Research Report 77
STRATIGRAPHIC ANALYSIS
OF A DEEP ICE CORE
FROM GREENLAND

by
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PREFACE

The work reported here is part of a long-term program involved in developing techniques and methods of deep ice core analysis. This study has been carried out over a period of several years in Greenland and at the laboratories of the U.S. Army Snow Ice and Permafrost Research Establishment (USA SIPRE), Wilmette, Illinois; the Department of Geology and Mineralogy, The University of Michigan, Ann Arbor, Michigan; and the U.S. Army Cold Regions Research and Engineering Laboratory (USA CRREL), Hanover, New Hampshire. The work accomplished at The University of Michigan was financed through USA SIPRE contract No. DA-11-190-ENG-89 and administered by The University of Michigan Research Institute (UMRI). The National Science Foundation (NSF) contributed financial support to both the USA SIPRE and the USA CRREL core analysis programs; this support and the direct interest in the entire program by A.P. Crary, Chief Scientist, Office of Antarctic Programs, NSF, is gratefully acknowledged.

The field work was made possible only through the collective effort of many individuals. The author particularly wishes to thank E. Swartz, B. Hamil and T. Fohl, field assistants during the 1957 season. W. Vest performed some of the later data reduction and E. BonDurant measured many of the black spherules. G.R. Lange, Project Drilling Engineer and J.R. Tedrow, Project Driller, both deserve credit for obtaining such valuable ice core. The cooperation of the U.S. Army 1st Engineering Arctic Task Force personnel and their Commanding Officer, Col. E.F. Clark, at Site 2 and Camp Tuto, Greenland, was invaluable.

The writer is especially indebted to H. Bader for his helpful criticism and encouragement in all aspects of these investigations, particularly during the early days, and for his continued personal interest, valuable suggestions and scientific inspiration.

The research presented here began in 1956 when the author was a member of the Basic Research Branch, USA SIPRE, J.A. Bender, Chief, and concluded while he was a member of the Environmental Research Branch, USA CRREL, R.W. Gerdell, Chief. The author wishes to thank them both for their valuable support. He also acknowledges the contribution made by S. Epstein and members of his laboratory at the California Institute of Technology by performing the oxygen isotope measurements under an NSF contract.

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SUMMARY

A deep rotary core drilling project in 1957 at Site 2 on the Greenland ice sheet (76°59'N, 56°04'W) provided ice core to a depth of 411 m. The vertical variation in bulk density, macroscopic structure, oxygen isotope ratios, ionic constituents, and extraterrestrial dust (black spherules) were analyzed using both field and laboratory techniques. These data permit the direct estimate of annual accumulation layers in the core. Continuous stratigraphic measurements and observations were made over the upper 110 m of the profile and detailed physical and chemical analyses were made on continuous 1.3 to 3.9-m core increments at 100, 200, 300 and 411-m depths. The average total ionic concentration in the ice sheet ranges between 0.65 and 1.35 mg/liter. The annual global mass deposit of black spherules as calculated from these studies varies from 2.10×10^5 metric tons in 700 year old ice to 6.57×10^5 metric tons in 12 year old firn. The oxygen isotope ratio variation provides the best means of estimating accumulation at depth. Results of the investigations indicate rates of net snow accumulation of 42.3, 34.2, 37.4, 41.1 and 41.6 g/cm² -yr at the surface, A.D. c. 1773, c. 1513, c. 1233 and c. 934, respectively. Accumulation data and other physical and chemical evidence allow climatological inferences to be made over the 10-century profile. The ice core record shows that snow accumulation and temperature in A.D. 934 were similar to today, followed by a gradual decrease in accumulation to a minimum around the late 18th century and an increase in both accumulation and temperature from A.D. 1773 to 1957 and following.

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I. INTRODUCTION

General Background

Of the former great ice sheets which covered nearly 30% of the earth's land surface during the Pleistocene epoch, there exist today only two prime and distant examples - the Greenland and the Antarctica ice sheets, located at opposite poles of the globe. These remnants of a past geological age modify and greatly contribute to the meteorological, climatological and hydrological conditions of the world, as did their former and more expansive counterparts. For example, the present polar ice sheets constitute the world's largest reservoirs of fresh water - in the solid state (Nance, 1960). About 78%, or some $20.5 \times 10^6 \text{ km}^3$ ($7.30 \times 10^6 \text{ mi}^3$), of the total volume of non-oceanic water is tied up in the frozen state in these two glaciers that blanket about 12% of the world's land surface.

Since historical times these massive continental-type ice sheets have been the subject of numerous exploratory and scientific expeditions from which much knowledge has been gained about the surface characteristics and stratigraphic layering of the upper few meters of firn (e.g., Nordenskiöld, 1885; Nansen, 1890; Koch and Wegener, 1930; Wright and Priestley, 1922; Sorge, 1935; Wade, 1945). Nevertheless, below the thin surface shell of the ice sheets lies an almost completely unexplored region about which little is directly known.

The nature of the inner structure of a polar glacier has always been of fundamental interest to glaciologists; the problem was obtaining suitable samples of deep ice for study. The serious attempts to core drill into glaciers around 1950 met with only marginal success, in terms of anticipated depth of penetration and core recovery.

The desire to develop a satisfactory method of continuous deep core drilling in polar ice received considerable stimulus and support in the United States during the planning stages of the International Geophysical Year (IGY) programs. In fact, one of the principal studies recommended by the Technical Panel on Glaciology of the U.S. National Committee was to develop a method of deep core drilling in polar glaciers (see Sharp, 1956a; Odishaw and Ruttenberg, 1958; Crary, Field and Meier, 1962).

The U.S. Army Snow, Ice and Permafrost Research Establishment (USA SIPRE) (now USA CRREL), then under the scientific leadership of H. Bader, accepted the responsibility for implementing the entire United States polar deep core drilling program. This included designing and modifying the drilling equipment, investigating and establishing techniques of ice core analysis, and developing bore hole instrumentation for temperature, flow velocity and deformational measurements. It was decided to conduct the initial tests at Site 2, Greenland (Fig. 1) during the summers of 1956 and 1957 (Lange, Langway and Hansen, 1959) and to apply the experience gained and techniques developed to the projected Antarctica IGY glaciological program (Bader, 1958; Patenaude, Marshall, and Gow, 1959; Ragle, Hansen, Gow and Patenaude, 1960).

Previous WorkPolar stratigraphic studies

The first systematic and quantitative field stratigraphic investigation of polar firn was made in Greenland at Station Eismitte in 1930-31 by Sorge (1933, 1935). He was first to clearly demonstrate that the non-uniform variations occurring in the physical properties of polar snow as a function of depth are related to periods of snow deposition and, most important, that a cyclical recurrence of these physical and stratigraphic characteristics corresponds to seasonal and annual accumulation. The primary parameters by which Sorge distinguished the limits of annual cycles were density variations and structural features (mainly ice layers and depth hoar horizons). To this day, these are the primary features that are examined and measured in performing a surface pit investigation, although considerable advances are now being made using indirect measuring methods. Sorge's work was shortly followed by the pioneering studies of H. W. Ahlmann (1933, 1935a, 1935b) and H. U. Sverdrup (1935) in Southeast Greenland and Spitzbergen where they established the basis for what is considered the beginning of modern glaciological techniques.

Stratigraphic interpretation of the upper firn layers (3 to 10 m) on polar ice sheets has been developed into an art that is now firmly established as a reliable method of estimating the amount of annual accumulation. Since Sorge's important investigation a great deal of surface pit work has been conducted in Antarctica (e.g., Schytt, 1958) and in Greenland (e.g., Lister, 1956; Benson, 1962; Langway, 1961; Ragle and Davis, 1962).

The only previous detailed stratigraphic study performed over an appreciable depth profile in a polar ice sheet was made by H. Bader at Site 2, Greenland, in 1954 (Bader, Waterhouse, Landauer, Hansen, Bender and Butkovich, 1955). In a 2 m square, 30 m deep hand-excavated pit, extended to 47 m by hand core augering, Bader interpreted the annual layers over a 70-year period. Schytt (1958) performed some physical measurements on a 100 m deep core obtained in Antarctica, but the core pieces were short, fragmentary and too sparse for stratigraphic considerations.

Early deep drilling

Although attempts to mechanically bore into glaciers for thickness measurements are reported to have begun in Switzerland as early as 1842 (see Miller, 1954), it was not until about 1950 that even limited success was achieved in deep core drilling. At this time three major core-drilling projects were conducted, almost simultaneously, on polar and temperate glaciers of the world.

During 1950 and 1951 members of the Expéditions Polaires Françaises (Heuberger, 1954) mechanically bored two holes on the south Greenland inland ice at Camp VI (69°42'N, 48°16'W, 1600 m elevation) and at Station Centrale (70°55'N, 40°38'W, 3000 m elevation) to depths of 126 m and 150 m, respectively. Some small diameter (3.7 to 4.8-cm) cores were recovered but little detailed information is available on their analysis. Also in 1950, members of the Juneau Icefield Research Project (see Miller, 1954) core drilled into the temperate Taku Glacier in Alaska (about 59°N, 134°W, 1090 m elevation), but here again the small diameter (5.2 cm) cores recovered were discontinuous and mainly of poor quality.

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Prior to 1956 the most successful polar ice coring program was accomplished by members of the 1949-52 British-Norwegian-Swedish Antarctic Expedition. Using a mechanical rig, a depth of nearly 100 m was reached on the shelf ice along the Dronning Maud Land coast (71°03'S, 10°56'W, about 40 m above sea level). Although core recovery was discontinuous some 4 to 5 cm long pieces of 8 cm (3.1 in.) diam core were recovered over the profile. The physical condition of the recovered core precluded any detailed stratigraphic analysis, but some significant studies on grain size, density, crystal orientation and air bubbles were performed (Schytt, 1958).

The Greenland Ice Sheet

The gross physical configuration of the Greenland ice sheet is now fairly well established (Bauer, 1955; Sharp, 1956b; Flint, 1957). The ice sheet represents about 12% of the total ice cover on the earth's surface and blankets nearly 85% of Greenland. Based primarily on the glaciological studies and the seismic results of the Expéditions Polaires Françaises (Bauer, 1955), it is known that the ice sheet has a surface area of 1.726×10^6 km² (0.666×10^6 mi²), a maximum surface elevation of 3290 m (10,800 ft), and a mean surface elevation of 2135 m (7000 ft). The mean thickness of ice cover is 1515 m (4979 ft) and the total volume of ice is estimated as 2.60×10^6 km³ (0.620×10^6 mi³) or, assuming an average density of 0.905 g/cm³, a volume of water of 2.35×10^6 km³ (0.560×10^6 mi³).

During the past few years the environmental and surface conditions on the Greenland ice sheet, that is, the annual snow accumulation and its distribution relative to latitude and elevation, and the mean annual temperature and its geographical variations, have been studied in detail in the south (Ragle and Davis, 1962), in the center (Benson, 1962), and in the north (Langway, 1961). A recent summary of our existing knowledge of the Greenland ice sheet, compiled from these and other studies (Bader, 1961), gives 36.7 cm (14.4 in.) of water equivalent as the present average annual accumulation for the entire ice sheet. This corresponds to an annual total volume deposit of 636 km³ (152 mi³) of water.

Our detailed knowledge of the regime of the Greenland ice sheet is still unsatisfactory. From the above information, however, we may state that less than about 0.03% of its total volume is added to the ice sheet each year and that the various ablational processes account for a loss of mass estimated at approximately 57% to 80% of the annual snow accumulation. Evaluating these data suggests that today the Greenland ice sheet has a slight positive mass balance.

Present Work

Drilling site

The most desirable location to drill for deep core in a polar glacier would be the simplest environment, that is, in a high elevation, net accumulation area where motion is minimal and summer surface temperatures do not cause excessive melting. In such a location the core profile would not be unduly masked by melt water percolation, flow would not obscure stratigraphic structure (only the natural load-metamorphic processes would affect the snow-firn-ice transitional profile), and fewer assumptions would be required in any core analysis.

Site 2, Greenland (Fig. 1), was selected as the location to perform the drilling trials, partly because it was already a field research facility for USA SIPRE maintained by the U. S. Army and capable of the logistical support required for this operation, but primarily because it fulfilled nearly all of the previously stated prerequisites of an ideal location.

Site 2 is located about 350 km (220 mi) east of Thule on the inland ice ($76^{\circ}59'N$, $56^{\circ}04'W$) at an elevation of 2000 m (6560 ft). The present mean annual surface temperature is $-25.4^{\circ}C$ and the temperature rarely reaches the melting point in the summer. The location is in what is generally considered a dry snow zone, i. e., where all precipitation falls as snow. According to Ahlmann's (1948) geophysical classification of glaciers, this location is of the high polar type; and in terms of Benson's (1962) modified geophysical classification, Site 2 is transitional to the dry snow facies and percolation facies or nearly on the dry snow line.

The surface in the Site 2 area is relatively flat with a general slope of less than about 0.1-0.2% to the southwest. Local and regional relief is limited to gentle undulations, resembling a modified swell and swale topography, with wave lengths of about 2 to 3 km and heights of about 10 to 20 m. The only small scale surface forms observed are sastrugi or snow dunes which are products of wind action and rarely exceed 6 to 10-cm heights. Seismic evidence shows that the subsurface bedrock at Site 2 is at about sea level (Bentley, Pomeroy and Dorman, 1957; Roethlisberger, Bentley and Bennett, 1965), which gives an ice thickness of nearly 2000 m. Available astronomical surface movement measurements (Musssetter, 1958, personal communication) indicate a surface velocity for the Site 2 region of about 10 to 20 m per year downslope.

Site 2 and vicinity (Camp Century, $77^{\circ}10'N$, $61^{\circ}08'W$, 1885 m; and Camp Tuto, $76^{\circ}25'N$, $68^{\circ}18'W$, 490 m) have been primary field testing and research areas for USA SIPRE and now U. S. Army Cold Regions Research and Engineering Laboratory (USA CRREL) since 1954, often for 12 months of the year, as well as for other governmental laboratories and university research teams. Glaciological, geological, meteorological, climatological, geochemical, geophysical and military engineering research has been and still is being actively pursued at these locations (see comprehensive USA CRREL bibliography).

Core drilling at Site 2

A Failing Model 314 rotary "1500" type drill rig with a 38-ft mast was modified, mounted on a 10-ton Otaco sled for transport over the ice sheet, and taken to Site 2 in 1956 for the deep core drilling (Lange *et al.*, 1959). The drill was powered by a 43 bhp Buda gasoline engine. Cooled compressed air ($-18^{\circ}C$ to $-5^{\circ}C$ and 4 kg/cm² or 60 psi at the drill head) was used as the drilling fluid. The bore hole was cased with 15.4 cm (6 1/16 in.) ID casing to a depth of about 50 m to prevent loss of air circulation in the permeable upper layers. A variety of drill bit tooth designs were used in the preliminary study; all cut a 10 cm (3 7/8 in.) diam core and a 14.6 cm (5 3/4 in.) diam hole. Core drilling was done with the drill string held manually in tension and the speed of rotation was varied from 40 to 75 rpm. The rate of penetration ranged from 6.4 to 25.4 cm (2 1/2 to 10 in.) per minute.

The first summer's drilling program was devoted essentially to developing methods of core drilling, but by September 1956 the ice sheet had been penetrated to a depth of 305 m (Lange *et al.*, 1959). Core recovery was not continuous but undisturbed samples were obtained over about 50% of the profile,

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many covering large vertical increments. Core quality progressively deteriorated with depth. Part of this was due to the removal of the increasing stresses at the bit-ice contact but some fracturing could also be traced to stress concentrations at small scratches incised on the surface of the core by the rotating bit.

In 1957, a new core was bored to a depth of 411 m a short distance from the original hole using the same basic drilling rig as in 1956 (Fig. 2). Core recovery during the 1957 operation provided nearly continuous undisturbed cores from 19 m to 110 m, and about 75% to 85% recovery from 110 m to 305 m; the remainder consisted of two 5-m lengths from 360 m and 411 m. Core quality improved considerably in 1957 (Fig. 3) because of experience gained in drilling and improvement in design of some of the tools (Lange, in preparation).

Because of the softness of the material in the upper layers, which caused difficulty in air circulation, rotary drilled cores were not recovered above 19 m. For density measurements and stratigraphic observations over this profile a 3 m deep pit study was performed about 1 km from the deep bore hole and a 25 m deep hand-augered 7.6 cm (3 in.) diam core was bored about 0.1 km from the deep bore hole (Langway, 1962). The 25 m deep hand-augered hole was also used for near surface temperature measurements and to calibrate the deep hole temperature measuring instruments (Hansen and Landauer, 1958).

Figure 2. Ice core drilling rig at Site 2, Greenland, 1957. Portion of 38-ft mast protrudes through plastic sheet covered plywood roof above snow surface. Canvas shelter erected on snow surface (at left) houses air compressors.

Figure 3. Undisturbed 10 cm diam rotary drilled ice core being removed from core barrel.

Ice Core Studies

Scope and value of the investigations

The recovery of the deep ice core presented an opportunity that had not existed before. Never had the snow-ice mantle of any glacier been so deeply penetrated, nor had such an appreciable quantity of relatively large diameter ice core been recovered with such continuity. In addition, since the core was obtained from a high polar glacier, it also contained entrapped within it all the foreign material - organic, inorganic, soluble, and insoluble - that fell with the snow or upon the snow surface. With this core one has a vertical profile of arctic history and the unique opportunity to examine systematically the physical and chemical internal nature of a polar ice sheet as a continuous function of depth. Once the age-depth relation has been established, an opportunity exists to investigate any climatological trends and even significant meteorological disturbances that affected the world's atmosphere, such as major temperature changes, volcanic eruptions, or cosmic showers, which in turn, if historically recorded, provide us with very desirable index horizons.

Many studies besides those to be discussed here were performed on the deep ice core samples from the 1956 and 1957 operations or in the bore holes as the cores were being recovered: e.g., crystal orientation, size and texture (Langway, 1966a); firn-fabric studies (Fuchs, 1959); measurements of the

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elastic constants (Nakaya, 1959); bubble pressure measurements (Langway, 1958); bore hole temperature, diameter and inclination measurements (Hansen and Landauer, 1958); core stress relaxation measurements (Kolb, 1957, personal communication); and on samples selected and prepared at the site or in the Wilmette laboratory for shipment to other interested scientists: e.g., deuterium analyses (Friedman, 1959, personal communication); bulk oxygen isotope analyses (Dansgaard, 1961); tritium analyses (Bergeman, 1957); occluded atmospheric gas analysis (Institute of Gas Technology, 1958); dissolved solids (Armour Research Foundation, 1958); bacteria content (Walter Reed General Hospital, 1959); and dissolved oxygen content (Northwestern University, 1957).

Some of the field studies, in particular the physical measurements, were repeated or duplicated on adjacent core samples under more carefully controlled conditions after the cores were transported to the USA SIPRE laboratory, Wilmette, Illinois. This was done to investigate possible structural alterations in the core brought about by transportation from Greenland with dry ice (-60°C) and to study the time effect on the deeper, higher stressed samples. Many other studies were extended and new ones were instituted at the laboratory.

Methods and techniques

For the purpose of analysis polar ice may be conveniently considered as consisting of three component parts: (1) the solid polycrystalline aggregate of individual ice crystals, (2) the occluded atmospheric air entrapped when the pore spaces close off, and (3) the foreign inclusions, particles or debris consisting of terrestrial and extraterrestrial particles. With this model in mind a complete program of analysis was developed for the investigation of the deep ice core (Langway, 1962).

Of major importance to the ice core studies was the development of methods, techniques or parameters to determine, identify, and if possible characterize the annual accumulation layers from the deep ice, particularly below 100 m. Because of the small amount of sample available in the 10 cm diam cross-section provided by the core, any such method would have to be based on measuring some distinctive physical or chemical variation in small vertical increments.

Objectives of report

This report describes physical and chemical studies that have been made on the deep ice core recovered at Site 2, Greenland, in 1957. It is not intended to cover all details of the many separate facets of the deep ice core studies, since some of the analyses, although interesting and important in their own right, have apparently little value in revealing annual layers.

