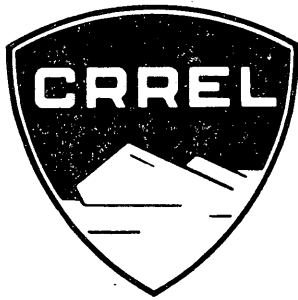


SR 188



Special Report 188

**SOLUBLE PARTICULATES IN ICE
FROM
SITE 2, GREENLAND**

George O. Linkletter

July 1973

**CORPS OF ENGINEERS, U.S. ARMY
COLD REGIONS RESEARCH AND ENGINEERING LABORATORY
HANOVER, NEW HAMPSHIRE**

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

**SOLUBLE PARTICULATES IN ICE
FROM
SITE 2, GREENLAND**

George O. Linkletter

July 1973

PREPARED IN COOPERATION WITH
NATIONAL SCIENCE FOUNDATION
GRANT 104

CORPS OF ENGINEERS, U.S. ARMY
COLD REGIONS RESEARCH AND ENGINEERING LABORATORY
HANOVER, NEW HAMPSHIRE

PREFACE

This report was prepared by Dr. George O. Linkletter, Assistant Professor of Atmospheric Physics, Desert Research Institute, University of Nevada.

The project was financed through a U.S. Army Cold Regions Research and Engineering Laboratory grant to the Department of Earth Sciences, Dartmouth College, and was supported in part by the Office of Polar Programs, National Science Foundation, under NSF grant AG 104. The laboratory investigations described were carried out at USA CRREL, Hanover, New Hampshire.

Numerous individuals on the USA CRREL staff helped with advice and useful discussion, particularly Dr. M. Kumai, Dr. S. Leung and Mr. M.A. Bilello. Mr. M. Bothner contributed valuable laboratory assistance. Dr. R.C. Reynolds and Dr. J.B. Lyons of Dartmouth College contributed discussion and advice throughout the project. Professor J.A. Warburton of the Desert Research Institute offered valuable advice during revision of an early draft of this report.

The author particularly wishes to thank Dr. C.C. Langway, Jr., of USA CRREL for his assistance, advice, and encouragement throughout the study and for making valuable suggestions on the preparation of this manuscript.

The contents of this report are not to be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official endorsement or approval of the use of such commercial products.

Revised manuscript received 10 May 1973.

CONTENTS

	Page
Introduction	1
Laboratory procedures	1
Results	3
Observed stratigraphy	3
Thin sections	3
Ice density	3
Cationic concentrations	4
Particle collections	6
Summary and discussion	10
Literature cited	11
Appendix A. Density of ice samples and the interpreted seasonal layers	15
Appendix B. Size class (diameter) and total particle concentration per gram of ice	17

ILLUSTRATIONS

Figure

1. Density variations with depth and the distribution of summer and winter layers	4
2. Measured variation, with depth, within the three size classes of particles studied	7
3. Diagrams showing the variation of potassium-bearing particles per gram of ice and of the K ⁺ ionic concentration appear to roughly parallel one another	9

TABLES

Table

I. Mean cation concentration	5
II. Summary of published chemical data for Greenland snow and ice	6
III. Size distribution of black spherules	8
IV. Morphological classification of soluble particles	8
V. Distribution of potassium-bearing particles	8

SOLUBLE PARTICULATES IN ICE FROM SITE 2, GREENLAND

by

George O. Linkletter

INTRODUCTION

Because the interior of the northern Greenland ice sheet is in the dry snow zone of a high polar glacier (Ahlmann 1953; Benson 1962), there is a virtual absence of melting. Aerosol particles, which reach the surface of the ice sheet as ice crystal nuclei or by other washout or dry fallout mechanisms, should be retained within the layer of snow in which they fall. Several investigators have found seasonal layering in snow in northern Greenland, and Langway (1962, 1967) has shown that certain physical and chemical parameters retain their cyclic behavior to at least 100 m depth.

Numerous studies on the chemistry of Greenland snow and ice have centered on major elemental concentration (Junge 1960, Langway 1962, 1967, Rodriguez 1964, McCorkell 1968, Murozumi et al. 1969, Federer 1970, Boutron 1971, Ragone et al. 1972). Fewer investigations have been concerned with stable isotope chemistry (Johnsen et al. 1972, Dansgaard et al. 1969). The concentration and, to a limited extent, the composition of insoluble particles contained in the snow and ice have also been studied (Kumai and Francis 1962, Langway 1962, 1967, Langway and Marvin 1964, Hamilton and Langway 1967).

The present investigation was conducted in an attempt to collect the soluble particles contained in a sample of Greenland ice, to devise procedures for the study of the size distribution and chemistry of these particles, and to investigate the relationship between the concentration and chemistry of these soluble particles and the elemental concentration of the ice.

LABORATORY PROCEDURES

USA CRREL provided 89 cm of continuous half-core of ice (split lengthwise) from Site 2, Greenland (76° 59'N, 56° 04'W). The ice was retrieved from 94.11 to 95.00 m below the snow surface during 1957 drilling operations. Core drilling procedures have been summarized by Langway (1967). Cooled, compressed air, not a liquid as in more recent drilling, was used as the drilling fluid. Interpolation from the Site 2 depth-density data indicates that the ice studied fell as snow in 1780 ± 5 years (Langway 1967).

Advance planning was necessary to maximize the number of tests possible with the half-core provided. Evaluation of possible interrelationships among test results, the amount of ice needed for each test, the destructive character of the tests, and the overall study objectives led to the routine outlined below.

1. *Observation of stratigraphy*: Each piece of ice (14-27 cm long, labeled and oriented for up direction as described by Langway, 1967) was examined for visible stratigraphy on a light table. All observed phenomena were logged to scale and classified.

