute HCl, and since several samples were taken across volcanic eruptions, a slight excess of chloride is expected. However, there are very few outliers with excess sodium so that the bulk of sodium can be assumed to originate from sea salt and nss. Mg²⁺ can be calculated using the sea salt molar ratio between sodium and magnesium: $[Mg^{2+}]/[Na^{+}] = 0.22$. The mean sea salt concentration in Hans Tausen ice does not show significant variation with depth. The Hans Tausen concentrations are $0.5 - 1.5 \mu equiv./kg$ as compared to GRIP Holocene values of 0.3 - 0.4 µequiv./kg, i.e. 2-3 times higher.

Discussion

The mean dust mass of the upper part of the Hans Tavsen core is around 80 μ g/kg. This is significantly higher than the 40 μ g/kg in GRIP Holocene ice (Steffensen 1997). On the other hand, annual accumulation is 0.11 m ice/yr as compared to GRIPs 0.22 m ice/yr. Thus the dust fluxes at Hans Tausen and GRIP are comparable. The size distributions are comparable with modes of 0.9 μ m at Hans Tausen and 0.85 μ m at GRIP. The dust in the GRIP core is of remote origin, since the site is on the central part of the Greenland ice sheet far removed from any local dust source areas. In fact, iso-



tope studies on the dust particles from the nearby GISP2 core suggest an Asian origin of the dust (Biscaye *et al.* 1997). Since GRIP and Hans Tausen sizedistributions and dust fluxes are comparable it suggests that the dust in the upper part of the Hans Tausen ice core is also of remote origin.

The GRIP dust sizedistributions and concentrations show very little variation in the Holocene period. Since the dating of the Hans Tausen ice core and the stable isotopic profile indicate that the whole ice core is from the Holocene (C.U. Hammer et al. 2001) then the increase in dust mass with depth in the Hans Tausen core has no counterpart in GRIP, and it is caused by increasing mass of large particle fraction. The mass ratio of large particles is high at high dust mass in the Hans Tausen core, which is contrary to the low mass ratios at high dust mass in the GRIP core. The large particle fraction with modes of 2 um or more appears sporadically through the Hans Tausen profile but becomes more and more dominant with depth. Below 300 m it dominates completely. The mean sizedistributions have modes close to 2.5 and such distributions have not been observed at GRIP or at Dye-3 at all.

function of depth for individual 5 cm samples in the segments analyzed. The variation in dust mass within each segment causes the results to appear as vertical lines, which gives an idea of the variability of dust mass. Note, that the dust mass scale is logarithmic.

Fig. 1. Dust mass as

Fig. 2. Mean microparticle size distributions of six selected 55 cm ice core segments. Bag numbers refer to the numbers in Table 1. Total dust mass is given above each plot. Dust mass in selected particle radius intervals are also indicated. The data points represent measurements. The full lines are the log-normal distributions fitted to the data. The mode and standard deviation of the lognormal fits are given at the bottom of the plots as "µ" and "(" respectively. The GRIP Holocene mean sizedistribution has been added for comparison.



Measurements of the sizedistribution of dust particles in air over arid dust producing areas in the U.S. yield lognormal distributions with modes of 2-3µm (Patterson and Gillette 1977). They argued, that these distributions are consequences of the physical mechanisms of wind action on the surface particles to produce dust aerosol. Dust aerosols in the free troposphere, i.e. 3-5 km altitude

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have modes of about 1 µm (Patterson et al. 1980). The 2-3 µm mode dust aerosols have been modified by gravitational settling and removal by condensation in clouds of primary the large particles. Therefore, we may assume that the large particle fraction in Hans Tausen are of local origin. We investigated if the presence of very large particles was due to changes by melting and refreezing processes, but we found also large particles in ice outside the melt layers. The dust in Hans Tausen ice appears to have two components: Dust from remote sources with log-normal modes of around 1 µm, and dust from local sources with modes around 2 µm. In most cases, one or the other component dominates; but in Bag 627 we were lucky to identify both components (see Fig. 2). The very large concentrations below 300m occur in ice with 100% indication of melt and could be caused by two things:

- 1) The ice cap was smaller at the time of deposition (C.U. Hammer 2001; Keller 2001) local sources were therefore closer, and
- 2) The layers below 300m have experienced significant run-off by melting.

This would cause the water phase to run off and leave the microparticles behind, increasing the dust concentration (Koerner 1997). This could also explain why $Ca^{2+}/dust$ ratio points from great depth in Fig. 3 are outliers. The Ca^{2+} has been washed out; but the dust remained.

Both factors appear to be significant. The decreasing frequency of dust layers with large particles with time (increasing frequency with depth) can be explained by less likelihood of local dust being blown unto the snow due to the growing of the ice cap and increased snow cover over the local sources. The "jump" in concentrations at 300m may mark a time in the development of the Hans Tausen ice cap where run-off by melting stopped. This is also indicated by the shift in the stable isotopic profile



around this depth (C. U. Hammer *et al.* 2001) and the end of the 100% indication of melt layers in the core (K. Nørregaard Madsen 2001)

There is far more Ca²⁺ in Hans Tausen than at GRIP. Also the relative concentration of nss. Mg2+ to Ca2+ is much higher. At the same time, the ECM measurements and ionic balance calculations indicate that the Hans Tausen ice generally is slightly alcaline. This is most likely due to the presence of large enough amounts of dissolved (Mg,Ca)carbonates in the ice samples to neutralize the strong acids such as sulfuric acid and nitric acid. Only in layers containing very large amounts of acid fallout from volcanic eruptions the Hans Tausen ice is acidic (H. B. Clausen pers. comm.). At Dye-3 and GRIP the ice from the Holocene remains acidic. The strong presence of dissolved (Ca,Mg)-carbonates in Hans Tausen ice is most likely from local sources of soluble carbonate dust particles from exposed carbonate rich sediments such as dolomite which are abundant in the Peary Land area (Dawes 1976).