Special emphasis is given to investigations made on samples from below 100 m which show potential value in defining annual cycles for stratigraphic interpretation. The equipment, methods and techniques of analysis are discussed. First a brief description is given of the field procedures of handling and processing the cores, and the stratigraphic field observations and measurements. Then the general characteristics and observations on the entire core are presented followed by the results of detailed laboratory investigations, namely: the macroscopic stratigraphy studies, the oxygen isotope studies, the chemical composition studies and the cosmic dust (black spherule) studies. The interrelationships and correlations of these stratigraphic parameters are presented and the results evaluated and discussed in terms of net accumulation

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and its variation over the entire profile. The geochemical or geophysical significance of each study is discussed in terms of the Greenland ice sheet and, when appropriate, its effect in other areas.

II. FIELD PROCEDURES

General Background

The field period for the recovery of the deep core extended from June 1957 to the end of August 1957. The core was examined and processed as it was being recovered and, although some strain was manifested below 220 m by transverse tensional fractures (joints), it was possible to continue all studies by selecting unfractured portions of the core when the investigation required an undamaged sample.

Subsurface Snow Laboratory

To provide cover and allow the field work to continue in the event of summer storms an L-shaped trench system was mechanically excavated in the firn and framed with timber and a plywood roof. The base of the trench was 5 m (16 ft) below the snow surface, 5 m wide and 30 m (100 ft) long on one leg and about 15 m (50 ft) long in the other direction. The longest portion of the trench system was used for the drilling rig and accessories (Fig. 4); the other leg was used for core analysis and core storage (Fig. 5). The air temperature in the snow laboratory varied between -18 C and -4 C.

Core Reference Datum

The reference surface for depth control was established by transit leveling in the July 1956 snow surface from an undisturbed location about 1 km distance away to the undersnow core breakout point. The same datum was used for both the 1956 and 1957 deep cores to simplify direct correlations in comparative studies.

For each core run the depth to the bottom of the bore hole was taken from the driller's log. This established the base depth for any or all core recovered during that run. For uniformity of recording, any missing length within the core barrel was assumed to have occurred at the top of the run.

Core Handling and Processing

The field work on the recovered core was divided into two main parts: (1) the logging, handling, and processing for storage and shipment and (2) the field tests, observations, and measurements; for the purpose of this report field investigations are confined to stratigraphic studies.

The ability to relate a given core sample to its true depth and orientation once the core had been removed from its confining environment was essential to the future studies contemplated. An accurate log was, therefore, the first task accomplished after receiving the core from the drillers.

The following description presents in chronological order the field procedures employed.

Figure 4. Ice core drilling rig located in undersnow shelter about 5 m below surface, Site 2, Greenland, 1957. Core barrel rests on tubular supports in foreground.

Logging methods

For each core run and each individual core piece an accurate record was kept of date recovered, physical condition, depth from the surface, orientation or questionable orientation, and any other specific data that might be of use in later detailed investigations. Special forms and data sheets were devised for core piece logs, core tube logs and density measurement logs.

Orientation procedure

Immediately after the core was received from the drilling team it was placed in wooden troughs with special care taken to keep the up-direction known. No azimuth control was obtained. While the core was still in the

Figure 5. Portion of undersnow core analysis laboratory, Site 2, Greenland, 1957. Wooden core-holding troughs are seen in center foreground on floor of snow trench, drilling rig is seen in the background.

wooden trough a small diameter hole (about 3 mm) was bored approximately 2 cm down from the upper edge through the whole diameter of each individual core section. This procedure eliminated any uncertainty about the up-direction.

Light table observations

From the wooden trough the various lengths of recovered core were taken to a light table and examined in fine detail by transmitting fluorescent light through them (Fig. 6). Subtle stratigraphic differences and discrete features not otherwise observable were detected in this manner. Here the most essential observations of megascopic stratigraphy were accomplished.

The stratigraphic data were plotted full scale on a narrow roll of graph paper which was extended adjacent to the core on a shelf attached to the light table (Fig. 6). This procedure greatly aided in the later evaluation of the stratigraphic observations and eliminated possible errors that could develop in any reduced scale plot of such data. In fact, by returning to

Figure 6. Examining core lengths on light table. Record of macroscopic stratigraphy is plotted full scale on rolled graph paper seen at lower right.

these original rolls it was possible later in this core study to confirm that two core pieces had been placed in the wrong bags, and thereby a serious discrepancy in the O-isotope data was corrected.

Cutting the core

The next step was to decide where the long lengths (up to 3 m) of core should be cut. Since continuous ice cores below 50 m had not previously been obtained or studied it was not known whether the density variation, so important an aid in determining near surface stratigraphy, would still be of use, yet to cut perfect ice core into smaller segments for density measurements might perhaps eliminate more important future studies on the samples. It was decided to make the cuts coincide with natural stratigraphic boundaries but, since bulk density determinations would be most valuable if accurately measured on large volume samples, an absolute minimum size for cutting was set at about 5 cm.

A preliminary incision was made at the desired core length with a hacksaw blade and each core piece was numbered with a soft, blunt-tipped #1 lead pencil. The numbers run consecutively, starting with the first piece recovered. For orientation, another small diameter bore hole was drilled through the diameters of the newly cut pieces of core which now ranged in length from 6 to 25 cm. The pieces were then cut with a mechanical band saw.

Bulk density measurements

The only physical measurement made on the core pieces in the field that had direct bearing on stratigraphic interpretation was density. A density determination was made on every undisturbed sample as it was recovered. Each piece was trimmed with a mechanical band saw (Fig. 5). Over the porous firn profile densities were determined by the volume-measuring method, and for the deeper impermeable ice the hydrostatic weighing method was used (Fig. 7).

Splitting, packaging and transporting the core

The entire 1957 core was sawed in half lengthwise for insurance against total loss during shipment. A wooden mold attached to the band saw table permitted the cores to be cleanly sawed into perfect halves. After splitting, each piece was inserted into a separate polyethylene bag (Fig. 8) with a data card that contained date recovered, piece number, depth from surface and other pertinent information; the bag was then tightly sealed. Each bagged piece was placed in a specially constructed aluminum foil storage shipping tube which had a near-vacuum tightness and temporarily stored in the snow trench (Fig. 9).

At the end of the 1957 season 160 m of selected half core was packed in dry ice and air transported from Greenland to the Wilmette, Illinois, laboratory. The core was kept in storage there at an average temperature of -30°C to await further detailed investigations.

Figure 7. Field apparatus for determining bulk density of core segments by the hydrostatic method. Vacuum-pressure pump on right is used to transfer and return weighing liquid from Lucite container (seen behind balance) used for weighing sample in liquid.

Figure 8. Drilling small diameter "up-orientation" holes at tops of core pieces. Polyethylene bags on work table contain individual half-core pieces.

Figure 9. Temporary storage of ice cores in aluminum foil covered containers in subsurface snow laboratory.

III. MACROSCOPIC STRATIGRAPHY

General Background

Each year in the dry snow zone of a high polar ice sheet the new snowfall buries the previous accumulation deeper, the density of the underlying firn increases by compaction, and with depth the firn gradually transforms into glacier ice.

The study of snow, firn or ice stratigraphy on a high polar ice sheet is comparable to the investigation of lake varves or any layered sequence in a sedimentary rock formation. In both cases individual layers are deposited and the specific characteristics or properties of the material allow one to differentiate between summer or winter deposition. In lake varves the differentiation is apparent to an experienced researcher and megascopic observation is generally all that is required to delineate between the dark and light layers which together represent an annual cycle. On the other hand, since snow and firn readily alter with temperature or other meteorological factors, interpretation of polar stratigraphy involves the careful consideration of sensitive diagenetic processes that transpire after deposition. A partial or complete metamorphism of the original snow structure often occurs. Nevertheless, by careful observations and measurements one is able to delineate multilayered sequences which represent annual accumulation cycles.

In this chapter we will first briefly discuss the factors affecting polar stratigraphy, the stratigraphic criteria themselves, and then the general observations made and the measurements taken on the entire deep core.

Polar Stratigraphy

Macroscopic stratigraphy refers to those structural characteristics in the firn-ice that are visible to the unaided eye, either by direct observation or by examination in transmitted light from below, or by the physical measurements of these properties. Stratigraphic interpretation in temperate glaciers often is aided by the presence of visibly suspended debris such as dirt horizons (Schytt, 1958) or pollen layers (Heusser, 1954) which reflect previous summer melt surfaces. The entire concept of polar stratigraphic interpretation, however, is based solely on the cyclical recurrence of certain seasonally related physical features preserved in the firn profile.

Factors affecting polar stratigraphy

An exposed vertical profile in a polar snow pack will reflect distinct layering or bedding. These layered structures are caused by original variations in the precipitation supply, changes in the rate of deposition, fluctuations in the surface temperature and other meteorological variables, such as wind conditions. Surface features of a snow cover may change rapidly through movement and erosion by wind (Hoinkes, 1961). Besides the initial meteorological conditions associated with its deposition a snow layer is also subjected to diagenetic, or post-depositional changes which add to the difficulty of stratigraphic interpretation.

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Even in the high polar regions diurnal and seasonal temperature waves penetrate and markedly affect the firn profile by creating reversing temperature gradients that assist mass vapor transfer. The entire upper 10 m is strongly affected by annual temperature fluctuations. Depending upon location, 10 m of Greenland polar firn (the depth of less than one degree annual temperature fluctuation) represents in the neighborhood of 6 to 12 years of accumulation.

During this time diagenesis of firn structure commonly masks the slight original relative grain size variations and consequently the stratigraphic usefulness of grain size. Cases do exist, nevertheless, where gross grain size differences, as exemplified by depth hoar crystals, are quite useful as stratigraphic aids. Depth hoar formation is fully discussed in the literature (e.g., Seligman, 1936; Bader et al., 1939; deQuervain, 1958; Giddings and LaChapelle, 1962) and appears to develop most favorably when a warmer snow surface is quickly blanketed by a colder deposit. In part the new snow layer restricts the upward heat transfer and accompanying vapor migration, causing the vapor to condense at the interface. Under ideal conditions a single distinctive depth hoar layer separates the summer-fall boundary of an annual accumulation cycle. Unfortunately for polar stratigraphic purposes, depth hoar layers may develop at any time of the year that a steep temperature gradient exists (Schytt, 1958).

Although surface melt phenomena play a dominant and destructive role in the stratigraphy of temperate glaciers (Leighton, 1952), in high polar glaciers slight melt features are identifying hallmarks of summer layers. Because of the generally low annual surface temperatures in a dry-snow zone, thin (less than 2 mm) ice layers form only on or close to the surface of summer snows by solar radiation (Schytt, 1958). On the other hand, icy crusts may form on winter snows by condensation from supercooled moisture laden air masses passing over the cold surface. Higher summer surface temperatures create more severe melt conditions and produce thicker ice layers, ice wedges and ice glands, which always form below the surface (Sverdrup, 1935; Ahlmann, 1935b; Moss, 1938), sometimes after percolating as much as 2 m in depth (Benson, 1959).

In addition to the temperature phenomena, the additive accumulation upon the relatively loose-packed original deposit causes settling and compaction which alters the initial structure and texture of a stratum. Once covered, a layer undergoes metamorphic processes, is compressed by the overburden, and densifies (Bader, 1960, 1962b). Nevertheless, in dry snow it appears that the progressive increase in density with depth does not obliterate the relative seasonal relationships of the prime stratigraphic parameter of density.

Developing criteria by which to distinguish seasonal accumulation cycles at a location is one of the most important aspects of a stratigraphic study. Figure 10, the profile of a late spring snow cover from the ablation zone of the ice sheet, displays an ideally developed single snow accumulation cycle. This example illustrates the detailed stratigraphic observations and measurements, and their interpretation, made in this case over a limited profile. It is a systematic sequence such as this, repeated annually, that one attempts to distinguish in deeper pits and from ice cores. Usually the contrast between seasonal or annual layers is less distinctive at greater depths than is shown in Figure 10.

Figure 10. Plot of general observations, measurements and interpretation of data made at a surface pit study (from Langway, 1961). This shallow pit was dug 26 km from the edge of the ice sheet in May. The snow cover here represents the net gain in deposition since the previous summer's ablation period. The strata are well defined and the distribution of the physical properties is nearly ideal over the profile. Relative stratigraphic symbols are as follows:

Grain Size Hardness

A - fine a - soft $\wedge \wedge \wedge$ depth hoar
 B - medium b - medium A_e = net accumulation
 C - coarse c - hard γ_p = mean density for profile

Note the good agreement between the physical measurements of density and hardness and the qualitative snow stratigraphy symbolized in the center column of the figure.

Stratigraphic criteria

Evidence of a summer layer in the dry-snow zone is generally reflected in firn strata by the inclusion of melt crusts or thin ice layers in porous and soft snow (usually coarser grained) and a relatively low bulk density. On the other hand winter deposits characteristically display finer-grained, hard and homogeneous wind-packed layers of relatively high bulk density, sometimes displaying interstratified wind crusts.

The classical physical stratigraphic criteria used to interpret seasonal firn layers at high polar regions (Sorge, 1933, 1935; Bader *et al.*, 1955; Schytt, 1958; Langway, 1961; Benson, 1962) are broadly listed in Table I.

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Table I. Seasonal stratigraphic indicators in dry snow.

<u>Structural feature</u>	<u>Summer layers</u>	<u>Winter layers</u>
Density	lower	higher
Melt phenomena*	yes	no
Wind crusts*	no	yes
Depth hoar*	yes	no
Grain size	coarser	finer
Hardness	less	more

*It is not unusual for feature to be found in other than expected seasonal layers.

As is listed in Table I, the main stratigraphic features used in the interpretation of annual layers in the dry-snow zone consist of melt phenomena (ice layers, ice wedges, ice glands and melt crusts) and density variations. Radiation crusts or sublimation phenomena (depth hoar and hoar frost), wind phenomena (wind crusts and wind slabs) and some metamorphic phenomena (grain size and hardness) are usually of secondary importance. In addition to the basic stratigraphic indicators it was observed during this study that light transmissivity is also a useful guide in interpreting stratigraphy in firn and ice cores.

Various stratigraphic features "observed" are difficult to categorize explicitly. The peculiarities of the weather add to the difficulty by making it nearly impossible to rely on the cyclical recurrence of certain structural features. The basic stratigraphic features discussed above are generally diagnostic and useful only when considered in relationship to the whole. General rules are difficult to set forth and, therefore, in addition to the physical measurements polar stratigraphy is to a great extent dependent upon the experience of the investigator and his knowledge of the contemporary environmental conditions at the site.

General Observations and Results

Stratigraphic characteristics

Using the terminology developed earlier for surface studies the prominent stratigraphic features observed in the ice core over the entire 411 m depth profile are qualitatively presented in Table II. The features are listed in approximate order of relative abundance (frequency of occurrence). The core profile is arbitrarily separated into depth increments from the surface to 70 m and from 70 m to 411 m.*

The single stratigraphic feature most frequently observed over the entire profile is a thin (1-2 mm) horizontal ice layer. Thicker (3-5 mm) ice layers are less numerous but more often found in closely spaced groups of two or

*This divisional break is at the approximate firn-ice transition (see p. 26).

three individual layers and sometimes inclined slightly from the horizontal. Ice wedges and ice glands are rarely observed. Wind crusts of firmly bonded fine grained layers (1-2 mm) are common in the upper surface firn but difficult to distinguish from thin ice layers with depth.

Table II. Structural features observed over the entire 411 m deep core profile.

Feature	Thickness (mm)	Observations above 70 m				Observations below 70 m			
		Numerous	Common	Present	Rare	Numerous	Common	Present	Rare
Thin ice layers (IL)	1-2		X				X		
Thick ice layers (IL)	3-5			X				X	
Ice wedges	10-25			X				X	
Ice glands	30-100				X				X
Depth hoar layers	10-20		X						?
Wind crusts	1-2		X						?
Relative light transmission	variable	X				X			
Definite indications of melt (DIM)	5-20			X				X	
Slight indications of melt (SIM)	5-20			X				X	

Other interesting and frequently observed features, noticed more often in the deep core, are structures designated DIM (definite indication of melt) and SIM (slight indication of melt). These features are horizontal strata, usually 5 to 20 mm thick, of relatively lighter appearing material commonly, although not always, having larger sub-rounded grains than the material on both sides. It is suspected that SIM and DIM features were originally depth hoar or icy firn strata. Evidence suggesting this is given in a later section.

Another useful stratigraphic indicator observed during this study is the property of light transmissivity. The transmission of light through the firn-ice cores revealed small increments that appeared uniformly lighter or darker than adjacent increments. In some cases the increments are bordered by other structural features, such as crusts or ice layers, but more commonly than not the material on both sides of a boundary is visibly homogeneous, the only observable difference being the light transmissivity. Since the boundary was horizontal, it was suspected that it was related to some original depositional phenomena and each boundary was carefully recorded.

It was learned in this study that the relative amount of light transmitted through a firn-ice core segment is related to the density of the sample. This situation is somewhat analogous to observations generally made in ice tunnels or on ice exposed at the margins of glaciers. Here the more bubbly ice is white (lighter) and the clear bubble-free ice is blue (darker) due to light reflection and absorption processes.

Similarly in the firn-ice core samples, light transmission is a function of the relative size and number of air bubbles (pore spaces). In the cores the ice-bubble interfaces form scatter points which retard light transmission by internal reflections in proportion to the porosity of the material. Looking at this stratigraphically the less dense segment (summer) has a larger volume of pore space, hence more interfacial scatter points, which reduce the relative amount of transmitted light and make the sample appear darker. The denser, less porous segment (winter) has a smaller volume of pore space, hence fewer scatter points, and appears lighter in transmitted light. Bulk porosity observations may be used, therefore, instead of direct density measurements as a seasonal parameter. The major advantage of using bulk porosity variations is, of course, that they can be qualitatively recognized with some reliability by only using a light table.

Porosity is the volume (V) of pores or air spaces contained in a sample and is expressed as a ratio of the total volume of the sample as

$$n = \frac{V_{\text{pores}}}{V_{\text{ice}} + V_{\text{pores}}} = \frac{V_{\text{pores}}}{V_{\text{total}}}$$

and may be calculated from the bulk density of a sample by

$$n = \frac{\gamma_i - \gamma_s}{\gamma_i} = 1 - \frac{\gamma_s}{\gamma_i}$$

where n is the porosity, γ_i is the density of pure bubble free polycrystalline ice and γ_s is the density of the sample.

Physical characteristics

Grain size variations are often recognized in the firn core above 70 m. The relative size differences are usually so discrete or grade so rapidly, however, that it was not possible in this study to record accurately the phenomena with any degree of assurance. It is simply difficult to establish a quantitative significance for grain size in the evaluation of seasonal layers.

Since grain size correlation with seasons is not readily apparent in the upper firn layer it was considered unlikely that any such relation would be found in the deeper metamorphosed ice. However, to investigate the slight possibility, but primarily for correlation with other planned detailed studies, continuous 1 1/2 to 4 m vertical thin sections from the 100 m, 200 m, 300 m and 411 m depths were made, photographed and the grain size variation studied. Based on these analyses (a total of about 100 sections) and other detailed studies reported here, observed crystal size variations in firn or ice contribute little towards the interpretation of annual layers, even when outstandingly clear relict structural bands are observed (Fig. 11).

Figure 11. Photograph of a vertical thin section (0.5 mm thick) taken full scale between crossed polaroids. Identification marking on upper left of photograph indicates top, sample number (478) and depth from surface (98.07 m). Note 4 to 6 mm thick band of smaller sized crystals about half-way down section. The considerable size variation shown in the individual crystals over all of this 14 cm high vertical section is evidence of the caution that must be exercised in accepting an average crystal size value from a horizontal section.

Ice fabric studies were conducted at the drill site, shortly after core recovery, on seven thin sections spaced between 100 m and 300 m (Langway, 1966a). These same sections and portions of the core immediately adjacent to them were studied later at the USA SIPRE laboratory to investigate any possible structure change during transport and storage. The only noticeable effects were shrinkage cracks in the 0.5 mm thick thin sections, undoubtedly caused by the dry ice used to preserve the cores during transportation. No measurable change occurred in the crystal orientation of the thin sections.

A complete crystal size analysis was made on each thin section used in the fabric study. Crystal size is reported here in terms of an average individual crystal area as observed in a random plane intersecting the sample. A 5X enlargement was made of the original photograph and each sectional diameter was measured directly on the enlarged photograph with a Zeiss semiautomatic particle size analyzer. The measured diameters were reduced to true size and the computed values converted to area to compare the results with other crystal size studies on ice. The results of this analysis are summarized in Table III.