2. *Thin section examination*: Thin sections were made down the length of the core and each section was photographed between crossed nicols while a centimeter grid overlay provided scale. The average grain size for each 1-cm vertical increment was obtained by counting the number of grains per square centimeter on 2X enlargements of the sections.

3. *Ice density determinations*: Each piece of core was then cut into a number of 4- to 5-cm-high vertical increments on a bandsaw used only for cutting snow and ice. The density of each of 21 small pieces was determined using the hydrostatic method. Density values are corrected to the in situ ice temperature, -25°C , and are considered accurate to $\pm 10^{-3}$ g/cm³.

4. *Measurement of cationic concentrations*: The concentrations of Na^{+} , K^{+} , Mg^{2+} and Ca^{2+} in each small vertical increment of a quarter core were measured in melted ice on a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer using a Boling burner head. The manufacturer's recommended procedures were followed for each cation, and no pre-analytical concentration was attempted. Four standards, diluted from a 10^{-3} g/ml stock standard, provided data for a least squares fit linear calibration line for each cation. The detection limits (concentration detectable with a 95% certainty) listed by Perkin-Elmer for the procedures followed in this study are: Na^{+} and K^{+} , 5×10^{-9} g/ml; Mg^{2+} , 3×10^{-9} g/ml; Ca^{2+} , 10×10^{-9} g/ml.

Contamination control studies were conducted prior to the actual analyses in order to devise a cleaning procedure and to insure that no contaminants would be introduced during handling of the samples. Using "clean ice" made from distilled, thrice deionized water, contamination-free results to the limits of detection noted above were found using the following procedures.

The small (60-100 g) pieces of ice previously cut on a bandsaw (used only for snow and ice) were placed in a plastic-coated lens holder which suspended the sample from two points. Warm, distilled, thrice deionized water was then sprayed on the sample from a filtering wash bottle. Three successive washings, each removing a layer of ice from the sample, were found sufficient to remove surface contamination from "clean ice" which had been purposely contaminated by contact with bare hands. Clean stainless steel tongs were used to transfer the ice to the pre-cleaned, wide-mouth polyethylene bottle in which the ice was sealed and kept frozen until a few hours before the chemical analysis was undertaken. Both the stainless steel tongs and the polyethylene bottles were cleaned by leaching in distilled, deionized water (one week's leaching followed by ultrasonic vibration, and one month's leaching in a new filling of water). Four pieces of "clean ice" were processed with the actual samples and none of the four cations being investigated were found in these blanks.

5. *Particle collection and examination*: Because of the expected small yield of particulate matter, contamination control studies were conducted using the "clean ice" described above. Each step of the cleaning (same as for chemical analysis samples) and particle collection procedure was monitored by including clean Millipore filters (47 mm, $0.45 \mu\text{m}$) with the sample and subsequently examining the monitor filters under an optical microscope.

A simple, easily cleaned vacuum system which maintained 2 mm Hg pressure and a temperature between -1° and -2°C was assembled in a coldroom. Each cleaned sample was placed on a Millipore filter in a plastic Petri dish using clean stainless steel tongs. This unit was then placed on the vacuum plate and the system sealed. Total sublimation of the 27- to 50-g pieces of ice required from 36 to 48 hours. Following sublimation, the system was opened by venting filtered air through a capillary tube in order to avoid disturbing the particles resting on the filter. Each sample filter was stored in a closed Petri dish until microscopic and chemical analyses were performed.

The number, appearance and sizes of particles on each filter were determined by examination under an optical microscope. A Wild point-counting stage attached to the microscope stage and an ocular grid (which outlined a 100- μm -diameter circle on the filter) delineated the area in which particles were counted. The limit of the optical microscope, between 1 and 2 μm , set the lower detection limit. Particles were classified by color (clear-white-tan versus black-dark gray-brown) and size ($\leq 5 \mu\text{m}$, 5 to $\leq 15 \mu\text{m}$, $> 15 \mu\text{m}$).

Chemical spot tests are well known for their use in the analysis of aerosols collected by airborne techniques (Lodge 1954, 1955, Lodge and Tufts 1956, 1957, Lodge and Fanzoi 1954), and have been discussed at some length by Feigl (1958).

Chemical spot tests were made on soluble particles in the sublimation collections in an attempt to 1) relate particle color and morphology to chemical composition and 2) study the variation of a given ion with depth. Individual particles were tested for chloride (AgNO_3 reagent, 1.5 μg detection limit), ammonium (Nessler's reagent, 0.3 μg), potassium ($\text{Na}_3\text{Co}(\text{NO}_2)_6$, 4.0 μg), sodium ($\text{Zn}(\text{UO}_2)_3(\text{CH}_3\text{COO})_9$, 2.5 μg), and calcium [$(\text{NH}_4)_4\text{Fe}(\text{CN})_6$, 25 μg]. Reagents were applied with microsyringes while the particles were viewed under the microscope. Three filters were used for individual particle tests.

The total particle population of each of the remaining 26 filters was tested for K^+ in order to observe the variation in the number of potassium-bearing particles over the length of the ice core. Each filter was saturated with sodium cobaltinitrite reagent for five minutes. Three successive washings on blotters saturated with distilled, deionized water removed the excess reagent, leaving only the insoluble particles and reaction sites. The filters were then examined under the microscope and reaction sites counted.

In an attempt to obtain an accurate determination of the chemical compounds which comprise the soluble particles, X-ray powder patterns were taken of four samples following standard procedures (Hurlburt 1963) and the ASTM card file. Particles to be X-rayed were lifted from the filters by touching them with a Vaseline-coated spindle which was in turn placed in the powder camera.

The analysis of the particle collections was conducted within a laminar-flow workbench producing air from which 99.97% of particles $> 0.5 \mu\text{m}$ had been removed.