With respect to sea salt, the high sea salt concentrations at Hans Tausen compared to GRIP is not surprising. Herron (1982) showed that sea salt concentraFig. 3. Dust mass plotted as function of Ca^{2+} concentration for 55 cm ("Bag") averages. Data are given in Table 1. For comparison the correlation between Ca^{2+} and dust for Dye-3 and GRIP (Holocene) and GRIP (Glacial ice) are shown as lines. Five outlying points are labeled with their corresponding depths.



Fig. 4. Non sea salt (nss.) Mg^{2+} concentrations plotted as function of Ca^{2+} concentrations for 55 cm ("Bag") averages. Data are given in Table 1. The full line represents linear regression of the Hans Tausen points. The dashed line is a similar regression line for GRIP data for comparison. tions decrease with altitude. However, the concentrations at Hans Tausen are slightly lower than estimated by the relationship of Herron. Also, Herron only discussed concentration data. If sea salt fluxes are calculated by inferring observed annual accumulations, the sea salt flux at Hans Tausen is significantly lower than would be expected at this altitude.

The Hans Tausen ice core is the only core from the northern coast of Greenland studied so far. The north coast borders the North Polar Sea. This ocean is mainly ice covered throughout the year, and it is not believed to be a significant source of marine sea salt aerosol. The sea salt flux at Hans Tausen ice cap (100 µequiv./m²/yr of Cl⁻) is comparable to the flux on the Central Greenland ice sheet (80 µequiv./m²/yr of Cl-). A detailed pit study at the drilling site revealed that in the surface snow at Hans Tausen ice cap the seasonal variation of sea salt concentrations shows winter highs and summer lows. This is similar to the seasonal pattern observed in Central Greenland (Steffensen 1988) and in aerosol measurements at Station Nord (on the Greenland North coast) (Heidam et al. 1993). This contrasts the seasonal pattern of sea salt concentrations in the aerosol at the coastal sites of East and West Greenland with summer highs and winter lows which is believed to be a consequence of the changing sea ice cover in the local sea (Heidam 1984). Thus the sea salt in the Hans Tausen ice core is believed to be from remote sources and in terms of sea salt the Hans Tausen ice resembles the Central Greenland ice cores. NaCl is readily soluble so in periods of heavy melting and run-off the sea salt is expected to run-off at the same degree as water. This means, that the concentration of sea salt is not expected to change due to heavy melting. This may explain why we do not see a change in sea salt concentration with depth in the Hans Tausen ice core. On the other hand, the lack of change with depth also indicates, that the North Polar Sea has never been a significant source of sea salt in the snow here, and has therefore probably not been ice free in the life time of the Hans Tausen ice cap.

Conclusions

Sodium is well suited as indicator of sea salt in the Hans Tausen core. The sea salt flux to the Hans Tausen ice cap is comparable to the flux to the Central Greenland ice sheet. The seasonal variation of sea salt concentrations in Hans Tausen snow shows winter highs and summer lows which is in agreement with the seasonal variations observed in Central Greenland and at Station Nord on the north coast of Greenland; but not in agreement with observations at coastal sites in West and East Greenland. The sea salt in Hans Tausen ice cap is believed to be from remote sources and not from the North Polar Sea. It appears, that the North Polar Sea has not been a significant source of sea salt for the Hans Tausen ice cap during its lifetime.

For the first time in Greenland we have identified two different fractions of microparticles characterized by their log-normal modes. Local dust with a

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log-normal mode of $2 - 3 \mu m$ and dust from remote sources with modes around 1 um. The influence of local dust decreases over time. Very high dust concentrations close to bedrock are thought to be due to run-off of melt water during the initial build-up of the ice sheet. Influx of soluble carbonate rich particles from local sources makes the ice slightly alcaline. The ratio between dust mass and Ca²⁺ has been changed in the deep part of the core due to melting and runoff. Sea salt and dust concentrations in the younger snow are comparable with Central Greenland concentrations. All together, these results support the overall interpretation that the Hans Tausen ice cap has been developing from a small glacier where melting and influence from local sources was dominant, into a larger glacier where the impurity content in the ice from the atmospheric aerosol is comparable with the contents in Central Greenland ice. The only "Hans Tausen finger print" that remains in modern Hans Tausen snow as opposed to Central Greenland snow is the high concentrations of (Ca,Mg)-carbonates from local sources.

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Fig. 5. Cl⁻ concentrations plotted as function of Na⁺ concentration for 55 cm ("Bag") averages. Data are given in Table 1. The full line indicates mean sea salt composition with a molar ratio between chloride and sodium of 1.17. determined by use of GPS. Meddelelser om Grønland Geoscience, this volume pp. 115-122.

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