These data plotted show a general linear increase in the average ice-crystal area from 2.7 mm^2 at 100 m to 4.9 mm^2 at 300 m. A previous report of the Site 2 firn grain-size variation between 8 m and 34 m (Fuchs, 1959) also shows a near linear increase over this interval, from about 0.5 mm^2 to about 1.0 mm^2 , respectively.

Table III. Ice crystal size (area) with depth.

Depth below 1957 surface (m)	Number of grains measured (n)	Average crystal size (area) (mm ²)
97	569	2.71
127	455	3.39
150	374	4.04
180	396	4.10
198	369	3.86
224	308	4.97
299	308	4.94

The texture of deep glacier ice (Fig. 12) is quite distinctive in cross section and easily distinguished from the texture of other kinds of ice, such as lake, sea, artificial and even deformed or marginal glacier ice. In cross section, the individual ice crystals appear fairly equant in shape, but are actually elliptical with an axial ratio (l:w) averaging about 1.8 in the size range between 2.5 mm² and 26.8 mm² (Langway, 1966a). The ice crystals are anhedral in form with slightly sutured and mosaic outlines. The larger crystals commonly interlock.

Adding to the distinctive character of deep polar glacier ice is the shape and arrangement of the occluded air bubbles. Air bubble inclusions in high polar ice are products of direct atmosphere capture by the permeable and plastically deforming dense firn. The bubbles become smaller, more spherical, and more uniformly distributed (spatially) with depth. Figure 13 shows the general shape and size change in air bubbles from the Site 2 core at various depth levels. An examination of these sections under crossed polaroids shows the inter- and intra-granular positions of the air bubbles. The average diameter of the bubbles at 305 m is about 0.3 mm and their number concentration (count per unit volume) at this depth is approximately 300/cm³, which gives a porosity value of about 0.4%.

Density profile

Density is a fundamental physical property of snow and ice, and a proven seasonal stratigraphic indicator in the upper firn layers. Consequently, density determinations were made on all suitable undisturbed core segments as they were recovered.

A total of 849 density measurements span the entire 411-m profile. From the surface to the depth of the zone of zero permeability, density was determined by the volume measurement and weighing technique. For the first 3 m, 500-cm³ snow-sample tubes were used and the samples taken horizontally at close intervals. Between 3 m and 24 m two different overlapping 7.6 cm (3 in.) diam vertical cores were hand-augered and continuous densities were measured. From 19 m to the depth of zero permeability, the mechanical drilling rig recovered cylindrical core (10.2 cm diam) of a quality which enabled accurate density determinations to be made. For all core samples above 70 m, volume was calculated from values measured to the nearest

Figure 12. Photograph of a vertical thin section of a deep ice core from 96.18 m in polarized light (left) and the same section in transmitted light (right). For linear scale a cm on edge grid overlies the section. Note in upper center of both photographs the 3 mm diameter "up-orientation" drill hole 2 cm down from upper end of the sections. (Circular-shaped hole seen in lower right of photographs was accidentally made during thin-section preparation.)

Figure 13. Occluded atmospheric air contained as air bubbles in high polar glacier ice (from Langway, 1958). Photographs taken using transmitted light. Air bubbles decrease in size with depth (M) and tend toward sphericity and spatial uniformity in their distribution.

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0.5 mm with a rule or vernier caliper. Below the permeable firn (about 70 m) density was measured with greater precision by using the hydrostatic method, which greatly aided stratigraphic analysis of the deeper core by discerning the smaller amplitudes of variation at these depths.

Core densities below 70 m were determined using the following equation

$$\gamma_s = \frac{w_a \cdot \gamma_l}{w_a - w_{lt}}$$

where

γ_s is the density of core sample, g/cm³

w_a is the weight in air, g

w_l is the weight in liquid, g

γ_l is the density of liquid, g/cm³

t is the temperature of liquid at w_l , C

The liquid used for the ice density determinations is 2, 2, 4 trimethylpentane. This liquid has a density of 0.71176 g/cm³ at -4.5 C and a coefficient of cubical expansion of 1.07×10^{-3} /C (Butkovich, 1953) which is linear within the temperature range at which these samples were measured. A beam balance, accurate to ± 0.05 g, was used for all bulk weighings, and a calibrated mercurial thermometer graduated to 0.1 C with 1-mm spacings was used for measuring the temperature of the liquid. Temperatures were read to the nearest 0.05 C. For the small mass (about 50 g) density determinations made on the core (see Appendix D, Table D6), weighing was done with an analytical balance, precise to ± 0.2 mg, and corrections for impurities, including the occluded air contained within the air bubbles, are considered.

Ice core samples were allowed to reach temperature equilibrium with the ambient air in the snow trench or laboratory cold room before measurements were made. The best value for the cubical expansion coefficient of ice between 0 and -25 C is given as 1.53×10^{-6} /C (Dorsey, 1940; Butkovich, 1957). All density values below 70 m are temperature-corrected to -25.0 C, the approximate *in situ* temperature at Site 2. The maximum error in the density measurement for the 500-cm³ tube samples and the 7.6 cm and 10.2 cm diam cores is about 2%. Using the hydrostatic method the maximum estimated error is about 5 parts per mil for the bulk samples and $\pm 2 \times 10^{-5}$ g/cm³ for the smaller bubble pressure samples.

Three overlapping density profiles are used to obtain a complete density profile from the surface to the bottom of the 411-m bore hole. Table IV presents a summary of the density measurements and Figure 14 shows the average density values for 1-m depth intervals plotted as a function of depth. The individual average meter values are given in Appendix D.

Besides our basic stratigraphic interest in density variations, insight into other important glaciological and physical processes is made available from the density determinations. The smoothed curve in Figure 14 reveals a gradual density increase from the surface snow through the firn and into high density polar ice. This transition is brought about at Site 2 primarily by load metamorphism, but surface temperature conditions and initial density

Table IV. Summary of density measurements, Site 2, Greenland.

Appendix D table no.	Source of samples	Depth range (m)	No. meas (n)	Type and location of sample and measuring method
D1	Pit study	0.03- 3.27	57	500 cm ³ density tubes; about 1000 m from deep drilling location; volume-weighting determinations.
D2	Pit study extension (hand augered)	2.85- 10.65	50	7.62 cm (3 in.) diam cores; about 1000 m from deep drilling location; volume-weighting determinations.
D3	Temperature bore hole (hand augered)	3.00- 24.31	136	7.62 cm (3 in.) diam cores; about 100 m from deep drilling location; volume-weighting determinations.
D4	Deep rotary drilling	19.62- 66.12	252	10.16 cm (4 in.) diam deep cores; volume-weighting determinations.
D5	Deep rotary drilling	66.21-288.29	313*	10.16 cm (4 in.) diam deep cores; volume-weighting and hydrostatic determinations.
D6	Deep rotary drilling (bubble pressure experi- ments)	72.5 -360.5	41	50-60 g samples; from deep cores; precise hydrostatic determinations.
Total				849

*262 continuous measurements between 66.21 m and 117.77 m and 53 intermittent measurements between 117.77 m and 288.37 m.

are important parameters. The overall form of the curve shows a non-linear increase in density with depth at a decreasing rate, asymptotically approaching the density of pure bubble-free polycrystalline ice (0.92002 g/cm³ at -25.0 C). The difference between the density of the sample and pure ice is the air content (porosity) of the sample. Density was not measured on bulk core samples below 288 m because of the scarcity of usable unfractured core. It was possible, however, to perform density measurements on smaller samples and in this way direct measurements were extended down to 360.5 m. The density measured at 360.5 m is 0.9172 g/cm³ and the calculated porosity is 0.301%.

The density profile can be conveniently divided into several naturally appearing sections or slope changes that are related to densification or compaction processes. In the upper layers load pressure causes densification by

Figure 14. Depth-density curve, Site 2, Greenland.

settling and a closer packing of the individual grains results with a reduction in the amount of air-filled pore spaces. The first major change in slope occurs at about the 10-m depth, with a density of about 0.55 g/cm^3 (Anderson and Benson, 1963).

Another important depth interval on the curve appears as a zone between the interval 68 m and 74 m where the densities average 0.821 g/cm^3 and 0.840 g/cm^3 , respectively. At these depths the formerly intercommunicating pore spaces become completely closed off from atmospheric circulation and form individual air bubbles. This close-off or zero permeability zone is the result of vertical plastic deformation of the firn. It is here, at a mean depth of 71 m and an average density of about 0.828 g/cm^3 , that by definition firn becomes glacier ice. The overburden at this point is around 4.8 kg/cm^2 . A detailed investigation of the pressures in the inclosed air bubbles as a function of depth (Langway, 1958) indicates that all subsequent increase in density with depth results from further plastic compression of the ice which causes a reduction in the void volume and an increase in the pressure of the inclosed air bubbles.

The overburden pressure at any point below the snow surface may be calculated by integrating the depth-density curve to that depth

$$\sigma_h = \int_0^h \gamma \, dh$$

where σ is the overlying weight of the snow, kg/cm^2

h is the depth below the surface, cm

γ is the density, g/cm^3

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Among other things this information allows the calculation of one component of the internal stresses within the glacier mass. By making some simple assumptions a depth-time of deposition curve can also be obtained at any given depth from the cumulative load pressure value (see Appendix A and B).

Appendix D presents the cumulative load pressure values as a function of depth obtained by numerically integrating the mean density values from meter intervals. A plot of load pressure versus depth indicates that at about 150 m the relationship is approximately linear and can be expressed as

$$\sigma_a = 12.50 + 0.92 (h - 1.5 \times 10^4) + P_a$$

where σ_a is the absolute load pressure, kg/cm²

h is the depth, cm

P_a is the average ambient air pressure at Site 2 (0.8 kg/cm²).

Assuming that the density is distributed uniformly throughout the interval 360.5 m to 411 m, by linear extrapolation, and using a density value of 0.917 g/cm³ at 411 m, the cumulative load pressure at the bottom of the bore hole is 35.65 kg/cm².

A number of investigators (e.g., Bader, 1953; Landauer, 1954, 1957; Bader, 1960, 1962; Waterhouse and Steeves, 1960; Benson, 1962) have studied density profiles from the Site 2 area in great detail and have formulated mathematical expressions and models by treating the depth curve in simple increments or by using complex functions to fit the available data. With the deeper density measurements available from this study it was possible to give better boundary conditions for theories of natural densification and the metamorphism of glacier ice (see Appendix A).

Discussion of Results and Conclusions Above 100 m

By observations and measurements of the stratigraphic features in the pit wall and by transmitting light through the hand-augered and mechanically augered cores from the upper 100 m of the firn-ice mantle, it was possible to interpret the annual stratigraphy, with progressive difficulty at depth, in much the same manner as is done in pit studies (Schytt, 1958; Langway, 1961; Benson, 1962). Furthermore, from precise density measurements related to the bubble pressure studies made on this deep core (Langway, 1958) it was possible to demonstrate empirically by direct measurement that the density of the firn-ice transition in polar ice (i.e., zero permeability) is in fact 0.828 g/cm³ and that this zone is located about 71 m from the snow surface at Site 2.

The classical stratigraphic indicators listed in Table I had been previously demonstrated to be useful criteria for interpretation of annual layers in a dry firn profile to 47 m (Bader et al., 1955). In this study, it was possible to extend the usefulness of the classical approach to approximately 100 m. A major factor in accomplishing the stratigraphic interpretations was the ability to trace continuously the structural features as a function of depth as the features and the surrounding material gradually metamorphosed from the undisturbed surface snow through the firn and into the high density glacier ice.

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Two interesting and valuable general observations are noted in the stratigraphic study and the bulk density measurements over the upper 100 m.

(1) Core segments appearing lighter in color on the light table are usually relatively more dense (winter layers) than the adjacent darker, less dense segments (summer layers).

(2) In the deeper portion of the upper 100-m profile (50 m to 100 m), core pieces containing what appear to be 1 to 2-mm ice layers or melt crusts are usually relatively less dense (summer layers) than adjacent core segments.

A count of the yearly layers from the surface to 100 m reveals 174 years of net accumulation. Details of this study will not be presented here, but an analysis and discussion of the pronounced melt features (i. e., ice layers, crusts, wedges and glands), their spacings in time, and their climatological significance will be included in a later chapter.

IV. DETAILED STRATIGRAPHIC STUDIES

General Background

At the beginning of these core investigations (summer 1957) no positive method for interpreting annual layers from deep ice was available. From experience it was obvious that the classical stratigraphic approach would not be satisfactory because of the lack of observable structure and the dampened range in density variations. In fact, there was some question whether relict layering or even microscopic property variations which could be related to original seasonal variations still existed in the deep ice.

Instead of the direct inspection and simple physical measurements used in the classical interpretation of the upper layers, the stratigraphic analysis of deep ice would require critical interpretation and indirect analytical techniques. Since many analyses were anticipated, pilot physical or chemical tests would have to be tailored and carefully conducted so that when one analysis had been established it would be possible to correlate these results with other analyses that would yield similar information and would be less costly and more adaptable to routine investigations. In order to gain full advantage of the available information contained within the ice cores any observed systematic cyclic sequence, periodicity or variation that might reveal or suggest seasonal or annual layers or other time intervals was closely investigated, and the feasibility of using this sequence to acquire additional data was studied. It was also desirable to establish a reliable standard method which could be used for comparative purposes with other indirect methods and to correlate results from other and deeper ice cores that were being planned.

The problem of interpreting deep ice core is essentially related to the depth at which the macroscopic stratigraphy becomes obscure, but it is also due in part to the physical damage done to the core during drilling. The depth at which the established seasonal parameters of density and melt features would cease being detectable and useful was unknown. The last structural feature was clearly observed at 220 m (a thin ice layer) but because the core was not continuous below this depth, and horizontal wafering and multiple fractures were common, reasonable interpretation of physical stratigraphy ends just below 100 m.

Since it was physically impossible to study the entire core in minute detail, it was decided to limit any detailed investigations to continuous 1-1/2

Figure 15. Schematic diagram showing the general plan and procedure for the detailed investigations on the deep ice core (from Langway, 1962).

to 4 m increments from about 100 m intervals (Fig. 15). Based on the upper core studies these increments would represent about 3 to 10 years of accumulation; not enough for detailed climatic investigation, but certainly enough to indicate order of magnitude trends. It would then be possible to interpolate between these levels, assuming no hiatus exists, and with caution draw some conclusions based on this information.

Macroscopic Stratigraphy at 100 m

The only satisfactory basis for evaluating and establishing the usefulness of an indirect method of stratigraphic analysis is a direct macroscopic correlation. The deepest undisturbed profile increment at which core was continuous from the surface layers and still contained vestiges of physical stratigraphy from which one could vaguely estimate annual layers was at 95.69 m. The prime question to resolve was whether any macroscopic variations existed over this profile that could be definitely correlated with primary deposition.

Results of Analysis and Discussion

Figure 16 presents a plot of the stratigraphy and density data from the 3.93-m profile between 95.69-m and 99.62-m depth. The horizontal lines between the core piece numbers at the left of the figure indicate the total vertical thickness of each core piece. This entire profile is continuous except for the thin mass removed by the band saw blade while cutting the core

into pieces. Several interesting relationships revealed in Figure 16 are discussed below.

Density measurements

Both field and laboratory density measurements of the 29 core pieces which make up this profile were performed using the hydrostatic method and are accurate to $\pm 2 \times 10^{-4}$ g/cm³. Density values range between 0.8752 g/cm³ (Piece 482) and 0.8953 g/cm³ (Piece 487), or a difference of only 0.0201 g/cm³ over the entire profile. The values given here are those remeasured in the laboratory nearly 8 years after core recovery. At this time all original measurements disclosed a consistent and slight decrease from their original values. This may be explained as a time dependent volume expansion of the ice (creep) after removal from its original confining stress environment, and the subsequent expansion of the gaseous air bubbles within the ice. Air bubbles in core samples from the 100-m depth originally contained pressures which did not exceed 2.3 kg/cm² (Langway, 1958). Apparently, the volume expansion is a second order physical relaxation phenomenon and has no bearing on the relative stratigraphic usefulness of the density measurements.

The slope (m) of the depth-density curve, dy/dh , has been determined for these data by a least squares analysis and a value of 15.74×10^{-6} g/cm³-cm is obtained.

Stratigraphic evaluation

Density variations. In the classical interpretation of pit stratigraphy it is customary to select the lower density increments as representing summer deposits and the higher density increments as depicting winter deposits. A cyclical seasonal evaluation of the density differences from the data shown in Figure 16 is in excellent agreement with the seasonal peaks as determined by the oxygen isotope ratio variations except for a small interval near the top (96.25 m to 96.75 m). Detailed discussion of the oxygen isotope ratio variations is given later.

Melt features. The more significant structural features of apparent temperature dependency - ice layers - are nearly all confined to the relatively less dense summer layers. Two features indicated as ice layers at 97.80 m and 98.50 m are contained in obviously denser winter layers and are therefore assumed to be the elusive wind crusts. A total of 24 ice layer features are distributed over the profile which indicates that less than 10% of the features regarded as ice layers are in reality wind crusts.

The SIM and DIM structures (see Chapter III, p. 19) are particularly interesting. A consideration of their possible origin leads one to conclude that they are related to elevated temperatures and hence are summer indices. This is supported by the fact that they are horizontal structures and often sandwiched between 1-2 mm and thicker ice layers. In all cases shown in Figure 16 the SIM and DIM features are contained in less dense summer layers. It is believed that the SIM and DIM laminae were originally either depth hoar or possibly icy firn layers which partly or completely collapsed and compacted during deep burial, yet still retained recognizable amounts of large rounded grains, and, to a lesser extent, angular forms associated with the original features.

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Concentrations of closely spaced multilayered melt features occur at levels represented by core pieces 469, 472, 478, and 480. Piece 480 has two relatively thick ice layers. It is particularly interesting to note that, even though they contain more melt features, these pieces still reveal bulk density values that are measurably lower than the adjacent winter layers.

Light transmissivity. The ability of a core piece to transmit light depicts in a gross way the density (or porosity) variations in small segments. This is a convenient measure and if substantiated would be a useful criterion in ice core stratigraphy, mainly because it provides a means of differentiating relative density differences of thin layered sequences without the necessity of cutting the core into very small thicknesses to perform measurements. As shown in Figure 16, a comparison between density, stratigraphic structures, and light transmissivity suggests that the darker sections correlate with the summer layers and the lighter sections correlate with the winter layers. Note also that the relative light transmissivity observations transect individual core pieces; that is, an end portion of one core piece and the beginning of the next core piece may show the same relative degree of light transmission (e.g., Pieces 476 and 477 are both light, Pieces 465 and 466 are both dark and Pieces 477, 480 and others have multilayered sequences). Another interesting fact illustrated in Figure 16 is that winter layers are generally more homogeneous appearing than summer layers. Winter accumulation rarely displays the structural features or the multilayering that are common in the summer layers.

Summary and Conclusions

Summarizing the observations and measurements at 100 m we can state that the slight variations in density are still real at this depth and represent original seasonal differences in deposition. When viewed by transmitted light on a light table, summer accumulation is generally multilayered (depicting more frequent and variable accumulation periods) and darker with prominent evidence of melt features, whereas winter accumulation is texturally more homogeneous and lighter with an occasional wind crust present. All seasonal structural features and light transmissivity are in good agreement with the density variations.

When the limits of annual accumulation are determined from the measured density variation, structural features and light transmissivity we count 9 years of accumulation over this profile. Using the variations of the O-isotope ratios as the basis for estimating annual increments we find 10 years of accumulation represented.

The real significance of Figure 16 is that it demonstrates that deep ice exhibits the same classical stratigraphic variations found in near-surface firn and that when undisturbed core is carefully analyzed, at least to 100-m depths, it may be interpreted in the same manner.

V. OXYGEN ISOTOPE STUDIES

General Background

Isotopes are atoms of an element that are chemically similar but have different atomic weights. These mass differences affect certain physical

properties, such as the rate of evaporation, vapor pressures and fractionation processes. It is possible to separate isotopes in the laboratory by physical and chemical methods. In nature, however, the lighter isotopes - especially hydrogen, carbon and oxygen - undergo a natural fractionation process and are often used as tracers to study atmospheric mixing processes (Craig, Boato and White, 1956).