RESULTS

Observed stratigraphy

Five definite stratigraphic features were observed in the ice sample (Fig. 1). All are classified as slight indications of melt (SIM). Four of the features occur in summer layers, while the fifth and smallest (probably a wind crust) is located in a winter layer.

Thin sections

Thin sections may be used to study texture, structure, and grain size. However, because the average grain sizes computed for 1-cm vertical increments showed no correlation with seasonal layers, ionic chemistry, or particulate content, a more rigorous investigation of the thin sections was not undertaken.

Ice density

Measured densities are presented in Appendix A and summarized in Figure 1. Langway (1967) has shown that variations in oxygen isotope ratio ($\text{O}^{18}/\text{O}^{16}$) delineate summer from winter layers in

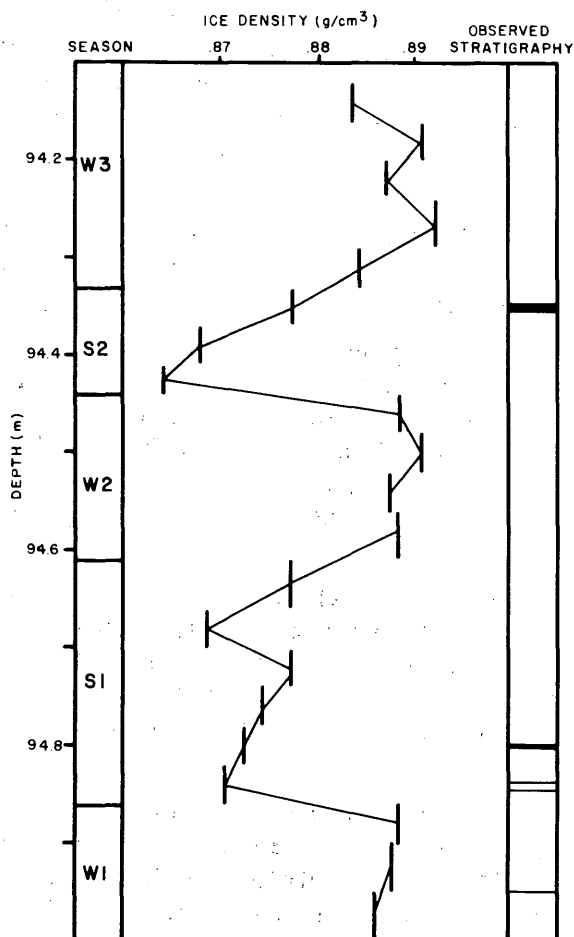


Figure 1. Density variations with depth and the distribution of summer (S) and winter (W) layers. Observed SIM are found primarily in summer layers.

Greenland snow and ice. In studies over the upper 100 m, Langway also found that variations in ice density can be correlated with oxygen isotope variations and thus also serve to delineate summer from winter layers. In Greenland dry snow areas, the density of winter snow layers is greater than that of summer layers. Based upon Langway's findings, the density values determined in the present study are interpreted to define five seasonal zones: two complete summers, one complete winter, and portions of two other winters. These zones are designated W1 (oldest winter), S1, W2, S2, and W3 (youngest winter). All other data are evaluated with respect to the seasonal divisions indicated in Figure 1.

Cationic concentrations

Measured values for Na^+ , K^+ , Mg^{2+} , and Ca^{2+} concentrations are listed in Table I. Computation of cation concentrations, based upon least squares fit standard lines, has led to values different from those previously reported for these samples (Linkletter 1970). Whereas Na^+ and K^+ values are lower than previously reported, Ca^{2+} and Mg^{2+} are slightly higher. Some of the most recent studies on the chemistry of polar snow and ice (e.g. Murozumi et al. 1969, Boutron 1971)

Table I. Mean cation concentration.

Based upon three analyses on each meltwater sample. The F.S.D. listed is an average of the deviations among the three analyses on individual samples for each cation. T = Trace; ND = Not Detected.

Sample	Concentration (10^{-9} g/ml)			
	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
454 A	43	40	.11	26
B	29	T	10	22
C	38	18	13	29
D	27	14	10	24
455 A	323	329	16	89
B	445	519	17	94
C	124	132	17	39
D	57	57	12	23
456 A	138	148	20	55
B	153	128	21	48
C	101	51	24	63
D	60	26	13	30
E	54	49	10	ND
457 A	47	40	8	30
B	19	5	6	ND
C	46	51	10	40
D	28	22	9	28
E	64	61	13	56
458 A	25	30	9	21
B	25	T	10	52
C	30	14	10	23
Mean	89	83	13	38
F.S.D.	2%	4%	12%	17%

suggest that some earlier reported values (e.g. Langway 1967) may reflect contamination rather than in situ ice chemistry. Some of the values listed in Table I may also reflect contamination. Although contamination control tests clearly proved that no contamination was occurring during laboratory handling, the tests did not investigate the amount of cleaning necessary to remove previous contamination of the ice samples. Recent work (Ragone and Finelli 1972) has shown that a 50% reduction in sample volume during washing is often necessary to remove contaminants. Only about 10% of the ice was removed from each sample during the washing procedure used in this study.

A sampling of published Greenland snow and ice chemistry data is presented in Table II. If concentrations measured in the present study (Table I) which exceed the means of values listed in Table II by two standard deviations of those values are rejected as being suggestive of contamination, a "corrected mean" can be calculated for each cation. Using this procedure, the rejection levels are: Na⁺ and K⁺ > 45 ppb, Ca²⁺ > 32 ppb, Mg²⁺ > 43 ppb. The "corrected means" are: Na⁺ 29 ppb, K⁺ 19 ppb, Mg²⁺ 13 ppb (no change), Ca²⁺ 21 ppb.

The probable reflection of contaminants by a significant number of the samples (Na⁺ 12, K⁺ 10, Ca²⁺ 9) precludes an analysis of seasonal trends, and the previously proposed annual variation of Mg²⁺/Na⁺ and Mg²⁺/K⁺ (Linkletter 1970) must be rejected at this time.

SOLUBLE PARTICULATES IN ICE FROM SITE 2, GREENLAND

Table II. Summary of published chemical data for Greenland snow and ice.

Reference	Location	Concentration (10^{-9} g/ml)			
		Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Junge (1960)	S2	30	10		35
Langway (1962)	S2	97	77		
Langway (1967)	S2	166	127	22	50
	AG	77	60	24	38
Rodriguez (1964)	CC	20	30		100
Ragone et al. (1972)	CC*	31	12	5	13
	CC†	41	16	28	124
Murozumi et al. (1969)	CC	20	3	5	6
Boutron (1971)	JJ	23	10	11	8
	Ce	36	25	10	11
	Ca	35	50	8	3
	Mi	30	9	44	11
	Cr	15	10	18	6
	Mean**	28	18	16	12
This study	S2				
Mean		89	83	13	38
Corrected mean		29	19	13	21

*Lower concentration zones.

†Higher concentration zones.

**Simple mean of published data exclusive of Langway (1962, 1967).

Particle collections

During the microscopic examination of the filters bearing particles collected by the sublimation of the ice samples, 2000 points were counted on each filter. Because this covered only 5% of the filter area, raw counts were multiplied by 20 to arrive at the total number of particles per filter. Standardization of the particle count data was achieved by calculating the number of particles per gram of ice. The data are presented in Appendix B and summarized in Figure 2. Recounting several filters suggested that the figures are accurate to $\pm 3\%$.

In evaluating these data, the following must be noted:

1. The $< 5 \mu\text{m}$ class is open ended because of the limits of resolution for the optical microscope. Figures for this class are probably dominated by data for the size range 2-5 μm .
2. Many of the particles classified as $> 15 \mu\text{m}$ are actually aggregates of smaller particles. No systematic method of determining the number or size of particles in a given aggregate was devised. The bulk of the aggregation is thought to be the result of the collision of particles on the surface of the sublimating ice.
3. Because the same basic cleaning and handling procedures were used here as for the ionic chemistry samples, the possibility of residual contamination cannot be ruled out.

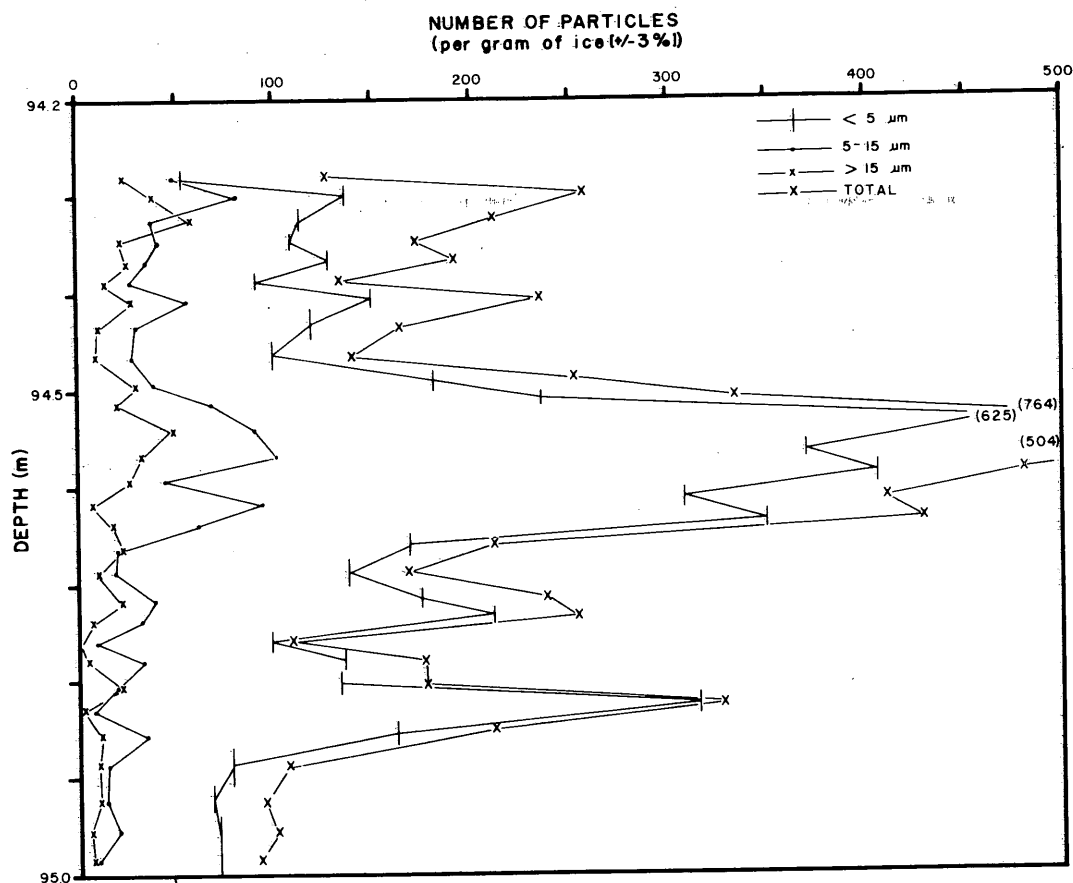


Figure 2. Measured variation, with depth, within the three size classes of particles studied. There is no apparent correlation of the number of particles per gram of ice with seasonal layers.

The four curves in Figure 2 show similar trends. Over the sample length there is no indication of a seasonal variation in particle influx. Total particles per gram of ice show no relation to the total cations measured (correlation coefficient 0.10).