The more important and most common oxygen isotopes are O^{18} and O^{16} ; the others (O^{14} , O^{15} , O^{17} , O^{19}) either have very short half-lives or exist in extremely low concentrations. The universal O^{18} to O^{16} ratio abundance from all waters and gases varies between 1:495 to 1:515 with an average of approximately 1:500 (Rakestraw, Rudd and Dole, 1951; Epstein and Mayeda, 1953; Dansgaard, 1954). In other words, about 99.8% of the oxygen in natural waters is O^{16} and about 0.2% is O^{18} . Although the average variation of the O^{18} and O^{16} concentrations in nature is slight, it has been demonstrated by mass spectrometric analyses that variations of the order of 0.1 part per mil can be detected.

Early work on the variations in the stable oxygen isotopes (O^{18} to O^{16} ratio) in natural waters (Epstein and Mayeda, 1953; Dansgaard, 1953, 1954) established some fundamental relationships between the O^{18}/O^{16} (O-isotope) ratios and atmospheric processes. The more important factors are the temperature of precipitation, the origin of the water vapor in the air mass, and the past history of the precipitation cloud system. Epstein and Mayeda (1953) formulated a simple multistage distillation model that explains the general behavior and trends of the O-isotope ratio variations quite well. In this model rain water has proportionally less of the heavy isotope (O^{18}) than does sea water since fractionation takes place during evaporation. Conversely, when recondensation occurs the first water precipitated is enriched in the heavy isotope. As a mass of water vapor rises over land and is cooled the precipitation becomes progressively lighter until the last condensate which falls is lightest of all. Successive increments of precipitation from an air mass were found to have more negative O-isotope values*; the state of the precipitation (rain or snow) does not appear to affect the results (Epstein, 1956).

Previous Work

The value of the O-isotope ratio as a glaciological tool was first reported by Dansgaard (1954) and Epstein (1956). From the O-isotope studies made on temperate glaciers in Canada, Alaska and the United States (Epstein, 1956; Epstein and Sharp, 1959; Sharp, Epstein and Vidziunas, 1960) it was shown that although large O-isotope ratio variations often existed in samples taken from a single storm, layers composed of winter precipitation generally have lower concentrations of O^{18} than layers of summer precipitation. In addition it was found that the isotopic composition varies within one glacier, and that the average O^{18} content of the temperate glaciers investigated decreased with increasing latitude. The initial Greenland firn samples then analyzed contained the lowest average O^{18} content measured.

Similar correlations of the O-isotope ratios were later reported from rain and snow by Dansgaard (1953, 1961, 1964) and from polar snow-firn by Gonfiantini and Picciotto (1959). Picciotto, DeMaere and Friedman (1960) established a direct correlation between the O-isotope composition of a polar

*See p. 35 for explanation of measurement units.

snowfall and its temperature of formation from radio-soundings at the base and the top of the clouds providing the precipitation. The results indicate that the O-isotope ratio measured in snow depends solely upon the temperature of formation and is not influenced by cloud height or type of precipitation.

Direct stratigraphic correlation between the O-isotope ratio variations and seasonal precipitation of deposited polar snows was first tested and demonstrated to be valid in the upper firn layers of the North Greenland ice sheet (Epstein and Sharp, 1959; Benson, 1962). The melt water samples were carefully collected by Benson from firn strata in pits where the annual limits of accumulation were well defined by classical methods, and the O-isotope ratio analysis was in excellent stratigraphic agreement. These results suggested that diagenetic changes in the firn had little or no effect in altering the O-isotope ratios of the original strata, at least in the upper few meters. This study firmly established the empirical seasonal correlation between O-isotope ratio variations and high polar firn stratigraphy. The more important diagnostic relationships evolved from this study are:

(1) the lower precipitation temperatures of winter are reflected in smaller (more negative) O-isotope ratio values and the higher precipitation temperatures of summer correspond to larger O-isotope ratio values (less negative),

(2) at a given location the seasonal variations in temperature cause a similar variation in O-isotope ratios,

(3) the amplitude of the seasonal O-isotope variation is approximately 100 to 200 times the experimental error of measurement.

These results suggested a very good possibility of using this technique to interpret deep ice layers if the layers had not undergone a homogenization or other destructive processes in the course of their deep burial which would affect the original O-isotope sequences.

Deep Ice Core O-Isotope Stratigraphy

The success obtained with the O-isotope method of stratigraphic analysis in the upper polar firn layers (Benson, 1962) was encouraging, but little was known of the effects of long term metamorphism on the surface-established O-isotope ratio variations. It was suspected, however, that any change in the O-isotope ratio variation would be less in polar glaciers than in temperate glaciers because of the temperature considerations (Epstein and Sharp, 1959).

Since deep polar ice had not yet been stratigraphically investigated by the O-isotope technique the first step in this investigation was to select carefully a deep continuous profile of ice core that would serve two purposes. It would establish a pilot study for the O-isotope method and at the same time it would also provide a correlation check for the classical stratigraphic technique at depth.

Core samples and preparation

O-isotope ratio measurements require only small quantities of liquid. This is, of course, ideal for stratigraphic purposes. The core pieces were selected from continuous vertical profiles at four depth levels at approximately 100 m (two series of samples), 200 m, 300 m and 411 m. Since additional studies were planned for the remaining core, each profile was carefully re-examined in detail before O-isotope sampling to insure maximum understanding of the relationships involved. At this time a continuous vertical thin section

was also prepared from each of the four depths for stratigraphic, structural (crystal orientation) and textural (crystal size and shape; bubble size and shape) correlation with the O-isotope and other data. Meticulous care was given to the various operational details and conditions of preparation.

Sample preparation started by trimming pie-shaped wedges from each solid core piece as is illustrated in Figure 15. These strips were then cut into 2 cm high increments and placed in pre-cleaned 50 ml capacity wide-mouthed glass containers with Bakelite screw caps. After an initial tightening of the caps the containers were brought out of the cold room and the samples allowed to melt at room temperature. Volumes of the melted samples averaged about 5-10 ml. Because any evaporation or loss of the original liquid would affect the subsequent O-isotope ratio, after a final tightening of the container a wax seal was placed on the cap-glass interface. A reference line was also marked at the liquid level on the outside of the container.

Starting in late 1957 the writer spent nearly 8 months of laboratory time in the careful preparation of the 439 individual samples and in making the thin sections.

Analytical procedures and measurements

All O-isotope ratio measurements discussed in this report were performed by S. Epstein or his associates in the laboratories of the Geological Sciences Division, California Institute of Technology.

A detailed discussion of the preparation techniques and the mass spectrometer used for analysis is given in Epstein and Mayeda (1953). Approximately 5 ml of sample melt water is used for measurement. Since the direct admission of water vapor into the mass spectrometer affects the vacuum system components and creates an unstable background the melt water sample is isotopically exchanged with carbon dioxide to equilibrium

using the Chicago PDB standard sample (i.e., CO_2 from a belemnite fossil from the Cretaceous Peedee formation in South Carolina).

After equilibrium has been achieved the O^{18} of the carbon dioxide is equal to that of the sample water multiplied by a fractionation factor. The carbon dioxide is then introduced into the mass spectrometer and the measurement carried out by comparing the isotopic components CO_2^{16} and $\text{CO}^{16}\text{O}^{18}$, of masses 44 and 46, respectively.

The results of measurement are expressed in δ units as per mil of relative concentrations with respect to mean ocean water. The unit is defined as

$$\delta (\text{‰}) = \frac{\text{O}^{18}/\text{O}^{16} \text{ sample} - \text{O}^{18}/\text{O}^{16} \text{ standard}}{\text{O}^{18}/\text{O}^{16} \text{ standard}} \times 1000$$

By definition $\delta = \text{zero}$ for mean ocean water. A $\delta = -30$ means that the $\text{O}^{18}/\text{O}^{16}$ (O-isotope) ratio of a sample is 3‰ or 30 per mil less than that of mean ocean water.

Results of Analyses

The δ values for individual O-isotope measurements from the three levels completed are plotted as a function of depth over each profile interval

in Figures 17, 18 and 19. For reference, core piece numbers are given on the left margin in the figures; in the case of the 100-m profile, the stratigraphic structure is shown on the right margin. Partly because of the physical condition of the samples no stratigraphic structures were observed in the core over the lower three depth profiles. The ice cores from 200 m, 300 m and 411 m all exhibited transverse fracture joints which occurred during drilling but these fractures had no effect on the preparation of samples or the O-isotope measurements (Epstein, personal communication). The O-isotope data from the 200-m samples are not yet available.

A study of the diagrams (Fig. 17, 18, and 19) shows features common to all depth levels. All curves display, to varying degrees, a sinusoidal distribution of the δ values with depth. In the lower half of the 100-m profile (the first batch measured), where continuous measurements were made, more scatter of δ values is observed, but even here the overall form of the curve shows distinctly individual maximum peaks and minimum troughs. At the two deeper levels (Fig. 18 and 19) every second or third melt sample was measured after a systematic distribution trend started to develop. Here the data plot as smoother functions, particularly at 300 m (Fig. 18). The wave lengths for the 300-m data are quite uniform and the cycles amazingly symmetrical. The same generally holds true for the 411-m data with the exception of the noticeable asymmetry associated with the third cycle from the top of the profile (Fig. 19).

Stratigraphic interpretations

O-isotope ratio variations have been demonstrated to be dependent primarily on the temperature of precipitation formation, which is roughly similar to seasonal surface temperature variations (Picciotto *et al.*, 1960) and have been empirically correlated with seasonal deposits in the Greenland upper firn (Epstein and Sharp, 1959; Benson, 1962). The cycles represented in Figures 17, 18 and 19 are therefore taken to be annual and the major peaks and troughs taken to represent snow deposits of maximum summer temperatures and minimum winter temperatures, respectively. Summer (S) and winter (W) are objectively established by selecting the absolute maximum and minimum positions on the curve for each cycle.

All structural parameters observed at 100 m correlate well with each other and are in good agreement with the O-isotope data (Fig. 16). From the 300-m and 411-m depths the O-isotope variation is taken as representing the best estimate of the annual accumulation at these depths.

Table V, Columns 9 through 14, presents a summary tabulation of the evaluation of the O-isotope data and the stratigraphic interpretation of the δ measurements made at each depth level shown in Figures 17, 18 and 19. Seasonal annual cycles (summer to summer or winter to winter) are calculated for each depth in water equivalents (Table V, Column 10 through 13), using the average density for that depth (Column 14). For the 100-m samples densities of actual core pieces were averaged; at the other levels an average density value was used. Some differences are observed between the average summer and winter seasonal values (Columns 10 and 12) due to the slight asymmetry in the form of some of the cycles. The differences in no case exceed 4%.

Other results and discussion

Besides the stratigraphic interpretation of the O-isotope data Table V presents a summary tabulation of the δ values. These data contain several

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Figure 17. O-isotope ratios at the 100-m depth. S = summer, W = winter.

Figure 18. O-isotope ratios at the 300-m depth.
S = summer, W = winter.

interesting features. The mean δ value (Columns 7 and 8) for the 251 samples measured is -30.3 with a maximum and minimum of -36.1 and -23.2 . The mean averages are -30.4 , -30.7 and -30.0 at 100 m, 300 m and 411 m, respectively. Since the samples from the consecutive depth levels are progressively older, the general change in the average δ value with depth would at first appear to suggest past climatic change; however, it must be remembered that because of glacier flow deep seated ice is not representative of the surface vertically above its position.

On the average the surface O-isotope ratio for any location should be constant. Assuming an idealized flow pattern for the ice sheet radiating out from the center (Nye, 1953, 1959; Weertman, 1957; Haefeli, 1961, 1963) the deeper ice originated at higher altitudes and its δ value should consequently be lower since average δ values decrease with declining surface temperature. If we take, for the present, a time-average accumulation rate for Site 2 of $40 \text{ g/cm}^2 \text{ -yr}$ and an average surface velocity of 15 m/yr , a first approximation will give an area about 15 km upstream as the depositional source for the ice at the 411-m depth. Since the general surface slope in the Site 2 region is about 0.2% the elevation 15 km upstream would be about 30 m higher than at Site 2. The general change in the average δ value of the O-isotope ratio versus elevation for North Greenland is given as 0.6 per 100 m (Sharp, Epstein and Vidziunas, 1950). This would amount to about a -0.2 decrease in the δ value in the snow falling 15 km upstream at 30 m higher elevation.

Figure 19. O-isotope ratios at the 411-m depth.
S = summer, W = winter.

From the plotted curves of Benson (1962) it is possible to estimate the average surface O-isotope ratio at Site 2 from measurements made along the same latitude on both sides of Site 2. Using these raw data and interpolating between the points one arrives at an average surface δ value for Site 2 of about -29.8. The difference between the surface and the 411-m δ values is nicely accounted for in this analysis, and the interpretation of the δ value for the 300-m samples is explained by a possible climatic change.

The maximum range in δ values, 12.9, is found in the 100-m samples and the range progressively decreases with depth to 8.4 and 7.5 at 300 m and 411 m, respectively. This progressive decrease in the numerical δ range with depth combined with a slight decrease, in the same direction, of the standard deviation (s) of the δ values (Column 7) and the general smoothing effect observed

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Table V. Summary data from stratigraphic evaluation of O-isotope ratios from 100 to 411 m deep ice core samples.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)
Approx sample depth (m)	Core piece number	Actual depth from 1957 surface (m)	Profile increment (cm)	No. samples prep	No. samples meas ^a (n)	O-Isotope ratio, δ (‰) (s)	Range in δ values	No. annual cycles	Average cycle as net annual accumulation		Average density (g/cm ³)		Average density (g/cm ³)
									Summer (g/cm ²) (s) [†]	Winter (g/cm ²) (s)			
100	461-488	95.59-96.62	393	191	136	-30.4 2.68	-36.1 to -23.2	10	32.4	8.9	32.8	10.6	0.8872
200	848-859	211.37-215.29	192	93	0	-- --	--	--	--	--	--	--	.9150
300	1215-1220	296.53-297.82	129	53	42	-30.7 2.11	-34.6 to -26.1	2-3	32.7	2.3	36.7	2.6	.9165
400	1335-1346	409.07-411.21	214	107	73	-30.0 2.07	-34.0 to -26.5	5	33.4	9.1	32.7	8.7	0.9175**
Total				928	454	251	-30.3	17-18	32.8		34.1		

^aO¹⁸/O¹⁶ measurements by S. Epstein, California Institute of Technology[†]Standard deviation; see p. 127^{**}Extrapolated from density value at 360 m

in the 300-m and 411-m curves is suggestive of a diffusion process with depth (time) with respect to the O-isotope ratios. There is a 65% decrease in the numerical δ range between 100 m and 300 m and a 9% decrease between 300 m and 400 m. To my knowledge the mechanics of this process have not been adequately evaluated nor has a satisfactory explanation been established.

The good correlation between the O-isotope variation and the macroscopic stratigraphy at 100 m encouraged a more analytical treatment of these data. Table VI presents the summary data of these analyses. Figure 20 shows curves of the core piece bulk density versus the average δ value for that piece (lower curve) and the weighted bulk density values versus the weighted average δ value for seasonal layers (upper curve). A third parameter is also incorporated into these curves. The open circles and partly or completely filled in circles next to the numbers represent the light transmissivity for each piece (lower curve) or seasonal interval (upper curve). The dark circles represent less light transmission (summer layers) and the open circles represent more light transmission (winter layers) through the core. The pie-shaped portions represent that fraction containing multilayers. For purposes of this analysis the O-isotope seasonal layers were calculated and are defined as the quantity of accumulation that bisects one-half the amplitude of the wave height on both limbs of the annual wave, i.e., the measure of accumulation as shown on the curves (Fig. 17, 18 and 19) that is statistically one-half the distance between a particular trough and a peak is either the spring or the fall boundary.

A comparison of the curves (Fig. 20) for seasonal layers and for core pieces (cut based on visual stratigraphic features, see p. 12) shows that no great advantage was gained by statistically treating the O-isotope data from this profile as seasonal layers. This fact is clearly shown in Table VII where the regression equations obtained by the method of least squares are given. Both curves are essentially the same. The very good fit for linear correlation of bulk density and O-isotope data over this depth interval is illustrated by the rather high correlation coefficient, r , and particularly by the Student- t test values (both significant at less than 0.001 level).

Summary and Conclusions

Interpretation of the O-isotope data from the continuous vertical profiles at different levels of the deep core reaffirms the results obtained from surface firn studies (Benson, 1962; Epstein and Sharp, 1959) in that a strong seasonal variation in δ is obvious, with the summer layer richer in O¹⁸ and the winter layers depleted in O¹⁸. The results also substantiate the fact that the original seasonal variation

Figure 20. Bulk density versus the average O-isotope ratio for the core piece (lower curve) and the weighted bulk density versus the weighted average O-isotope ratio for seasonal layers (upper curve). Open circles represent winter layers, closed circles summer layers.

Table VI. Summary of O-isotope, density and stratigraphic data from 100 m deep ice cores.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Core piece no.	Depth to top (m)	Length of piece (cm)	O-Isotope ratio* (n) (δ)	Density (g/cm ³)	Megascopic stratigraphy†			
					Relative appearance in transmitted light	Structural features		
						Depth to top (m)	Unit	Thickness (mm)
461	95.69	10	3 32.6	0.8913	Lighter	95.86	SIM	5
462	95.79	23	5 31.1	.8838	Darker?	95.98	I L	1
463	96.02	16	4 29.9	.8763	Darker	96.03	DIM	5
464	96.18	7	2 32.9	.8895	Lighter	96.14	I L	1
465	96.25	13	2 34.0	.8880	Darker	96.44	I L	1
						96.59	I L	1
466	96.38	16	4 29.5	.8834	Darker	96.62	SIM	5
467	96.54	19	4 26.6	.8818	Lighter	96.88	SIM	14
468	96.73	12	2 29.6	.8906	Lighter	96.89	I L	2
469	96.85	10	3 28.0	.8781	Darker	97.20	I L	1
470	96.95	12	2 30.8	.8915	Lighter(L)	97.22	I L	1
						97.26	I L	1
471	97.07	10	3 31.9	.8954	Lighter	97.26	DIM	20
472	97.17	19	4 28.2	.8752	Darker(L)	97.28	I L	1
473	97.36	10	3 30.8	.8923	Lighter?	97.65	SIM	8
474	97.46	15	6 31.9	.8878	Lighter(L)	97.86	I L	2
475	97.61	17	8 28.6	.8762	Darker	97.91	I L	1
						97.96	SIM	4
476	97.78	10	4 32.7	.8928	Lighter	98.00	SIM	4
477	97.88	19	5 30.5	.8863	Lighter(L)	98.09	I L	1
478	98.07	12	6 28.2	.8823	Darker(L)	98.12	DIM**	4
479	98.19	12	6 31.8	.8916	Lighter	98.14	I L	2
480	98.31	13	7 30.7	.8892	Lighter(L)	98.33	I L	1
						98.38	I L	1
481a	98.44	13	7 32.4	.8928	Lighter(L)	98.38	SIM	10
481b	98.57	15	4 29.0	.8865	Lighter(L)	98.39	I L	4-5
482	98.72	15	5 24.2	.8752	Darker(L)	98.40	I L	2-5
483	98.87	17	8 27.8	.8933	Lighter	98.49	I L	1
484	99.04	9	4 33.0	.8918	Lighter	98.67	I L	1
						98.81	SIM	7
485	99.13	10	6 29.9	.8895	Lighter	99.09	I L	1
486	99.23	14	6 29.3	.8880	Darker	99.25	I L	1
487	99.37	13	6 34.2	.8953	Lighter	99.27	I L	1
488	99.50	12	5 35.2	0.8934	Lighter	99.32	SIM	4
						99.57	I L	1
						99.58	I L	2

Bottom:99.62

Total profile: 393 136 30.4 0.8872

*O¹⁸/O¹⁶ measurements by S. Epstein, California Institute of Technology

†SIM = slight indication of melt; DIM = definite indication of melt; I L = ice layer or other crust; (L) = layers present of different light transmission

**Only structural feature over profile observable in section between crossed polaroids.

Table VII. Coefficients for the regression of bulk density versus average O-isotope ratios.