Although insoluble particles are common in the collections, they were not studied in detail. Insoluble particles were observed during all filter examinations and are estimated to constitute approximately 90% of the total particle population visible under the optical microscope. No insoluble particles greater than 20 μm were observed, with 80% or more being < 5 μm diameter. Most of the insolubles had a flat, plate-like appearance. Particles with such shapes found as snow crystal nuclei on the Greenland ice sheet are identified as clay minerals by electron microscopy and electron diffraction (Kumai and Francis 1962). Increase in size of insoluble particles is paralleled by a tendency toward a more rounded shape. All black spherules encountered during the counting and scanning of the filters were noted and their diameters measured. Of the 37 spherules found, 5 were shiny and the others displayed varying amounts of pitting. No distribution pattern was evident in this sample. The sizes found are summarized in Table III.

The soluble particles on the filters can be divided into five morphological classes (Table IV). Types 1, 2 and 3 were found on all filters, whereas types 4 and 5 had an irregular distribution which could not be correlated with any known factor. Types 2 and 3 were by far the most common. Tests on individual particles failed to establish any relation between chemical composition and particle morphology.

Table III. Size distribution of black spherules.

	Size range (μm)					
	< 5	6-10	11-15	16-20	21-25	> 25
Shiny	0	2	1	0	1	1
Pitted	10	10	6	1	0	5
Total	10	12	7	1	1	6

Table IV. Morphological classification of soluble particles.

Shape	Color	Size range	Positive tests	Comments
(1) Acicular	White-light brown	3-25 μm	NH_4 , K, Na	Many insoluble inclusions
(2) Cubic	Yellow-brown	5-40 μm	K, Na, Cl	Greasy appearance
(3) Irregular	Yellow-brown	3-25 μm	K, Na, Ca, Cl	Greasy appearance
(4) Spheroidal	Tan	5-25 μm	K, Na, Cl	Semi-soluble skin, striated
(5) Spheroidal	Tan	5-20 μm	K, Na	No skin, shiny

Table V. Distribution of potassium-bearing particles.

Sample	K-particles/g ice	Avg values/g ice
455 A1	36.82	
A2	18.21	W3 27.52
B1	36.01	
B2	*	
C1	6.28	S2 16.18
D1	6.25	
456 A1	18.54	
A2	5.74	
B1	4.43	
C1	5.38	W2 9.48
C2	4.36	
D1	10.07	
D2	9.76	
E1	17.60	
E2	6.21	
457 A1	12.98	
A2	2.34	
B1	1.81	
B2	1.29	S1 6.34
C1	9.11	
D1	3.40	
D2	5.28	
E1	3.45	
458 A1	5.70	
B1	2.02	W1 3.15
C1	1.74	

*Used for individual particle tests.

Winter average 10.80
 Summer average 8.62
 Total average 9.39

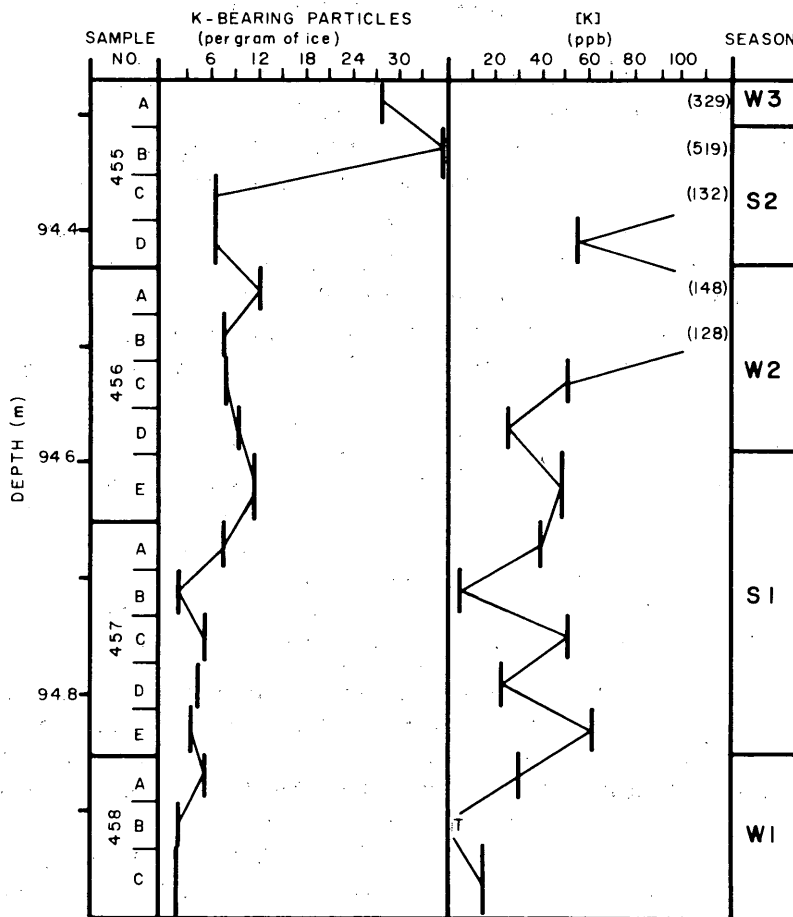


Figure 3. Diagrams showing the variation of potassium-bearing particles per gram of ice and of the K^+ ionic concentration appear to roughly parallel one another (correlation coefficient 0.93).

Whole-filter spot tests were made for potassium on 26 filters. The reaction spots and rings (referred to as reaction sites) were counted, and the raw counts converted to K-reaction sites per gram of ice (Table V). No regular seasonal variation was found. Curves for K-reaction sites per gram of ice and K^+ concentration (atomic absorption values) appear roughly to parallel one another (Fig. 3). In fact, their correlation coefficient is 0.93.

It was noted that many of the K-reaction sites contained a small amount of insoluble material and could thus be classified as mixed nuclei. Almost all of the larger K-reaction sites had insoluble material present, whereas a lower percentage of the small reaction sites had insoluble material associated with them. Mixed nuclei are thought to be of continental origin (Twomey 1954, Junge 1957), as are potassium salts in general (Mason 1957).

All four samples that were X-rayed produced identical diffraction patterns, but definite identification of the material could not be made. However, it is possible to say that solubles of types 2 and 3 are neither primarily simple salts (e.g. KCl , $NaCl$, etc.) nor their common hydrates. Whether complex salts could form during the experimental sublimation process is not known.

SUMMARY AND DISCUSSION

Using variations in density, seasonal layers have been defined down the length of an 89-cm ice core from Greenland. Two and one-half years of snowfall are present in the ice sample studied. Four melt features in the core are located in summer layers. One apparent melt feature in a winter layer is interpreted as a wind crust. Grain size shows no correlation with the seasonal layers.

Careful contamination control procedures used in this study clearly demonstrate that the ice samples were not contaminated during analysis. These procedures did not, however, ensure that any previously acquired contamination had been removed completely. More recent work by Ragone and Finelli (1972) suggests that approximately the outer half of the ice sample must be removed to be rid of all surface contamination. Approximately 10% of the ice was removed from each sample during cleaning in the present study.

Based upon a comparison with published Greenland snow and ice chemistry values (Table II), it appears that 12 Na^+ , 10 K^+ and 9 Ca^{2+} values are too high to be accurate measures of the concentration of these cations in uncontaminated ice. If these values are rejected, "corrected mean" concentrations become Na^+ 29 ppb, K^+ 19 ppb, Mg^{2+} 13 ppb, and Ca^{2+} 21 ppb. The rejection of the apparently unreasonable data eliminates the possibility of investigating seasonal trends for cation concentration or cationic ratios. Because of this reevaluation, the seasonal trends for $\text{Mg}^{2+}/\text{Na}^+$ and $\text{Mg}^{2+}/\text{K}^+$ reported by Linkletter (1970) can no longer be considered valid.

Sublimation of small ice samples yields collections of particulate matter, both soluble and insoluble, contained in the ice. These collections are well suited for microscopic examination and microchemical testing, and the resulting data are thought to be less influenced by contamination than those for soluble components only. Recent work by Hamilton and Langway (1967) found an excellent positive correlation between small particle (0.6-3.0 μm diameter) concentrations and seasonal oxygen isotope variations. Counts on larger particles in the present study show no regular seasonal cycle. No correlation was found between particle concentration and cationic concentrations.

In the year represented by layers W2 and S2 (which had a snow accumulation of 36.8 g/cm^2), it would be expected that about 1500 particles in the 5- to 15- μm -diameter class would be found in a 1-cm^2 column over the year's increment. This is based upon the 40 particles/g ice average for that year. This means an average influx rate of 28 of these large particles per week. Using Langway's (1967) calculated washout time and the particle data from the present study, a concentration of 1.1×10^{-4} 5-15- μm -diameter particles per cm^3 of air over Site 2 is calculated. A similar calculation yields 0.6×10^{-4} particles greater than 15 μm per cm^3 of air. Junge (1963) has reported the concentration of particles greater than 6.4 μm , over both continents and oceans, to be $290 \times 10^{-4}/\text{cm}^3$ of air. This is approximately 160 times the value which this study estimates for the interior of northern Greenland.

A calculation based upon the number of K^+ -bearing particles and the "corrected" concentrations and relative abundance of the cations found in this study suggests that approximately 4% of the particles studied were hygroscopic salts. The difference between this figure and that of Kumai and Francis (1962) (0.6%) probably can be explained by the difference in aerosol sizes studied (Junge 1957) and the fact that whereas Kumai and Francis considered only snow crystal nuclei, this study included "wet" removal and dry sedimentation contributions. Wet deposition appears to be the dominant mechanism for the removal of marine aerosols from the atmosphere (Junge 1963, Murozumi et al. 1969). Comparison of the above suggests that more than 80% of the soluble salts in the Greenland ice sheet derive from wet removal of marine aerosols from the atmosphere.

Only a few studies have been made of the seasonal variation for the physical and chemical parameters of the Greenland ice sheet. Although seasonal variation of the oxygen isotope ratio and of the snow density are well known, other variables are less understood. Langway (1967) reported seasonal variation for Cl/Na, SO_4/Cl , and specific conductance that indicate a fall-winter maximum for solubles. However, Langway's data are thought by some to reflect contamination (Murozumi et al. 1969, Boutron 1971). Based upon the study of a single one-year layer of snow and the assumption that marine aerosols have the same elemental proportions as sea water, Murozumi et al. (1969) reported a fall-winter maximum for marine aerosols and a spring maximum for continentally derived dust. A pronounced cycle with a winter maximum has been found for 0.6- to 3.0- μm -diameter insoluble particles (Hamilton and Langway 1967). Although no regular cycle for the $> 2 \mu\text{m}$ particle concentration was evident in this study, both fall layers and one of the spring layers are marked by distinct concentration maxima.

The seasonal variability of the weather systems affecting Greenland (Dorsey 1951, Putnins 1970) provides a mechanism for variable transport of aerosols to the ice sheet. Whereas weak zonal circulation and only infrequent storms characterize the summer, intense storm activity accompanies the return to strong zonal circulation in the fall. Because winter circulation has a strong meridional component, it is the most important time for warm maritime air penetration over the ice sheet. In addition, seasonal cycles of sea ice and open water around Greenland, and of snow cover and exposed soil in coastal Greenland and the Arctic islands, suggest a source of variability in aerosol composition and concentration.