Curve	Intercept b	Slope m	Correlation coefficient r	Standard error estimate S_y	Student t-test t
Individual pieces	0.8330	-17.77×10^{-6}	0.70	0.0046	5.05
Seasonally grouped and weighted	0.8417	-14.81×10^{-6}	0.70	0.0037	4.24

in O^{18} is preserved in deep polar ice. It has been shown that bulk ice core samples containing a more negative average value also have a greater density, that bulk ice core samples with a more positive δ value have less density, and that, when observed, the other stratigraphic indicators agree very well with the summer-winter O-isotope determinations of seasonal layers.

The curves obtained by plotting the O-isotope data versus depth are smoother than those shown at the surface by Benson (1962, p. 41-43) and do not appear to reflect a sharp stratigraphic break at the fall boundary. The good symmetry of the curves, especially at 300 m, is quite evident. Since it is known that precipitation does not fall constantly, it must be assumed that the symmetry is a result of generally uniformly spaced snowfall during all seasons, or that a diffusion process smooths out perturbations. If the latter case is true, there is no effect on the stratigraphic usefulness of the data as long as the maximum and minimum peaks are well defined.

Interpretation of the variation in δ values at each depth level in terms of accumulation gives net accumulation values that are of the same order as the present surface accumulation at Site 2. At 100 m a direct comparison of the O-isotope determined seasonal layers and the megascopically determined seasonal layers shows excellent detailed correlation and gives less than a 10% difference between the methods, in terms of average annual estimates of net accumulation.

In conclusion, it appears that the O-isotope variations provide a very good means of estimating annual accumulation from carefully sampled continuous deep core profiles in polar dry snow regions. The method is particularly desirable because of the small quantity of ice required for the analysis.

VI. CHEMICAL COMPOSITION STUDIES

General Background

The investigation of the ionic constituents in glacier ice is essentially a study of chemical trace substances in precipitation. For gross considerations a glacier may be viewed as a homogeneous mass of snow and ice, but, in fact, pronounced small-and large-scale differences and non-uniform variations exist in many of its physical and chemical properties.

Atmospheric precipitation is the source of all of the accumulation that makes up the mass of a glacier and this precipitation is generally in the form of snowfall. Snowflakes first form in the atmosphere as minute ice crystals as a result of condensation of water vapor on a nucleus or possibly by a grouping of a large number of water molecules (Mason, 1957). Further growth of the ice crystals occurs, producing the often complicated snowflake structure (Nakaya, 1951; Mason, 1959), while falling through the atmospheric layers of various temperatures and supersaturations.

By coalescence and subsequent metamorphic processes innumerable snowflakes eventually are transformed into glacier ice. Chemically glacier ice is predominantly solid H_2O , but trace quantities of water soluble and insoluble substances are also present. The most important of these trace substances are the aerosol (i.e., dispersed solid or liquid matter having a size range of a few molecules to about 20 micron radius) and particulate materials. These particulate materials are incorporated in polar snow deposits during snowfall as crystal nuclei and by wash-out, and also during non-precipitation periods as dry fallout. The water soluble derivatives of the total aerosol and particulate materials are all combined in a glacier melt water sample and are the components that make up the ionic constituents.

Since glaciers are fundamentally products of atmospheric processes, we have approached the studies presented in this chapter from the point of view that the bulk composition of a melted sample, particularly an annual or seasonal increment, is representative of the average bulk concentration of the same constituents in the air for the same time interval. With this in mind an enormous amount of geochemical information may be garnered from a systematic study of the ionic constituents of a polar glacier as a function of time and geographical location. Similar analogies have been extensively used with rain water analyses (e.g., Junge and Werby, 1958; Junge, 1958b; Gambell and Fisher, 1964; Whitehead and Feth, 1964; Carroll, 1962) and have provided valuable insight for further understanding general geochemical processes related to cloud physics, atmospheric chemistry, trace and residence time studies and general atmospheric budget and cycle considerations.

All categories of water soluble or insoluble substances found in glacier ice may be of either terrestrial or extraterrestrial origin. In this chapter we shall discuss the dissolved solids or soluble inclusions which are presumably products of terrestrial processes; in the next chapter we shall discuss those particles which are considered to be of extraterrestrial origin.

Previous Work

Until very recently the amount of data available on the chemistry of temperate region snow and glacier ice has been surprisingly limited, and even less is available on subpolar and polar material.

Table VIII presents the few reported chemical analyses performed on snow, firn and ice from temperate, subpolar and polar regions. Renaud (1949) appears to be among the first to have seriously studied the chemistry of temperate glacier ice. His results showed that temperate glacier ice is composed of a crystal of pure ice surrounded by a relatively saline skin; that the outer saline skin of ice grains has conductivities of about 40 to 120 μ mhos/cm; and that the purer inner core has values of about 1 to 3 μ mhos/cm. Kothe (1953) reported on a study of the chloride concentrations of snow and deep ice samples from an Alaskan glacier. Although the chloride content varied between 0.3 and 4.5 mg/liter, no seasonal or depth correlation was evident. Later work by Gorham (1958a, b) on glaciers

in Spitzbergen and Norway substantiated the low-level salt concentrations found by Renaud and provided some data on the chemistry of surface snow and crevasse openings in glaciers. Gorham found Na and Cl in much the same proportion to one another as in sea water and concluded that sea spray is the important source of salts since Cl can be assumed to be almost wholly marine in origin. He reported sea salt as the dominant component of the Spitzbergen samples with some mineral dust content from local moraines. In Norway, Gorham found a higher salt content in the winter's snowfall than in the older glacier material and explained this by percolating melt during previous summer periods. Georgii and Weber (1962) investigated the trace substances in the atmosphere, particularly SO_2 , and the snow-ice chemistry of alpine and subarctic glaciers. Their results showed SO_4^{2-} concentrations in "several-hundred-year" old glacier ice from Austria (0.057 mg/liter) to be lower by a factor of about 10 than those in fresh fallen snow (0.4 to 1.0 mg/liter), and a parallel situation regarding the conductivity values on the same samples. Georgii and Weber also investigated the chemistry of melted ice core samples from Axel Heiberg Island which covered a vertical 40-year firn profile. Here the results showed an average SO_4^{2-} concentration of about 0.03 mg/liter without any significant variation with time.

The chemical composition of recent snows falling in the northern Sierra Nevada was studied in detail by Feth, Rogers and Roberson (1964). The main results of their study pertinent to this report seem to be in the comparative analyses of new snow (less than 48 hours old) and old snow (on site an "appreciable time" prior to collection). The dissolved solids content in old snow averaged 25% higher than in new snow (from an original average of 4 or 5 mg/liter to 6 or 7 mg/liter), and, particularly striking, the SiO_2 component increased from an average of zero in the new snow to a maximum of 1.7 mg/liter in old snow. SiO_2 was detected in 52 out of 79 of the Sierra Nevada samples, with an average concentration of 0.2 mg/liter.

The first reported study on the chemical composition of polar glacier snow-firn is given by Junge (1960) on samples taken from Site 2, Greenland. Junge was primarily interested in the world sulfur budget but he also measured other ions in the same samples covering the time period 1917-1957, all obtained from a 30 m deep pit. No increase was found in the SO_4 concentrations over the time period studied, which he explained by the fact that, since industrial SO_2 has only a few days residence time, it is washed out before reaching Greenland. However, Junge pointed out the importance of sulfate in the atmosphere in remote places for the composition of crystal nuclei. His results are important and will be discussed further later in this chapter. Langway (1962) reported on the chemistry of 700 year old glacier ice from the Site 2 location and also showed the predominance of the sulfate ion.

Investigations into the chemistry of the Antarctic ice sheet are quite scarce Sugawara (1961) briefly reported on samples of snow from Antarctica but gave wide ranging values for nearly all the ionic constituents in the two samples measured (only the results given for the one reasonably credible analysis are presented in Table VIII). Brocas and Delwiche (1963) performed a systematic study of the geographical variation in the concentrations of chloride, sodium and potassium in snow-ice samples from Queen Maud Land, Antarctica. They found that Cl and Na concentrations decrease from the coast (68°S) to the interior ice sheet (72°S) from 2.3 mg/liter to 0.47 mg/liter for Cl and from 1.54 mg/liter to 0.56 mg/liter for Na, whereas K concentrations showed no important variation. Additional chemical data from two glaciers peripheral to the Antarctic ice sheet are given by Angino, Armitage and Tash (1965). A total of four samples, two from ice chipped off the

Table VIII. Chemical data available on previous analyses of snow, firn and ice from temperate, subpolar and polar regions.

Collection site (reference)	No. samples	Type samples	Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ⁻	NO ₃	NH ₄	SiO ₂	pH	Specific conductance (μmhos/cm)
(milligrams per liter)														
<u>Temperate</u>														
Switzerland (Renaud, 1949)	3	firn & ice	-	-	-	-	-	-	-	-	-	-	-	1 to 37
Alaska (59°N, 134°W) (Kothe, 1953)	24	snow, firn & ice	-	-	-	-	-	~0.4	-	-	-	-	-	-
Finland (Viro, 1953)	10	snow	-	0.43	-	0.35	-	-	-	-	-	0.51	-	-
Norway (Gorham, 1958a)	5	snow & ice	0.08	0.04	-	-	-	-	-	0.01	0.02	~0.008	5.8	1.9
Austria (Georgii and Weber, 1962)	4	ice	0.31	-	-	-	-	0.43	0.057	0.021	0.038	-	5.2	3.3
Sierra Nevada (Feth, et al., 1964)	79	snow	0.46	0.31	0.16	0.39	2.90	0.50	0.93	-	-	0.16	-	-
<u>Subpolar</u>														
Spitzbergen (Gorham, 1958b)	14	snow & ice	2.01	0.21	0.31	0.39	<5.5	3.34	<1.1	0.012	-	-	6.1	-
Axel Heiberg (79°47'N, 92°20'W) (Georgii and Weber, 1962)	41	snow & firn	0.05	-	-	0.07	-	0.07	0.028	0.013	0.029	-	5.2	1.9
<u>Polar</u>														
Greenland														
Site 2 (76°59'N, 56°04'W) (Junge, 1960)	42	snow & firn	0.03	0.01	-	0.035	-	0.037	0.25	-	-	-	-	-
Site 2 (76°59'N, 56°04'W) (Langway, 1962)	29	ice	0.097	0.077	-	-	-	0.156	0.315	-	-	-	-	3.84
Antarctica														
Showa Base (68°30'S, 40°30'E) (Sugawara, 1961)	1	snow	5.3	-	0.61	0.42	-	8.3	0.8	-	-	-	-	-
Queen Maud (70°26'S, 24°19'E) (Brocas and Delwiche, 1963)	100	snow, firn & ice	1.28	0.28	-	-	-	1.31	-	-	-	-	-	-
McMurdo Sound (77°26'S, 162°40'E) (Angino, et al., 1965)	1	ice	6	4	<1	7	12	<14	0	-	-	0	7.0	76

Taylor and Wilson Piedmont glaciers and two from melt water streams draining away from these glaciers, were measured for ionic content. The results showed wide variance in nearly all constituents and the results of only one of the glacier samples is given in Table VIII.

Factors Influencing the Chemistry of Glaciers

Sources of supply

Since precipitated snow is a chemical composite containing substances of diverse origin many factors determine its composition. Probably the most important factors are the source of the nuclei and the history of the air mass carrying the precipitation (Eriksson, 1957; Gorham, 1958a).

Although some uncertainty exists about the chief source of atmospheric ice nuclei, it is generally recognized that the constituents are oceanic, continental and extraterrestrial. The important airborne aerosol and particulate materials include sea-spray particles, mineral dust, volcanic debris, organic dust, industrial waste (pollution) and cosmic dust in various proportions and concentrations.

Salt particles are continually being released into the air from breaking waves as sea spray, and onshore winds transport the sea salt particles in concentrations which vary with wind velocity and oceanic churning. Coastal and inland marine evaporite deposits also provide salt particles. Wind-transported terrestrial mineral and organic dusts and gases of natural and industrial sources contribute a considerable portion of aerosol and particulate matter to the atmosphere (Aufm Kampe and Weickmann, 1951; Kumai, 1961; Kumai and Francis, 1962a; Bigg and Miles, 1964; Rex and Goldberg, 1958). Less is firmly established on the role played by, or the chemistry of, the extraterrestrial component of the atmospheric constituents (see Chapter VII) but Adderley and Bowen (1962), and Bigg and Miles (1963, 1964) clearly show a relation between lunar phase and precipitation.

Crystal nuclei

It is an accepted fact in cloud physics that nearly every cloud droplet, raindrop or snowflake has a nucleus upon which water vapor condenses or sublimates to form the appropriate habit for the existing temperature and humidity conditions (Mason, 1957).

Collisions between crystals and partial melting may produce irregularities. The shape, size or composition of the crystal nuclei do not appear to govern the snow crystal form (i.e., needle, hexagonal, dendritic). The air temperature and humidity at which the crystals grow seem to be the major factors controlling the habit of a snow flake.

The most effective nuclei are presumably hygroscopic electrolytes, gaseous ions and nonhygroscopic dusts (Hutchinson, 1957). Snow crystals generally have a single solid center nucleus with a diameter size range of about 0.3 to 25 microns, averaging about 1 to 3 microns, and numerous smaller condensation nuclei having a diameter size range of 0.005 to 0.1 micron (Kumai, 1957; Kumai and Francis, 1962b). The center nucleus is generally an aerosol particle upon which the water molecules initially condense in the upper atmosphere; the condensation nuclei are usually smaller aerosols which are swept out by the snowflake in its journey earthward (Kumai, 1964). Multi-nuclei are sometimes observed in the branches of large snowflakes due to the coalescence of individual supercooled droplets.

Atmospheric processes

Air masses not only bring the different kinds of weather but also are the transporting agent that circulates, supplies and disperses the aerosols and particulates which are usually characteristic of their place of origin (Carroll, 1962).

The important chemical materials found in polar glacier ice originally served as ice crystal nuclei, but substantial contributions are apparently also made by dry fallout, settled by gravity during non-precipitating weather. For example, Junge and Gustafson (1957) report that about 25% of the Cl^- content of the Boston area precipitation is the result of dry fallout. A similar study by Larson and Hettick (1956) showed that during one 36-hour non-precipitation period at Savoy, Illinois, dry fallout contributed 112 mg of dissolved solids in a collecting pan (10^{-2} mg/cm²) or nearly five times more than the average 10 mg/liter concentrations found in normal rain water analyses. Studies of the distribution of sea-salt particles in the atmosphere (Toba, 1965) show that direct impact of particles on ground obstacles may contribute even more material than the dry fallout process.

Wash-out, or removal of material from the air by capture in falling rain or snow crystals is another source of chemical materials, but the process is only applicable to airborne matter below the bases of precipitation clouds (U.S. Atomic Energy Commission, 1955). Georgii and Weber (1962) report that approximately 20 to 40% of the total trace substance concentration in rain at ground level is by wash-out as well as partial evaporation of the droplets as they fall through unsaturated air.

Transport mechanisms

Besides water vapor the terrestrial materials carried by the wind are mainly substances ejected directly into the air (e.g., volcanic debris and products of thermonuclear explosions), are photo-chemically generated in the atmosphere from original earth sources (Junge, 1960, 1963; Mossop, 1965), or are swept up by the wind from the earth's surface. Apparently, any type of material may be carried by winds if it is small enough (Sverdrup et al., 1946). These substances may be of local origin or transported from great distances.

Although much is to be desired in our knowledge of the transport processes of airborne particles we gain some insight into the mechanism by looking at the literature concerning the exchange and fallout of radioactive debris from test explosions (Storebø, 1960; Prawitz, 1964; Carlson and Jones, 1965), the areal distribution of ejected volcanic ash from violent eruptions (Thorarinsson, 1949; Fisher, 1964; Muller, Juhle and Coulter, 1954), and the disposition of material from dust storm activity (Laprade, 1957; Game, 1964). Thermonuclear fission products are injected high into the stratosphere and spread rapidly in their latitude band of injection but migrate slowly towards the poles (Martell, 1959). The fall velocity is low for these small radioactive particles and stratospheric residence times are given by Stebbins (1960) as 5 months for polar latitude injections and 10-20 months for tropical latitudes, depending upon the altitude reached. The presence of artificial radioactive fallout from the same bomb test found in both the Antarctic (Picciotto and Wilgain, 1963) and Greenland firn layers (Croaz, Langway and Picciotto, 1966) testifies to the worldwide wind distribution of artificial materials if they are injected high enough into the atmosphere.

The distribution of volcanic ash over an extensive area is common following violent eruptions (Symons, 1888; Griggs, 1922; Brooks, 1932; Wexler, 1950). Direct measurements show that the dust injected into the stratosphere by the

Krakatoa (1883) and Katmai (1912) eruptions depressed normal incidence of solar radiation by at least 10% over intercontinental distances for several months (Wexler, 1951). A recent study (Mossop, 1964) shows that volcanic dust remains in the stratosphere at altitudes of over 20 km for at least a year. It is estimated that it takes from 2 to 5 years to remove about 90% of the dust emitted into the atmosphere during violent volcanic eruptions (Mitchell, 1963; Volz, 1964). The dominant wind direction is considered the most important single factor in the distribution of ejected debris. Selective transportation of the less dense, more acidic material plays a lesser but still significant role in the final relative distribution of the volcanic ash (Nayudu, 1964).

Dust wind-swept up from the Sahara desert has been collected in the high Swiss Alps (Glawion, 1938; Roethlisberger, personal communication). Rex and Goldberg (1958) have reported on the atmospheric transport of 1 to 20 μ diam quartz particles from continental sources which are found distributed in mid-Pacific Ocean pelagic clay deposits.

Seasonal variations in precipitation

Many investigators have reported seasonal and geographical variations in the chemistry of rain water samples due either to periodic availability of more aerosol or particulate materials or to gross variations in the seasonal rate of rainfall (Rossby and Egnér, 1955; Junge and Gustafson, 1957; Eriksson, 1952a, 1952b, 1959, 1960; Junge, 1956; Carroll, 1962; Fanning and Lyles, 1964). These investigations often show that concentrations of the various ionic constituents are extremely variable particularly near the coasts and generally decrease in salt content inland. A higher concentration of salts is often found in winter's rain allegedly due to the more turbulent nature of the ocean during this period. Furthermore, it is well established that wash-out locally reduces the concentrations of atmospheric constituents and that the total concentrations of dissolved solids decrease as a function of time during individual storms (Larson and Hettick, 1956; Siksna, 1959; Whitehead and Feth, 1964; Gambell and Fisher, 1964).

The chemical composition of snow, as with rain, can be expected to vary geographically as well as during an individual shower and seasonally in the same location (Carroll, 1962), but the tedious task of collecting precipitation samples for chemical studies as a function of individual storm, season or year is greatly reduced by sampling polar snows. It is particularly useful since very little reaction takes place to the soluble salts, colloidal or particulate matter after it is deposited on a cold glacier (Junge, 1960).

An early attempt was made by Kothe (1953) to find a seasonal correlation in the chloride concentrations in snow-ice samples from a temperate glacier. He anticipated the possibility of a higher concentration of sea salts in summer snows because of the seasonal increase in oceanic vapors brought inland by prevailing winds. The results, however, are inconclusive because of the melt conditions associated with a temperate glacier, the wide depth spacing of the samples, and perhaps the analytical procedures and equipment used in the analyses. In any event, no apparent success was attained and little variation was found between seasons or depth.

The study reported in the next section was made in an attempt to resolve the possible stratigraphic significance, to determine the limits of variability in the chemical constituents, and to investigate any major precipitation trends which might have occurred in ancient precipitation. No data are available on a systematic study of glacier ice over a continuous depth profile for this purpose. The work reported by Georgii and Weber (1962) was performed on an ice core that was stratigraphically dated (Müller, 1963), but the samples were taken to represent annual layers and therefore the chemical results do not reveal seasonal variations.

Deep Core Stratigraphy Using Chemical Variations

If, as suggested by the shape of the O-isotope ratio distribution with depth, the accumulation is fairly evenly distributed throughout the year, sampling for chemical analysis is no problem, and one need only sample uniformly at evenly spaced close intervals to obtain a representative variation. If, however, there is a non-random seasonal period that is generally lacking in snow accumulation, the concentration distribution will be strongly influenced by dry fallout. Stratigraphically, this situation would be desirable if the mechanisms producing this uneven distribution were consistent. The actual distribution of falling snow during the year for the periods represented by these chemical analyses is, of course, not known.