Suggested seasonal trends for the chemistry and particulate content of the Greenland snow and ice generally fit with the seasonal weather variations. For example, the winter maximum for 0.6- to 3.0- μm -diameter insoluble particles occurs at the time of greatest meridional transport of air masses. It has already been suggested that these particles originate from distant sources because of the uniformity of their cycle (Murozumi et al. 1969). The irregular variability of the larger particles studied here, along with their more limited transport distances imposed by inherently greater fall velocities, suggest a more local source. The autumn maxima would occur when the intense fall storms move over the not yet snow-covered coastal source areas. The irregularity of the variation in these large particles is probably traceable to their more limited and necessarily regional source areas and the need for sufficiently strong winds to transport the particles into the interior of Greenland.

Murozumi et al. (1969) have suggested that approximately twice as much sea salt (67 γ/kg) as dust (35 γ/kg) occurs in Greenland snow and ice. They have discussed the evidence and arguments of other investigators which conflict with their data. Both the counts made on particle collections and the calculations based upon microchemical tests on the particles, and "corrected" cation concentrations in the present study indicate that more than 90% of the particulates $> 2 \mu\text{m}$ diameter are dust particles.

LITERATURE CITED

- Ahlmann, H.W. (1953) *Glacier variations and climatic fluctuations*. New York: Amer. Geog. Soc. (Bowman Memorial Lecture, Series 3).
- Benson, C.S. (1962) Stratigraphic studies in the snow and firn of the Greenland ice sheet. U.S. Army Snow, Ice and Permafrost Research Establishment (USA SIPRE) Research Report 70, 93 p.
- Boutron, C. (1971) Contribution à la chimie des neiges de l'Antarctique. Détermination d'éléments tracés au niveau ppb par spectrométrie d'absorption atomique. Thèse. Univ. de Grenoble, 88 p.

LITERATURE CITED (Cont'd)

- Dansgaard, W., S.J. Johnsen, J. Møller and C.C. Langway, Jr. (1969) One thousand centuries of climatic record from Camp Century on the Greenland ice sheet. *Science*, vol. 166, no. 3903, p. 377-381.
- Dorsey, H.G. (1951) *Arctic meteorology: A compendium of meteorology* (T.F. Malong, Ed.). Amer. Meteor. Soc., Boston, p. 942-951.
- Federer, B. (1970) Neutron activation determination of the aerosol content of Greenland snow. *Geofis. Pura Appl.*, vol. 79, p. 120-127.
- Feigl, F. (1958) *Spot tests in inorganic analysis*. New York: Elsevier, 600 p.
- Hamilton, W.L. and C.C. Langway, Jr. (1967) A correlation of microparticle concentration with oxygen isotope ratios in 700-year-old Greenland ice. *Earth and Planetary Science Letters*, vol. 3, p. 363-366.
- Hurlburt, C.S. (1963) *Dana's manual of mineralogy*. New York: J. Wiley and Sons, p. 139-145.
- Johnsen, S.J., W. Dansgaard, H.B. Clausen and C.C. Langway, Jr. (1972) Oxygen isotope profiles through the Antarctic and Greenland ice sheets. *Nature*, vol. 235, no. 5339, p. 429-434.
- Junge, C.E. (1957) *Facts and problems of chemical composition of condensation nuclei in unpolluted and polluted atmospheres in artificial stimulation of rain. Proceedings of the First Conference on Cloud Physics and Precipitation Particles* (H. Weickmann and W. Smith, Eds.). New York: Pergamon, p. 31-35.
- Junge, C.E. (1960) Sulfur in the atmosphere. *J. Geophys. Res.*, vol. 65, p. 227-237.
- Junge, C.E. (1963) *Air chemistry and radioactivity*. New York: Academic Press, 382 p.
- Kumai, M. and K.E. Francis (1962) Nuclei in snow and ice crystals on the Greenland Ice Cap under natural conditions and artificially stimulated conditions. *J. Atmos. Sci.*, vol. 19, p. 474-481.
- Langway, C.C., Jr. (1962) Some physical and chemical investigations of a 411 meter deep Greenland ice core and their relationship to accumulation. In *Symposium of Oberurgl. Variations of the regime of existing glaciers* (W. Ward, Ed.). Int. Assoc. Sci. Hydrol., Pub. 58, p. 101-118.
- Langway, C.C., Jr. (1967) Stratigraphic analysis of a deep ice core from Greenland. U.S. Army Cold Regions Research and Engineering Laboratory (USA CRREL) Research Report 77, 130 p.
- Langway, C.C., Jr. and U.B. Marvin (1964) Comparison between snow-imbedded and industrial black spherules. USA CRREL Research Report 154, 17 p.
- Linkletter, G.O. (1970) The use of cationic ratios in determining annual stratigraphic layers in polar ice. ISAGE Symposium, Int. Assoc. Sci. Hydrol., Pub. 86, p. 16-18.
- Lodge, J.P. (1954) Analysis of micron-sized particles. *J. Anal. Chem.*, vol. 26, p. 1829-1831.
- Lodge, J.P. (1955) A study of sea salt particles over Puerto Rico. *J. Meteor.*, vol. 12, p. 493.
- Lodge, J.P. and H.M. Fanzoi (1954) Extension of the gelatin method for detection of micron-sized particles. *J. Anal. Chem.*, vol. 26, p. 1829.
- Lodge, J.P. and B.J. Tufts (1956) Techniques for the chemical identification of micron and submicron particles. *Tellus*, vol. 8, p. 184-189.
- Lodge, J.P. and B.J. Tufts (1957) *Techniques for the identification of micron and submicron particles in artificial stimulation of rain. Proceedings of the First Conference on Cloud Physics and Precipitation Particles* (H. Weickmann and W. Smith, Eds.). New York: Pergamon, p. 43-46.