Core samples and preparation

A plot of the first results from the O-isotope measurements on samples at the 100-m and 300-m depths indicated that the 300-m core samples produced the most systematic variations and the simplest data to interpret seasonally. The 300-m core samples were, therefore, selected for the initial chemical analyses for stratigraphic purposes.

Hygienic procedures were followed in handling and preparing the samples from the solid half core. The specimens were handled with clean white nylon gloves and stainless steel tongs. Each 15 to 26 cm high core piece was cut into 3 to 4 cm thick increments, as shown in Figure 15, and carefully trimmed on all sides. The band saw was swept clean of all shavings after each cut. After trimming, each specimen was placed in a pre-cleaned wide-mouthed polyethylene container for shipment. A water level line was marked on the outside of the container. The melt water was not filtered before analysis since preliminary tests indicated sodium was sorbed from certain filter media (R. Werby, personal communications).

Analytical procedures and equipment

The analytical work presented here was performed by specialists in water chemistry using instrumental methods of analysis. In the course of these investigations two different laboratories were employed. Since slightly different procedures and equipment were used at each laboratory the stated precision of measurement varies. The analyses presented in this section were performed* as follows:

Sodium was determined using a Beckman DU flame photometer and photomultiplier. Two sets of measurements were made for sodium: on the original liquid as received and on about 3 ml of a five-fold concentrate. A reproducibility of about 2% was attained. Potassium was determined using the same flame photometer as above with a red phototube, also on about 3 ml of a five-fold concentrate. The precision for Na^+ and K^+ is $\pm 10\%$.

Chloride was determined nephelometrically using a Coleman Model 7 nephelometer on about 15 ml of a three-fold concentrate. Replicate measurements were made on all samples and, considering the variations, a precision of $\pm 25\%$ is given for Cl^- . Sulfate was determined nephelometrically using the same equipment. Replicate measurements were made on three-fold concentrates and, again due to large variations, a precision of $\pm 25\%$ is given for SO_4^{2-} .

*Werby Laboratories, Inc., Boston, Massachusetts.

Conductivity measurements were made using an Industrial Instrument Company conductivity bridge, Model RC16. No carbon dioxide aeration was performed. Measurements are precise to $\pm 1.0\%$.

Statistics and units

Considering all the physical and meteorological factors involved in the snow accumulation process as well as the sampling and instrumental errors in determining such low level chemical constituents, a thorough and strict statistical treatment of the chemistry data is not considered appropriate. Yet, in order to simplify the evaluation and to present general trends, it was necessary to use certain statistical measures and to perform some simple manipulations. The main statistical parameters used on these data are given in Appendix C.

The concentrations of dissolved ions are expressed in milligrams per liter (mg/liter) or weight per volume units. Specific conductance, a measure of the total dissolved salt content of a sample, is given in micromhos per cm units ($= \mu\text{mhos/cm} = \text{ohm}^{-1} \times 10^6$). The individual concentrations of the principal dissolved salts (Na^+ , K^+ , Cl^- , SO_4^{2-}) are summed and the total as reported given for each sample.

For determining the limits of seasonal accumulation for the grouped chemistry data, the same layer dimensions were used as in evaluating the 300-m O-isotope data (see p. 40).

Results of Analyses and Discussion

The results of the chemical analyses of the melt water from 29 continuous increments of ice from the 300-m depth are given in Table IX. The conductivity and certain calculated ratios for each sample are shown in the lower part of the table. Some of these data are plotted as a function of depth in the curves shown in Figure 21; the statistical layers as determined by the O-isotope ratio distribution are delineated by brackets to the right of the specific conductance curve. Since the literature contains arguments supporting both the higher concentration of sea spray particles in winter precipitation and a similar correlation with summer precipitation, no initial assumptions were made regarding the expected seasonal concentrations of the various constituents. The basis for the seasonal correlation at depth is the O-isotope analysis performed on adjacent core sections as shown in Figure 15.

A plot of the individual ionic concentrations given in Table IX versus depth showed no apparent seasonal correlation. This is in part due to the somewhat wide variation often obtained for a single ionic measurement. The average ionic concentrations obtained by summing the individual concentrations over seasonal increments do show an interesting relation however. Table X presents the data given in Table IX averaged over the entire 1.29-m profile and Table XI gives these same data with the concentration averages and ranges now grouped by seasons. Based on the evaluation of the O-isotope data (Chapter V) this profile includes the precipitation from three complete winters, two complete summers and portions of two other summers.

Figure 21. Plots of ionic ratios and specific conductance values versus depth of melt water samples from continuous increments of ice core from approximately the 300-m depth. Brackets to right of specific conductance curve represent seasonal accumulation layers as determined from interpretation of O-isotope data.

Table IX. Chemical analyses of principal dissolved solids in melt water samples from detailed ice core study at 300-m depth, Site 2, Greenland.

Cure piece number:	1215				1216					1217				1218					1219					1220					
Depth to top of piece:	296.53m				296.68m					296.88m				297.10m					297.34m					297.60m (Bottom: 297.82)					
Sample number	1	2	3	4	5	6	7	8	9	10	11	12	13&14	15	16	17	18	19	20	21	22	23&24	25	26	27	28	29	30	31
	(milligrams per liter)																												
Na ⁺	0.106	0.121	0.087	0.125	0.080	0.105	0.088	0.107	0.130	0.088	0.093	0.083	0.087	0.110	0.121	0.096	0.131	0.124	0.084	0.089	0.086	0.124	0.116	0.101	0.090	0.057	0.052	0.052	0.063
K ⁺	.084	.082	.085	.096	.068	.087	.075	.088	.100	.078	.074	.079	.082	.084	.086	.086	.101	.097	.078	.075	.065	.090	.084	.072	.070	.044	.042	.039	.043
Cl ⁻	.15	.18	.14	.18	.10	.16	.14	.18	.18	.14	.14	.15	.17	.20	.21	.15	.17	.18	.14	.15	.16	.19	.19	.14	.18	.10	.10	.11	.10
SO ₄ ⁻	.38	.38	.36	.35	.36	.36	.34	.31	.33	.35	.28	.33	.35	.26	.29	.29	.35	.31	.29	.30	.32	.28	.29	.27	.33	.29	.27	.26	.30
Total, as reported:	0.72	0.76	0.67	0.75	0.61	0.71	0.64	0.68	0.74	0.66	0.59	0.64	0.69	0.65	0.71	0.62	0.75	0.71	0.59	0.61	0.63	0.68	0.68	0.58	0.67	0.49	0.46	0.46	0.51
Specific conductance, (micromhos/cm), at 25C	4.42	4.53	3.91	4.80	3.75	3.91	3.91	4.27	5.32	3.38	3.46	3.34	3.36	4.07	4.73	3.63	5.00	3.78	3.49	3.62	3.88	4.54	4.13	3.75	3.19	2.71	2.55	2.70	2.78
Ratios by weight:																													
Cl/Na	1.4	1.5	1.6	1.4	1.2	1.5	1.6	1.7	1.4	1.6	1.5	1.8	2.0	1.8	1.7	1.6	1.3	1.4	1.6	1.7	1.9	1.6	1.6	1.4	2.0	1.8	1.9	2.1	1.6
K/Na	.79	.68	.98	.77	.81	.83	.85	.82	.77	.89	.80	.95	.94	.76	.71	.90	.77	.79	.90	.84	.76	.74	.72	.71	.78	.77	.81	.75	.68
SO ₄ /Cl	2.5	2.1	2.6	1.9	3.6	2.2	2.4	1.7	1.8	2.5	2.0	2.2	2.1	1.3	1.4	1.9	2.1	1.7	2.1	2.0	2.0	1.4	1.5	1.9	1.8	2.9	2.7	2.4	3.0
Cl/K	1.8	2.2	1.7	1.9	1.5	1.8	1.9	2.0	1.8	1.8	1.9	1.9	2.1	2.4	2.4	1.7	1.7	1.9	1.8	2.0	2.5	2.2	2.1	1.9	2.6	2.3	2.4	2.8	2.1

Table X. Average chemistry of 1.29-m core profile from 300 m.

Ion	Average concentration (mg/liter)	Standard deviation	
		(s)	(%)
Na ⁺	0.097	0.024	25
K ⁺	.077	.017	22
Cl ⁻	.156	.032	21
SO ₄ ⁻	0.32	0.037	12

Table XI. Average chemistry of 2 summer and 3 winter layers from 300 m.

Ion	Winter		Summer		
	Average (mg/liter)	Range	Average (mg/liter)	Range	
Na ⁺	0.109	0.080-0.131	0.092	0.082-0.124	
K ⁺	.085	.068- .101	.078	.065- .097	
Cl ⁻	.17	.10 - .21	.15	.14 - .18	
SO ₄ ⁻⁻	.31	.26 - .36	.32	.28 - .35	
Total, as reported:	0.67	0.58 -0.75	0.64	0.59 -0.71	
Specific conductance, (μmhos/cm, 25 C)	4.25	3.63 -5.32	3.67	3.34 -3.88	
Ratios {	Cl/Na	1.5	1.2 -1.8	1.7	1.4 -2.0
	K/Na	.78	.71 - .95	.86	.76 - .95
	SO ₄ /Cl	1.9	1.3 -3.6	2.1	1.7 -2.5
	Cl/ $\bar{K}$	2.0	1.5 -2.4	2.0	1.8 -2.5

Table XI shows that the average ionic concentrations of Na⁺, K⁺ and Cl⁻ are less in the summer snows with some overlapping in their ranges, whereas the SO₄⁻ ion appears to have nearly the same average concentration for both periods with wider variability during the winter period. The total as reported and conductivity values both show larger winter values. On the other hand, the ratio values are lower in the winter with the exception of Cl/K (for simplicity ionic charge is not shown for the ratios) which seems to average as a constant. The SO₄/Cl ratio is interesting in that although the SO₄⁻ ion is rather uniformly variable for both summer and winter and averages about the same during the year, the SO₄/Cl ratio has an extremely wide range in the winter snows.

Although no outstanding correlations are evident in the ratio curves shown in Figure 21 there are some discrete relations. Note that the K/Na ratios are plotted at twice the abscissa scale used for the other ratios. The K/Na ratio variation is slight over the profile with an average value of 0.79, but the curve does show a faint correlation of higher K/Na ratios associated with summer snows. The Cl/Na ratios show a better stratigraphic correlation, similar to the distribution of the K/Na but with minimum values more pronounced at the fall boundary. Observed in the Cl/Na curve is a distinct fall minimum with a gradual increase in the value to a spring-summer maximum and then a decrease to the next fall minimum.

The SO_4/Cl ratio plot is the most variable of all, yet the general form of this curve appears to parallel the form of the O-isotope curve to a good degree with the more positive values representing summer layers and the minimum values corresponding to winter layers. To a lesser extent the Cl/K ratio variations suggest seasonal relations and seem to reflect a fair, but dampened, mirror image of the SO_4/Cl ratios except for the lower 20 cm of the profile.

The electrical conductivity of water, a dilute salt solution, is the sum total of all the individual contributions from each ion present. Figure 21 shows a plot of the conductivity measurements made on portions of the same liquid samples from which the ionic constituents were determined. Several interesting features are exhibited in the rather narrow limits of the conductivity values shown in this figure.

A careful study of the conductivity curve shows that two out of the three autumn periods represented have extreme maximum conductivity values and, in general, the winter values are higher than the summer values. Except for two samples (Table IX, no. 4 and 17) the form of the conductivity curve would be a mirror image of and in good agreement, with a slight shift, with the general form of the O-isotope curve, particularly the lower 2/3 of the curves. In other words, the fall-winter periods have generally higher total dissolved salt concentrations than do the spring-summer periods. The data plotted in Figure 21 indicate that summer layers have conductivities of between 2.5 and 4 $\mu\text{mhos/cm}$ and that the winter layers are in the 4 to 5.5 $\mu\text{mhos/cm}$ range.

Summary and Interpretation of the 300-m Results

To summarize the chemical results from the 300 m deep samples we find that SO_4^{--} is the major anion and represents 49% of the total measured dissolved salts; Na^+ is the major cation, constituting 15% of the total, with Cl^- , 24%, and K^+ , 12%, the remaining constituents. The K^+ content is relatively high, averaging 0.08 ± 0.02 mg/liter over the profile, and is about 80% to 100% of the Na^+ concentrations. In sea water K^+ is only 4% of the Na^+ , which suggests that the K^+ concentrations in the core samples are probably of non-oceanic origin.

The K/Na and Cl/Na ratios show similar variations with minor differences, notably in the upper 30 cm of the profile. The Cl/Na ratio variation is more pronounced, however, with the maximum values occurring, in all but one case (Table IX, sample no. 5), at the fall boundary. The SO_4/Cl ratios have the widest dispersion, and appear to have a direct correlation with the O-isotope variations, that is, the higher values reflect summer snows and the minimum values the winter snows. The Cl/K variations are in fair inverse agreement with the SO_4/Cl distribution.

The specific conductance of fall-winter layers is generally higher than spring-summer layers, with maximum peaks appearing at the autumn boundaries. The absolute values of specific conductance for these samples range between 2.5 and 5.5 $\mu\text{mhos/cm}$, an extremely weak salt solution when one considers that the purest water made in the laboratory is about 0.05 $\mu\text{mhos/cm}$ and that ordinary distilled water runs about 1 to 5 $\mu\text{mhos/cm}$ (Hem, 1959).

The precipitation chemistry data for any location must be evaluated in light of its geographical setting and the meteorological and physical factors affecting the site. The Greenland ice sheet is supplied with precipitation brought in by rising maritime air masses (Matthes, 1946). Junge and Werby (1958) have shown that the influence of sea spray on precipitation is significant around coasts and very noticeable up to 500 km inland. Site 2 is, therefore, apparently under a strong marine influence since it is only 250 km from the coast but at an elevation of 2000m. The effect of altitude is to deplete salt particles from air rising upslope (Woodcock, 1953; Squires and Twomey, 1957) with a more pronounced effect noted with a steeper slope (Eriksson, 1957). The storm winds that nourish the Site 2 area track predominantly from the southwest (Haywood and Holleyman, 1961) and pass over the open water of Baffin Bay and Melville Bay, from where some, if not all, of the hygroscopic sea spray particles found in the deposited snow have been carried aloft by the winds.

Although snowfall occurs during all the months of a year on a high inland polar glacier actual deposition is not a continuous process. Only limited data are available on directly measured long-term (more than one year) distributions of snowfall at inland Greenland sites (Georgi, 1935, 1959; Loewe, 1936; Matthes, 1946; Hamilton, 1958a, b; Haywood and Holleyman, 1961). Considerable variation is reported and, although some investigators suspect that summer precipitation accounts for most of the yearly layer, evidence from recent semiannual stake accumulation measurements on the inland south Greenland ice sheet ($66^{\circ}28'N$, $46^{\circ}14'W$; elevation 6890 ft) indicates that this is not necessarily the general situation. From stake measurements and density profiles, Reed (1964) and Szathmary (1965) show that nearly 60% of the average total accumulation (four winters and two summers measurements) at this south Greenland site falls in the winter; in other words 50% more accumulation occurs in the winter months (average 4.3 g/cm² -mo) than in the summer months (average 3.1 g/cm² -mo).

This study has shown that the winter layers have on the average a larger concentration of dissolved solids as well as a greater range in the measured values of the ionic constituents and conductivities, with maximum values tending to occur in the autumn. There are probably at least two possible explanations for this situation.

The seasonal concentrations might be explained by a general increase in the airborne sea spray components during the late summer-early fall period due to the progressively worsening ocean surface conditions, followed by an abrupt freezing over of the ocean surface. The ocean in the region of North Greenland is ice-covered more than half of the year, and undoubtedly the nearby freeze-up restricts or diminishes the local supply of sea spray particles. However, open leads can furnish some moisture (Langway, 1961) and in addition the ocean surface to the south is unfrozen and a bountiful source of spray particles. In general winter conditions should favor a more abundant concentration of salt particles in the atmosphere (Woodcock, 1953), and the greater variability found in the ionic concentrations in the winter snows could be explained by sharp alternations of violent snowstorms (Matthes and Belmont, 1950) and the more vigorous wave

breaking conditions at sea (Blanchard and Woodcock, 1956). It is not clear what exact influence these factors have on the airborne salt concentrations in North Greenland. The slope of the conductivity curve does not drop off noticeably in late autumn as would seem likely if the ocean surface quickly froze over and abruptly cut off the total source of sea spray particles. This is, of course, not the only factor involved.

A second, and perhaps simpler, explanation is that, because of the comparatively low liquid water content of precipitation clouds in the winter, there would be a tendency for the precipitation to contain a higher relative concentration of solubles per unit volume of snow. Junge (1958b) estimates in general that a factor two or more increase may be expected in the constituent concentrations of polar latitude precipitation. This second interpretation would only require that more precipitation occurs in the winter than in the summer to make up for the apparently equal thickness of summer-winter layers found in the 300-m core samples.

Of all the chemical components in precipitation, only Cl^- is considered to have a single well defined oceanic source (Eriksson, 1959; Hutchinson, 1957; Mason, 1957; Junge and Gustafson, 1957), although it has been reported that tropospheric reactions of salt particles (Junge, 1957) or oxidation by ozone (Rossby and Egnér, 1955) may produce gaseous Cl_2 and lower the Cl^- concentrations. Because of the well known boundaries the Cl^- component of precipitation is often used to draw conclusions regarding the distribution of aerosols. In general, Cl^- , SO_4^{--} , Mg^{++} and Na^+ are generally considered to be of marine origin and K^+ , Ca^{++} and SiO_2 of terrestrial origin.

Nearly all of the Cl/Na ratios shown in Table IX are slightly less than found in sea water (1.8), a situation similar to that found by Junge and Werby (1958) at inland areas of the United States except that they found slightly higher winter values than summer values. Table XI shows an opposite relationship for Site 2. The Cl/K ratio is essentially constant. The greater concentration of cations in the winter snows when the nearby mineral dust sources (Thule-Tuto area) are snow-covered can only mean either a loss of Cl^- by decomposition of sea spray particles (Sugawara, Oana and Koyama, 1949) or the addition of cations from distant mineral dust sources (Kalle, 1954; Rex and Goldberg, 1958).

Assuming Cl^- to be completely oceanic in origin it is possible to calculate the excess in ionic constituents (above sea water ratios) by subtracting from the measured ion the theoretical net value based on the average sea water ratio corresponding to the measured Cl^- value (Junge and Werby, 1958). Taking the average values from Table IX we obtain an excess of Na^+ amounting to 0.01 mg/liter. Since K^+ is less than 2% of the Cl^- in sea water all K^+ in the Site 2 samples may be considered excess. Combining Na^+ and K^+ from these samples we obtain about 0.09 mg/liter (or about 14% of the total) as excess constituents attributable to mineral dusts.

A basic assumption made here is that sea spray is a major contributor of the crystal nuclei in the atmosphere and a dominant component of the aerosol of the arctic air mass. A knowledge of the proportion of snowflake nuclei which are in fact sea spray would shed some light on the analysis. Air samples from the Site 2, Greenland, area have been studied by Kumai and Francis (1962a) and Fenn (1960) for aerosol and particulate concentrations. Kumai and Francis' work consisted of direct study of the snow-crystal nuclei by collecting individual snowflakes on a mesh, evaporating the snowflake by sublimation, and investigating the remaining solids. The results of the analysis of 356 snow crystal nuclei collected

by Kumai and Francis at Site 2 during the Summer of 1960 (Table XII) are the most complete data available on polar snow-crystal nuclei. The size of all snow crystal nuclei measured at Site 2 was found to range in diameter from 0.1 to 13 microns with an average of about 1 micron. It is interesting to note that hygroscopic particles (i.e., sea spray) compose only 0.6% of the total substances serving as crystal nuclei, and that no identified products of industrial combustion are found.

Table XII. Summer snow crystal nuclei from Site 2, Greenland (from Kumai and Francis, 1962a).

Material	Number	%
Mineral dust particles (siliceous clays)	302	85.0
Hygroscopic particles	2	0.6
Unidentified particles	39	10.7
No nucleus	13	3.7
Total:	356	100.0

Fenn (1960) and Fenn and Weickmann (1959) measured the concentration and size of airborne particulate matter at Site 2 by means of an aerosol spectrometer and a cascade impactor, which collects solid and liquid particles only in the size range from 0.03 to 3 μ diam. From two different samples consisting of 13.5 liters of air (8 hours sampling time) Fenn found the particle concentration in each sample to average about 1 to 3 particles/cm³ in the diameter range of 0.9 to 1.8 μ , averaging about 1 μ . These results, and those by Fenn and Weickmann (1959) show that aerosol concentrations over the Greenland ice sheet in the summer are never higher than 20 particles/cm³ and that the freezing nuclei concentration is only 1/4 to 1/3 of those measured in the United States; they also suggested, as was demonstrated by Kumai and Francis, that the arctic air masses do not contain industrial aerosol.

A later study at Camp Century in March 1960 (Fenn, 1960) showed no distinctive particle deposit, which indicates that the aerosol concentration in winter air was below the background level of 20 particles/liter (0.02 particles/cm³) or at least 3 orders of magnitude less than during the summer season.

To summarize the crystal nuclei discussion we find that hygroscopic sea spray particles constitute a very small percentage of the total aerosol of North Greenland air masses in the summer, and even less in the winter, yet the chemical analyses presented here show greater concentrations of dissolved solids in the winter. These findings are consistent with several factors. Junge and Gustafson (1957) and others have shown that about 98% of the total mass of sea spray particles in maritime air is found in the giant sizes (diameters above 2 μ). Kumai and Francis' (1962a) work involved particles having an average diameter of about 1 μ and so therefore apparently did not include the dominant sizes of sea spray particles. Likewise, the summer-winter concentrations found by Fenn (1960) pertain only to particles between 0.9 and 1.8 μ diam. Particles in the large size ranges (0.2-2.0 μ diam) need not have direct bearing or correlation with giant sized particles.

Geochemistry of the Ice Sheet

In addition to the detailed investigation of the stratigraphic usefulness of chemical variations in the ice core it is also of great interest to determine the internal nature and the variations in the chemical constituents of a polar ice sheet as a function of time and geographical location. The Site 2 deep ice core provided the samples for the temporal study as well as for the internal composition and various surface and shallow cored samples provided the material for the secular investigations.

Sampling and preparation

Because of the low level ionic concentrations, even with hygienic care taken during handling, the difficulties associated with the collection and storage of representative glacier samples will undoubtedly introduce some errors in the final analysis. An understanding of the collection procedures may help make evident possible unavoidable errors.

Handling of all deep ice core samples closely followed the procedures outlined for the stratigraphic chemical studies. The annual snow samples were collected by first digging a pit into the snow, and stratigraphically determining the annual layer. The face wall of the pit was then trimmed back and a channel sample taken over the annual layer of the newly exposed face with a polyethylene scoop. The loose aggregate was shoveled through the neck of a precleaned 10-liter wide-mouth polyethylene bottle. After melting, the water level was marked on the outside of the container, the caps tightened and a special Teflon pressure-sensitive tape was used to seal the cap-container. Other samples were collected at Camp Century in liquid form from subsurface water wells used to supply camp needs. Here samples were taken both at the water surface and with depth in the water well, not under the best circumstances for collection. All solid field samples were melted in closed polyethylene containers, transported from Greenland to Hanover, and then shipped to the laboratory for analysis.

A consideration of the geochemical role of polar glaciers is incomplete if only the dissolved chemical constituents are measured. In the next chapter the solid components will be discussed. In this section, since the melt water was not filtered before chemical analysis, the results include not only the original dissolved materials, but also the contributions of any sorbed fall-out materials in the snow.

Analytical procedures and equipment

The chemical analyses presented in this section were performed by different water analysts* than those discussed in the previous section. The instrumental methods of analysis and precision are given below.

Sodium and potassium were determined by flame photometry with a precision of $\pm 2.5\%$. Chloride was determined with an automatic chloride titrator having a precision of $\pm 2.5\%$. Magnesium was determined by atomic absorption spectroscopy with a precision of $\pm 1.25\%$. Sulfate was determined nephelometrically using the Keily and Rogers method with a precision of $\pm 5\%$. Silicon dioxide was determined by emission spectrographic techniques and the method as outlined in ASTM D1689-61T with a precision of 0.25% . Calcium was determined† by atomic

*Waltham Laboratories, Inc., Waltham, Massachusetts

†Courtesy of N. Johnson and G. Likens, Dartmouth College.

absorption spectroscopy with a precision of about $\pm 5\%$. Conductivity measurements were made using a Serfass conductivity bridge with a precision of $\pm 1.0\%$.

Statistics and units

Statistical treatment of the chemical data in this section is consistent with the chemical data discussed earlier. In addition, because a more complete ionic analysis was performed, equivalents per million (epm) are calculated for each analysis for the purpose of comparing the positive and negative ions. Since water is a chemically balanced system, the sum of the equivalents of cations in solution should equal the sum of the anions, if all the major ions have been determined. In any event chemical balance is an indication of the gross validity of the analysis. As reported by Rainwater and Thatcher (1960) large errors in the determination of trace constituents can go unnoticed and a deviation of up to 5% may result from the accumulation of small unavoidable errors in analysis of water containing as little as 20-30 mg/liter of dissolved solids. Glacier melt water with a total dissolved content of about 1-2 mg/liter would be expected to have a greater error. Angino *et al.* (1965) report an unsatisfactory correlation for the epm calculations on Antarctic ice samples. Because of the extremely low concentrations numerical epm values are carried to three decimal places. Standard deviation, *s*, is used for these samples as a measure of variability or dispersion of the concentration and not as an indication of precision.

Results of Analyses and Discussion

Time and geographical variations

The results of the chemical analyses of the core samples from various depth (time) levels are presented in Table XIII. The core samples represented were randomly taken from the approximate depths indicated. All chemical constituents are given as ions except for SiO_2 which is also not included in the summation of the total dissolved solids because of the uncertainty (Hem, 1959) as to the form silicon takes in solution (colloidal or the ionic silicate). Included in the table are the concentrations in mg/liter, the total dissolved salts and the calculated milliequivalents per liter (epm). Specific conductance for each sample and certain calculated ratios are presented in the lower half of the table.

Although no simple relationship exists between the composition of precipitation and the composition of sea water (Hem, 1959), the ions measured in the samples comprise the major ionic constituents of the oceans. The combined sum of constituents in these samples represents 99.29% of the total variety of all dissolved solids found in average sea water (Column 10) and 49.84% of the total variety of all dissolved solids found in average river water (Column 11) and the predominant fraction of dissolved solids found in natural aerosols (Junge, 1956).

The chemical composition of samples at the progressive depth levels is variable. In most cases the height of the half-core (i. e., split) piece used for a sample represents less than one full year's accumulation, and accordingly the analysis represents the precipitation chemistry for that fraction of a year. On the average the time period involved is approximately one-third of a year and therefore the variability revealed in the results also includes a seasonal variation. Total dissolved salts measured in the core samples range from 0.58 mg/liter to 1.77 mg/liter (average 1.22 mg/liter) or 1.7×10^{-5} to 5.1×10^{-5} less than the concentrations in sea water.

Table XIII. Chemical analyses of principal dissolved solids in melt water samples from 20 to 411 m deep ice cores, Site 2, Greenland.

(1) Sample depth	(2) 20m		(3) 100m		(4) 150m		(5) 200m		(6) 250m		(7) 300m		(8) 350m		(9) 411m		(10) Average sea water*			(11) Average river water†
	(mg/l)	(epm)	(mg/l)	(epm)	(mg/l)	(epm)	(mg/l)	(epm)	(mg/l)	(epm)	(mg/l)	(epm)	(mg/l)	(epm)	(mg/l)	(epm)	(mg/l)	(epm)	(weight percent of all solids)	(weight percent of all solids)
Na ⁺	0.310	0.014	0.135	0.006	0.188	0.008	0.117	0.005	0.119	0.005	0.181	0.008	0.125	0.005	0.156	0.007	10,556	459.0	30.61	5.25
K ⁺	.183	.005	.092	.002	.174	.004	.121	.003	.060	.002	.130	.003	.095	.002	.159	.004	380	9.7	1.10	1.92
Mg ⁺⁺	.017	.001	.035	.003	.045	.004	.022	.002	.013	.001	.016	.001	.017	.001	.009	.001	1,272	104.6	1.69	1.42
Ca ⁺⁺	--	--	.045	.002	.060	.003	.050	.002	.035	.002	.060	.003	.045	.002	.050	.002	400	20.0	1.16	12.50
SiO ₂	.122	--	.289	--	.642	--	.257	--	.257	--	.235	--	.235	--	.118	--	(5) 4	--	--	10.92
Total cations	--	0.022	--	0.013	--	0.019	--	0.012	--	0.010	--	0.015	--	0.010	--	0.014	--	593.3	--	--
Cl ⁻	0.249	0.007	0.532	0.015	0.479	0.014	0.710	0.020	0.071	0.002	0.355	0.010	0.497	0.014	0.621	0.018	18,980	535.3	55.04	6.50
SO ₄ ⁼⁼	.54	.011	.22	.005	.82	.017	.28	.006	.28	.006	.39	.008	.28	.006	.51	.011	2,649	55.1	7.68	9.11
Total anions	--	0.018	--	0.020	--	0.031	--	0.026	--	0.008	--	0.018	--	0.020	--	0.029	--	590.4**	--	--
Total, as reported††	--	--	1.06	--	1.77	--	1.30	--	0.58	--	1.13	--	1.06	--	1.51	--	34,241***	--	99.29	49.84
Specific conductance (micromhos/cm), at 25C	3.60		2.34		2.89		1.89		2.00		1.99		1.95		3.15		52,880			50.100
Ratios by weight:																				
Cl/Na	0.8		1.8		2.5		6.1		0.6		2.0		4.0		4.0		1.80			1.24
K/Na	.59		.68		.93		1.0		.50		.72		.76		1.0		.036			.36
SO ₄ /Cl	2.2		.41		1.7		.39		3.9		1.1		.56		.82		.14			1.4
Cl/K	1.4		5.8		2.8		5.9		1.2		2.7		5.2		3.9		49.9			3.4
Na/Mg	18.2		3.8		4.2		5.3		9.2		11.3		7.4		17.3		8.3			1.5
Mg/Cl	.07		.07		.09		.03		.18		.04		.03		.04		.067			.51
Ca/Na	--		0.33		0.32		0.43		0.29		0.33		0.16		0.32		.038			2.4

*H. U. Sverdrup, et al. (1946) from Table 15, p. 173.
††H. U. Sverdrup, et al. (1946) from Table 15, p. 173.

*H. U. Sverdrup, et al. (1946) from Table 15, p. 173.

†D. A. Livingstone (1953) from Table 41, p. 641.

The anions and cations theoretically balance; if average bicarbonate (HCO₃⁻, 2.1 epm), bromide (Br⁻, 0.8 epm) and fluoride (F⁻, 0.1 epm) are added, totaling about 0.6 percent by weight.††Less SiO₂ component.*Total dissolved solids in average (19 parts per mille Cl⁻) ocean water, 34,482 mg/liter.

A plot of the individual ionic constituents, total dissolved salts, specific conductances and the ratios of the various ions as a function of depth showed no obvious systematic trends. The curves did indicate, however, that SO_4^{--} and K^+ vary proportionally and that a maximum total ion concentration exists at 150 m (especially SO_4^{--} and SiO_2), and to a lesser extent at 411 m (except for SiO_2). Minimum concentrations are observed at 250 m, notably Cl^- . For the profile, Na^+ averages about 38% of Cl^- , SO_4^{--} about 95% of Cl^- , K^+ about 30% of Cl^- , and Mg^{++} about 13% of Na^+ and 5% of Cl^- . Except for Na/Mg and Mg/Cl, all ratios differ considerably from sea water. The Cl/Na ratio is on the average (2.6) higher than for sea water (1.8). Ca^{++} is about 30% and K^+ is about 76% of the Na^+ suggesting a common source for these cations.

Table XIV presents the results of the chemical analyses made on samples of snow, firn or ice from various locations and of different ages on and in the Greenland ice sheet. The number, type (snow, firn or ice), depth, years of accumulation and the approximate data that the samples fell as snow are given in the upper left hand corner of the table. Geographical location and elevation of sample sources are tabulated as footnotes. Column 3 presents the average values of the data given in Table XIII, Column 4 presents the averages of data used earlier in this study for stratigraphic interpretation (Table IX) and Column 5 gives the data for Greenland reported by Junge (1960); all other results are part of this investigation.

It is interesting to compare the average values of Column 4 in Table XIV with the single value of Column 7 in Table XIII. Both sets of samples are from approximately the 300-m depth. Except for the similar SO_4^{--} concentrations, the values given in Table XIII are nearly a factor 2 higher, in all constituents including total salts, than those given in Table XIV. This is not as serious as first might seem. The different samples are not from the identical horizon, and, as mentioned earlier, the single sample (Table XIII) could mainly represent a winter layer, which tends to contain a higher concentration of salts.

At this writing no chemistry data are available for a single year's surface accumulation from Site 2. A core sample from the 20-m depth which fell as snow in 1920 is given in Column 2. Junge's data (Column 5) are the average composition of firn from the surface to the 30-m depth (1957 to 1915). The chemical composition of snow and firn from Camp Century (about 130 km, or 80 miles, westerly from Site 2) is presented in Columns 6, 7 and 8. These samples come from the 1963-64 surface accumulation and two different subsurface water wells, about 1 km apart, both representing approximately the same time period. The total dissolved salt content of the water well samples ranges between 0.84 and 0.90 mg/liter, but large variations exist in individual constituents.

Column 9 of Table XIV gives the chemical results from melted horizontal ice cores and larger samples from the Tuto tunnel located at the margin of the North Greenland ice sheet. Carbon dating measurements made on 1-ton ice samples adjacent to some of the chemistry samples discussed here (Langway *et al.*, 1965; Oeschger *et al.*, 1966) indicate that the age of the ice 300 m from the tunnel portal is about 3000 years BP and that the age of the ice 200 m from the tunnel portal is about 5000 years BP. A comparison of the chemistry of the Tuto tunnel ice with that of other inland locations shows that, except for Cl^- (high at Tuto) and SiO_2 (low), all constituents fall within the ranges of the given standard deviation. The Cl^- concentrations are much higher in the tunnel samples, 61% of the total constituents, than in the inland samples; and for the

Table XIV. Mean composition of melt water samples of snow, firn cores and ice cores from various locations of the Greenland Ice Sheet.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Locations*	Site 2				Camp Century			Tuto Tunnel	Dye 3	
No. samples	1	8	29	14-44	2	1	7	6-12	3	
Type sample	Firn	Firn-Ice	Ice	Snow-Firn†	Snow	Firn	Firn	Ice	Snow	All
Depth(s)	20m	20-411m	300m	0-30m	0-1.2m	30-70m	25-70m	Horizontal cores	0-1.4m	Locations
No. years covered	1	986	3.2	40	1	100	110	--	1	(weighted
Date (A.D.)	1920	934-1920	1203	1915-57	1963-64	1810-1910	1810-1920	3-5x10 ³ BP**	1963-64	average)
(milligrams per liter)										
	(x)	(x)	(s)	(x)	(s)	(x)	(s)	(x)	(s)	(x)
Na ⁺	0.310	0.166	0.064	0.097	0.024	0.029	0.011	0.135	0.019	0.122
K ⁺	.183	.127	.043	.077	.017	.011	.006	.047	.003	.112
Mg ⁺⁺	.017	.022	.012	--	--	--	--	.016	.013	.012
Ca ⁺⁺	--	.05	.01	--	--	.035	.019	.045	--	.035
Cl ⁻	.249	.439	.206	.156	.032	.037	--	.568	.301	.533
SO ₄ ⁻⁻	.54	.42	.20	.04	.04	.25	.14	.17	.001	.025
SiO ₂	0.122	0.269	0.163	--	--	--	--	0.158	0.071	0.086
Total, as reported: ††	1.35***	1.22	--	0.65	--	0.36	--	0.98	--	0.84
								0.90	--	1.32
										0.78
										0.76
Specific conductance (micromhos/cm), at 25°C	3.60	2.98	0.84	3.85	0.73	--	--	2.65	0.18	1.78
								1.87	0.12	3.24
										2.28
Average ratios by weight:										--
Cl/Na	0.80	2.6		1.6		1.3		4.2		4.4
K/Na	.59	.76		.79		.38		.35		.92
SO ₄ /Cl	2.2	.95		2.0		6.8		.30		.05
Cl/K	1.4	3.4		2.0		3.4		12.1		4.8
Na/Mg	18.2	7.5		--		--		8.4		10.2
Mg/Cl	.07	.05		--		--		.03		.02
Ca/Na	--	0.30		--		1.2		0.33		0.29
								1.3		1.3

*Site 2: 76°59'N, 56°04'W, 2000m (6560 ft)

Camp Century: 77°10'N, 61°08'W, 1885m (6180 ft)

Tuto Tunnel: 76°25'N, 68°18'W, 490m (1605 ft)

Dye 3: 65°12'N, 43°47'W, 2426m (7960 ft)

†C. E. Junge (1960)

**Radiocarbon date

††Less SiO₂ component***Includes average Ca⁺⁺ value for location, Column (3)

only Greenland location investigated, the K/Na ratio is similar to sea water. From the radiocarbon dates it appears that the source area for the tunnel ice, assuming an average flow velocity of 3 m to 5 m per year to the west, is 15 to 25 km from the coast. The K/Na ratio and the Cl^- concentrations would then be in agreement with those found in the precipitation of temperate regions, that is, more Cl^- is deposited near the coast.

The Dye Site sample (Column 10) is the only South Greenland sample available. It represents the 1963-64 accumulation profile and the total as reported favorably compares with the 1963-64 accumulation at Camp Century in North Greenland. In detail, however, Ca^{++} and SO_4^{--} appear to be found in concentrations an order of magnitude less in the south, with all other constituents agreeing within a factor of 2.

The SiO_2 concentrations in the Greenland samples are of special interest and will be discussed in more detail. Local exposed rock and soil is a significant factor in the mineral supply inland (Gorham, 1961, p. 821). Fenn and Weickmann (1959) and Kumai and Francis (1962a) have vividly demonstrated that for North Greenland dry dust particles carried by wind from permafrost ground act as excellent freezing nuclei and that there are few particles other than dust in the arctic air masses, at least in the Aitken nuclei and the large nuclei (less than 2.0μ diam) aerosol sizes. Kumai and Francis have shown that 85% of the total nuclei at Site 2 are composed of clay minerals, primarily kaolinite, montmorillonite and illite.

It is well known that adsorption to and solution from glass container walls is a large source of error in trace SiO_2 analyses but solutions stored in polyethylene containers, as were these samples, show no contamination effects (Smales and Wager, 1960, p. 223). Most silica in natural waters is probably derived from the decomposition of silicate minerals, particularly feldspars (Rainwater and Thatcher, 1960, p. 259), and although the solubility of the clay particles that originally formed the snow nuclei is unknown, some insight is gained from laboratory studies on the solubility of quartz and solid silicates (Morey, Fournier and Rowe, 1964). Hydrolysis and dissolution of relatively insoluble silicate minerals are accelerated by fine-grinding to colloidal sizes (Keller, Balgord, and Reesman, 1963). The snow crystal nuclei are originally in a fine degree of comminution with a high specific surface area and it is probable that after a glacier sample is melted at room temperature the solid clay minerals in contact with the water solution at room temperatures tend to dissolve. The solubility of amorphous SiO_2 in water at 25C is about 115 ppm and laboratory tests indicate that the solubility value increases with time (Morey et al., 1964).