LITERATURE CITED (Cont'd)

- Mason, B.J. (1957) *The physics of clouds*. London: Clarendon Press, 481 p.
- McCorkell, R.H. (1968) Dissolved iron, nickel, and cobalt in Greenland ice. Smithsonian Astrophysical Observatory preprint in Meteoritics.
- Murozumi, M., T.J. Chow and C. Patterson (1969) Chemical concentration of pollutant lead aerosols, terrestrial dusts, and sea salts in Greenland and Antarctic snow strata. *Geochim. Cosmochim. Acta*, vol. 33, p. 1247-1294.
- Putnins, P. (1970) The climate of Greenland. In *Climates of the polar regions* (S. Orvig, Ed.). *World survey of climatology*, vol. 14. New York: Elsevier, p. 3-128.
- Ragone, S.E. and R.V. Finelli (1972) Procedures for removing surface contaminants from deep ice cores. USA CRREL Special Report 167, 7 p.
- Ragone, S.E., R.V. Finelli, S. Leung and C. Wolf (1972) Cationic analysis of the Camp Century, Greenland, ice core. USA CRREL Special Report 179, 9 p.
- Rodriguez, R. (1964) Development of glacial subsurface water supply and sewage system. U.S. Army Engineering Res. Develop. Lab. Technical Report 1737.
- Twomey, S. (1954) The composition of hygroscopic particles in the atmosphere. *J. Meteorology*, vol. 11, p. 334-338.

**APPENDIX A. DENSITY OF ICE SAMPLES AND
THE INTERPRETED SEASONAL LAYERS**

<i>Sample</i>	<i>Length (cm)</i>	<i>Density (g/cm³)</i>	<i>Season (Interpreted)</i>	<i>Mean density</i>
454 A	4	0.884		
454 B	4	0.891		
454 C	4	0.887	Winter	
454 D	5½	0.894	W3	0.888
455 A	4	0.886		
455 B	4	0.878		
455 C	4	0.868	Summer	
455 D	3	0.865	S2	0.870
456 A	4	0.887		
456 B	4	0.891	Winter	
456 C	4	0.888	W2	0.889
456 D	5	0.889		
456 E	5	0.877		
457 A	4	0.870		
457 B	4	0.878	Summer	
457 C	4	0.875	S1	0.874
457 D	4	0.873		
457 E	4	0.870		
458 A	4	0.889		
458 B	5	0.888	Winter	
458 C	5	0.886	W1	0.888

Mean winter density 0.888

Mean summer density 0.873

**APPENDIX B. SIZE CLASS (DIAMETER) AND TOTAL
PARTICLE CONCENTRATION PER GRAM OF ICE**

<i>Seasonal layer</i>	<i>Sample</i>	<i>< 5 μm</i>	<i>5-15 μm</i>	<i>> 15 μm</i>	<i>Total</i>
W3	454 S7	54	49	24	127
	454 S8	137	81	38	256
	454 S9	114	39	59	212
	455 S1	109	42	22	173
	455 S2	128	37	27	192
S2	455 S3	91	28	14	133
	455 S4	150	56	29	235
	455 S5	119	32	12	163
	455 S6	99	29	10	138
W2	456 S1	182	40	31	253
	456 S2	236	68	20	334
	456 S3	625	90	49	764
	456 S4	370	101	33	504
	456 S5	407	46	27	480
	456 S6	308	94	8	410
	456 S7	350	62	18	430
	456 S8	169	21	22	212
S1	456 S9	138	20	11	169
	457 S1	175	40	23	238
	457 S2	212	33	8	253
	457 S3	98	10	1	109
	457 S4	136	34	7	177
	457 S5	134	21	22	177
	457 S6	316	9	3	328
W1	457 S7	162	36	13	211
	457 S8	78	17	12	107
	458 S1	68	15	12	95
	458 S2	72	22	7	101
	458 S3	72	11	9	92

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) U.S. Army Cold Regions Research and Engineering Laboratory Hanover, New Hampshire 03755		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE SOLUBLE PARTICULATES IN ICE FROM SITE 2, GREENLAND			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)			
5. AUTHOR(S) (First name, middle initial, last name) George O. Linkletter			
6. REPORT DATE July 1973		7a. TOTAL NO. OF PAGES 19	7b. NO. OF REFS 30
8a. CONTRACT OR GRANT NO. NSF Grant AG 104		9a. ORIGINATOR'S REPORT NUMBER(S) Special Report 188	
b. PROJECT NO.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.			
d.			
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.			
11. SUPPLEMENTARY NOTES Co-sponsored by National Science Foundation 1800 G Street NW Washington, D.C. 20550		12. SPONSORING MILITARY ACTIVITY U.S. Army Cold Regions Research and Engineering Laboratory Hanover, New Hampshire 03755	
13. ABSTRACT <p>Collections of soluble and insoluble particles made by sublimation techniques from small pieces of polar ice are well suited for microscopic and microchemical analysis. Examination of an 89-cm vertical profile of a polar ice core from a depth of 100 m at Site 2, Greenland, indicated no seasonal cycle in the abundance of particles $>2 \mu\text{m}$ in diameter. Microchemical spot tests made on individual particles indicated the presence of NH_4^+, K^+, Ca^{2+}, Na^+ and Cl^-. Whole filter spot tests for K^+ indicated no systematic variation in the concentration of potassium-bearing particles. Approximately 4% of the particles $>2 \mu\text{m}$ in the ice studied were soluble salts of Na^+, K^+, Mg^{2+} and Ca^{2+}. The concentrations of Na^+, K^+, Ca^{2+} and Mg^{2+} were measured in melted fractions of the same core profile by atomic absorption spectrophotometry. Variation of the K^+ concentration and variation of the number of potassium-bearing particles per gram of ice have a correlation coefficient of 0.93 over the $2\frac{1}{2}$ years of accumulation studied.</p>			
14. Key Words Glaciology Particle density (concentration) Land ice Particle size distribution			