A clay nucleus with an average diameter of 1μ and a density of 2 g/cm^3 has a mass of 10^{-12} g. Kumai (1965) has shown that an average snowflake at Site 2 has a mean mass of 8.22×10^{-6} g and therefore 1 g of snow has 1.22×10^5 snowflakes. Assuming each flake has one center nucleus (the lower limit) there are 1.22×10^8 nuclei per kg of snow (or kg of melt water) which is equivalent to 0.122 mg of nucleus substances per liter. If 85% of the total particles are clay of which approximately 50% is the SiO_2 component and if the dissolution is complete we would obtain an average contribution of SiO_2 from snow crystal nuclei amounting to about 0.05 mg/liter. This is a factor 3 lower than the weighted average dissolved SiO_2 concentrations found at Site 2 and Camp Century (Table XIV, Columns 1-8) which suggests that dry fallout is an important source of SiO_2 in polar snow, as is reported for snows in temperate regions (Feth et al., 1964; Viro, 1953; Gorham, 1958b). In addition the comparatively high cation content of glacier samples is partly explained by the cation exchange or dissolution of clay minerals.

As a check on the preceding interpretation we may approach the problem of the total concentrations of nuclei in a reverse manner, that is by computing the number of nuclei there must be to account for the measured dissolved solids concentrations. Using all the chemistry data available for Site 2 (Table XIV, Columns 1-4) we obtain a weighted average of 0.56 mg/liter for the total as reported dissolved salt concentrations, and an average corrected net snow accumulation rate of about 39 g/cm² -yr. From this we compute an average dissolved salt concentration (deposition) of 21.8×10^{-3} mg/cm² -yr. Assuming as before an average particle diameter of 1 μ and a density of 2 g/cm³ we obtain an average mass/particle of 10^{-12} g. Combining the above gives us a calculated deposit of 22×10^6 average size particles per cm² per year from the measured dissolved salt concentrations (over 4 times more per year than is obtained by a similar calculation using Kumai's measured number concentration of nuclei/g of snow. This also suggests that larger fallout particles or multi-nuclei are contributing to the concentrations). If we take an average airborne aerosol concentration of 2 particles/cm³ (Fenn, 1960) in the troposphere above Site 2 (a height of approximately 5000 m), a volume of air 1 cm² cross section will contain 10^6 particles. This means that a complete washout of the airborne salt particles occurs on the average about twice a month at Site 2. A similar analysis by Fenn (1960) gives essentially the same results; though he used an average concentration value of approximately one-half of ours for the dissolved solids concentration a compensating error occurred by his using nearly twice the correct snow accumulation value.

Geochemical budget

Taking the mean concentrations of the dissolved solids given in Table XIV, Column 11 as being representative of the distribution throughout the entire ice sheet and 2.35×10^6 km³ for the total volume of water equivalent (Bauer, 1955), we calculate the total ionic weight-volumes of dissolved solids tied up in the ice sheet (Table XV.) The plus and minus figure after the weight value in metric tons represents the percent standard deviations obtained from the values given for the pooled standard deviation in Table XIV. For the case of Na⁺ this means that the estimate of the total abundance ranges between 37×10^6 metric tons and 325×10^6 metric tons.

Table XV. Abundance of various chemical constituents in the Greenland ice sheet.

Ion	Concentrations (mg/ton)	Total mass ($\times 10^6$ metric tons)
Na ⁺	77	181 $\pm$ 76%
K ⁺	60	141 $\pm$ 33%
Mg ⁺⁺	24	56 $\pm$ 58%
Ca ⁺⁺	38	89 $\pm$ 42%
Cl ⁻	270	634 $\pm$ 74%
SO ₄ ⁻	290	682 $\pm$ 45%
SiO ₂	130	306 $\pm$ 69%
Total	889	2089

The total soluble salt content of the ice sheet is 1.78×10^9 metric tons. If uniformly distributed over the surface of the ice sheet this amount of salt would provide 103 mg/cm^2 , with a thickness of about 0.5 mm. In comparison with the total dissolved material in the ocean, the soluble material in the Greenland ice sheet is an infinitesimal fraction, 3.56×10^{-8} . For example, in the oceans there is 5.5×10^{14} metric tons of calcium alone, and twice as much of the relatively scarce element uranium (4.2×10^9 metric tons) than all the combined dissolved materials in the ice sheet. The annual total deposit of dissolved salts incorporated with snowfall in Greenland amounts to 4.8×10^5 metric tons.

Since the annual accumulation of the ice sheet is in slight positive balance it may be concluded that there is also a slight net gain in the dissolved solids being stored in the glacier.

Summary and Conclusions

Interpretation of the chemical variations from the continuous vertical core profile at 300 m has allowed us to develop certain criteria regarding the seasonal distribution of dissolved solids. We find at 300 m that a higher concentration of chemical constituents is associated with winter snow deposits and a lower concentration is found in summer snow deposits. These results are in agreement with rain water analyses in temperate zones and, because of the marine influence on Greenland, are most likely related to winter conditions at sea. The stratigraphic interpretation of the chemistry data is restricted somewhat by the limited time period involved but the results indicate that the specific conductance of a melt water sample, which could be accurately measured in the field, offers some promise of being a useful guide to estimate seasonal accumulation layers.

In general the relative abundances and ratios of the ions from samples over the ice sheet differ markedly from those in the oceans except for the Na/Mg and Mg/Cl ratios. If we assume that Cl^- is totally of marine origin and all other dissolved solids are present in proportion to their presence in average ocean water we obtain a quantity of excess cations which, as indicated by crystal nuclei studies, are presumably terrestrial mineral dusts.

In this study we find that the average SO_4^{2-} concentrations at various ice sheet locations vary slightly but are generally of the same order as given by Junge (1960) for Site 2. The low SO_4^{2-} value obtained for South Greenland may be in error. Over 38% of the total quantity of soluble salts measured from all Greenland locations is SO_4^{2-} , confirming Junge's hypothesis that sulfur plays a predominant role in the arctic aerosol. Combined SO_4^{2-} and Cl^- average 75% of the total dissolved salts for the samples, with the cations Na^+ , K^+ , Mg^{++} and Ca^{++} contributing the remainder. The average Cl^- concentrations appear to decrease slightly inland (from limited data) but one must recall that deep ice samples do not accurately represent the present surface location.

It is interesting to consider the evidence for or against the Ewing-Donn (1956, 1958) ice age theory as given by the chemical analyses of ancient ice samples (Table XIV, Column 9). Briefly, the theory involves a condition that the Arctic Ocean be periodically ice free. When this situation is attained the increased ocean surface moisture source for the polar atmosphere would favor growth of

an ice sheet. With this theory, at the end of the last glacial stage, approximately 10,000-12,000 years ago, the open Arctic Ocean should have frozen over terminating the growth of glaciers (consequently the plentiful sea spray, snow crystal nuclei sources). If this were the case, it is possible that the salt concentrations in the snow would be higher during the Wisconsin stage, when the Arctic Ocean was ice free for the entire year, than afterwards. Results from the 5000 year old tunnel ice samples show a high Cl^- content in contrast to today's inland surface stations. The approximately 1000 year old ice from the bottom of the 411 m deep core also has a higher Cl^- concentration. Both facts suggest that the Cl^- concentrations are decreasing, which somewhat supports the theory. However, the tunnel samples are not quite old enough to provide a definite test of the ice age theory. In addition, since the original source area of the tunnel ice is near the coast, one would normally expect an elevated Cl^- content in these samples. Further studies are needed on older tunnel ice, or deeper ice core presently being recovered at Camp Century, to establish the validity of these findings.

In conclusion it may be stated that although the absolute concentrations of total chemical constituents of polar snows are very low, averaging less than 1 mg/liter, non-uniform variations do exist which can provide an indirect means of interpreting seasonal layers. The relative chemical purity of polar glacier ice, even the present-day deposits, in comparison with rain water and snow falling over continental areas, is evidence that industrial exhausts from North America do not appreciably contribute to the arctic air masses.

VII. COSMIC DUST STUDIES

General Background

The accelerated interest in space research during the last decade has created a parallel interest in the study of all forms of extraterrestrial materials. Besides meteorites, it is generally acknowledged that extraterrestrial dust is the only other form of material from outer space that we currently have for investigation. It is further recognized that each year the earth sweeps or intercepts many more tons of extraterrestrial dust during its orbit about the sun than it does stony or iron meteorites (Opik, 1956).

For many years it has been realized that the dry snow areas of a polar ice sheet provide an excellent repository for extraterrestrial debris (Nordenskiöld, 1874) and would be an ideal place to investigate total atmospheric fallout. Far from exposed nunataks or peripheral mountain chains and free from excessive terrestrial soils, industrial pollution or human contamination, one has the unique opportunity of collecting extraterrestrial dust samples from the earth's surface containing a minimum amount of extraneous material.

With the present refinement of snow pit stratigraphy and the recovery of the deep ice cores it is doubtful if there exists a more practical approach to estimate with as much reliability the present and past annual deposits of extraterrestrial dust. Furthermore, by using physical stratigraphic control, it is possible to study the relationships of extraterrestrial dust influx to such things as periodic cometary showers, cyclical or sporadic meteorological phenomena, magnetic polar effects and geographical distribution of dust concentrations.

One type of particle that has been extensively studied in the past and identified in nearly all collections of extraterrestrial dust is the opaque and non-opaque spherical form. They are easy to identify microscopically in a heterogeneous mixture of particles, and also the natural terrestrial processes which can produce inorganic spherical forms are almost nonexistent.

Previous Work

It is interesting to note that one of the first studies of extraterrestrial dust on earth was made on samples from the Greenland ice sheet. During an early Greenland expedition Nordenskiöld (1885) reported the presence of extraterrestrial spherules. He believed that there was a greater variation in dust falls than was generally assumed and that polar regions are especially well suited to search for such material. Murray (1876) and Murray and Renaud (1884) were the first to describe in detail the microscopic characteristics of black spherules which they collected from Pacific Ocean deep-sea sediments.

Since these initial studies of Nordenskiöld, Murray and Renaud, spherical particles have been collected by numerous investigators although often identified by different names. These collections include those obtained from the earth's surface (Buddhue, 1950; Thomsen, 1953; Hodge, 1956; Crozier, 1962), including sites of meteorite falls (Krinov and Fonton, 1952; Yavnel, 1957; Rinehart, 1958; Kirova, 1961); from ocean sediments (Bruun, Langer and Pauly, 1955; Laevastu and Mellis, 1955; Opik, 1955; Fredriksson and Martin, 1963); from ancient rocks and sediments (Crozier, 1960; Skolnick, 1961; Mutch, 1964a, 1964b); and from airborne collecting devices (Hodge and Wildt, 1958; LaGow and Alexander, 1960; Fireman and Kistner, 1961; Hodge and Wright, 1961; Hemenway and Soberman, 1962).

After the early work in Greenland, polar regions appear to have been neglected as collecting grounds for extraterrestrial particles until about 1955. Since then, however, a deluge of information has been obtained from polar and subpolar samples (Stoiber, Lyons, Elberty and McCreham, 1956; Nishibori and Ishizaki, 1959; Hunter and Parkin, 1960; Thiel and Schmidt, 1961; Langway, 1963; Wright, Hodge and Langway, 1963; Schmidt, 1963, 1964; Parkin, 1964; Langway and Marvin, 1964; Hodge, Wright and Langway, 1964; Fireman and Langway, 1965; Giovinetto and Schmidt, 1965; Tilles, 1965; Fireman, DeFelice and Langway, 1965).

Buddhue (1950) reviewed the subject of all forms of extraterrestrial dust up to 1948 and Hoffleit (1952) compiled an extensive bibliography in 1952 which was extended by Hodge, Wright and Hoffleit (1961) 10 years later. An up-to-date expanded survey report and summary of all data available on microscopic extraterrestrial particles to 1964 has recently been compiled by Schmidt (1965).

The advent of the electron probe microanalyzer (Castaing, 1951; Birks, 1963) was an important turning point in the study of extraterrestrial particles and much emphasis has been placed on the nature and chemistry of individual particles during the last 10 years (see Schmidt, 1965).

Origin of Extraterrestrial Dust

According to LaPaz (1958, p. 235) evidence is available to indicate that meteorite falls have occurred on earth since the beginning of time, yet in the last 150 years only about 1600 recognized meteorites have been collected in the entire

world. Of this total a mere 683 were actually seen to fall. On the direct measurement of these falls the nature and composition of all extraterrestrial material is firmly based.

Besides meteorites the earth annually collects upon its surface tons of extraterrestrial dust (of asteroidal, cometary, interstellar and meteoritic sources and possibly moon dust expelled by meteorite impact) at a rate of deposit that is presently subject to question, of a size range that is not well established, and of an elemental composition that is rather poorly defined. All dust is probably derived from the solar system, but the interstellar regions may also contribute. Black spherules have received considerably more attention than other forms of extraterrestrial dust, but even here many aspects are still speculative and topics of controversy.

Although the state of our knowledge concerning the genesis of extraterrestrial dust is limited, Krinov (1960) has thoroughly discussed the various forms of dust which may reach the earth. Krinov proposed a classification system which divides incoming dust into three main classes: (1) meteoric (atmospheric disintegration products of falling meteoric bodies), (2) meteoritic (produced by the crushing impact of meteorites on earth) and (3) cosmic (micrometeorite particles which because of their large surface area to mass ratios radiate heat fast enough so as not to alter their form or structure).

According to this classification the meteoric fraction of extraterrestrial dust consists of solidified droplets, globules and spheroidal forms of material that either ablated from falling meteors in the atmosphere (and generally have different chemical compositions than their parent bodies because of oxidation and diffusion during flight) or are individual particles that entered the earth's atmosphere at a velocity high enough to cause fusion. It is postulated that the spherules found in the Greenland samples are of the meteoric class.

Deep Ice Core and Near Surface Studies

Presented here are the results of an investigation of black spherules extracted from the Site 2 deep ice core and also from stratigraphically determined shallow firn layers at Camp Century. An attempt is made to establish criteria by which one may distinguish between the terrestrial and extraterrestrial origin of these particles, since the chemical composition and physical properties of black spherules are important clues to the origin of all cosmic dust. This study involves the investigation of the physical properties, concentrations, distributions, and chemical composition of the spherules.

Samples and preparation

Several distinct advantages are presented by investigating the dust content in the layered sequences of a polar ice sheet. In comparison with deep sea or indurated sediments, one can extract the dust from its embedded matrix with great ease and without damage to the particles simply by melting. Also, in contrast to airborne collections, an unlimited time interval is available from glacier samples merely by extending the depth profile. These factors allow a greater variety and number of particles for examination and experiments.

The ice core samples for the dust studies were selected from near the 300-m depth to take advantage of the information obtained from the O-isotope and the soluble chemistry investigations. It was also desirable to study old ice which was

deposited as snow long before the industrial revolution (early 19th century) had contributed to atmospheric pollution to avoid any possibility of artificial origin of the dust. A pilot study performed on Camp Century firn samples (Langway, 1963) provides the data for the detailed stratigraphic distribution of spherules.

Various methods were tested and experiments performed for determining the most feasible procedures (Langway, 1962, 1963). Included in these studies were: sampling techniques, methods of extracting and separating the material from the parent sample, and the identification and analysis of single and composite groups of isolated particles. Collection devices and separating procedures included high-speed centrifuging, micro- and macro-filtering, settling tanks, a vacuum-suction device and a magnetic collecting apparatus. The simplest and most convenient method of particle separation for small samples was found to be a careful melting of the glacier sample and micro-filtering.

A total of 73 half-core pieces (Nos. 138-210) from between 282.3 m and 295.6 m (a 13.29-m continuous profile) were selected and prepared in the field for the extraterrestrial dust investigations. Samples were brushed clean and rinsed with deionized micro-filtered water in the trench laboratory. Pieces were then placed in precleaned seamless polyethylene jugs, covered with a friction cap, and brought into the warm subsurface laboratory to melt at room temperature. Each melted sample was filtered through a 0.45 μ diam retention membrane filter using a 600-ml seamless stainless steel funnel and accessory apparatus* (Fig. 22). The funnel and polyethylene jug were capped at all times except during transfer of the liquid. The effluent was passed through a deionizer and then refiltered; this water was used for rinsing and cleaning. Immediately after filtering, the membrane filters were placed in a sterile Petri dish and oven dried at 90C, then the dish was capped and sealed. Precautionary measures used to minimize sample contamination during field processing included the inclosure of the entire area of the warm laboratory used for this work with sheet polyethylene, from floor to ceiling, and the wearing of clean room laboratory apparel. To avoid any loss or jarring of the filtrate from the filter surface, all samples were hand carried from the field to the laboratory.

Analytical procedures and equipment

Except for a cursory microscopic examination in the field all microscopic studies were performed within a dust-free inclosure (Fig. 23) at the Hanover, N.H., laboratory. The inclosure was modified with microscope bellows and all Petri dishes were placed inside this dust-free inclosure before their covers were removed.

The entire filter was examined at X100 magnification using a mechanical stage and a Bausch and Lomb zoom microscope with oblique illumination provided by two 6-V lamps at 120 degrees. From the initial survey of the particles on each filter disc the particles could be grouped into a few classes based on form, color and surface characteristics. The spherules, although representing only a small percentage of the total particles present, were easily identified. Diameters of all spherules greater than 5 μ were individually measured to the nearest micron with an eyepiece reticle at X200 magnification.

*Millipore Filter Corp., Bedford, Massachusetts

Figure 22. Field apparatus used for rinsing, melting, filtering and storing cosmic dust samples.

Figure 23. Microscopic examination of filtrate containing cosmic dust within dust-free work space.

For the chemical analyses representative particles were selected from each of the broadly characterized groups, although in this chapter only the spherical forms are discussed. Each particle selected for chemical analysis was photographed for permanent record. Particles were transferred from the membrane filters onto a beryllium substrate using a straight needle, aluminum or molybdenum micro-tool and a modified Leitz micromanipulator, all within the dust-free box. An amyl-acetate and collodion mixture (3:1) was used as the mounting medium. Microchemical analyses were performed by the electron probe micro-analyzer technique.*

Density determinations were made on composite groups of selected spherule samples (Camp Century magnetic collection) using a Berman balance and toluene as the immersion fluid. A potentiometer with bridge was used to measure the temperature of the liquid.

Results of Analyses

Physical properties

Microscopic examination. The most obvious physical properties of particles when observed in ordinary reflected light, and of fundamental importance in recognition, are color, form, luster, size and surface characteristics. Microscopic examination of the residue from a filtered glacier melt water sample reveals particles of various shapes and sizes. Obvious contaminants such as polyethylene fibers and chips, cellular wood fragments and cloth fibers are easily recognized and present no problem in identification. Irregularly shaped inorganic particles are another matter.

The most striking particles and the easiest to identify microscopically are the droplet-globules and spheroidal forms (Fig. 24). The morphology of these particles varies and, although perfect spheres are most common, especially in the smaller size ranges (less than 40 μ diam), droplet or tear shapes, oval forms and flask or dumbbell configurations are not rare. Some spherules are hollow and a few of the larger ones (greater than 50 μ diam) have protuberances — much smaller spheres or globules attached to their surfaces. Other spherules are brittle and reveal a hackly fracture when crushed. Some broken spherules reveal a frothy or scoriaceous internal structure.

Microscopic examination also shows that most spherule-globules are opaque and predominantly black or grayish in color, although dull or vitreous amber, brown, red, and white (transparent and translucent) spherules are present. The luster of the metallic spherules is usually dull, but black glassy varieties are frequently found (Fig. 25). Most colored spherules have a vitreous to sub-vitreous luster. Surface features of the spherules range from smooth and shiny to rough or pitted and dull. No systematic striations or pits were noticed. Almost every black or metallic spherule examined displayed some magnetic susceptibility.

In earlier papers (Wright, Hodge and Langway, 1963; Hodge, Wright and Langway, 1964) a morphological classification system was developed for all extraterrestrial particles. In this study it was possible to microscopically classify the spherules into three broad types. Table XVI presents a modified version of the earlier classification for spherules only.

*Advanced Metals Research Corp., Burlington, Massachusetts.

Figure 24. Black metallic spherules from magnetic collection, Camp Century, Greenland; largest spherules are about 1 mm diam.

Figure 25. Largest black glassy spherule (230 μ diam) found at Camp Century. Note surface indentation near perimeter at bottom of spherule.

Although the spherules appear different, as will be shown by the chemical analyses, their chemical nature is not apparent from a microscopic examination.

Density measurements. Density determinations (Table XVII) were performed on composite groups of black metallic spherules (Type 1, Fig. 24) and larger metallic particles magnetically collected from firn samples at Camp Century. These spherical particles have a size range between 5 and 800 μ diam, but are otherwise identical in appearance and chemically similar to the Site 2 spherules.

Table XVII shows that the spherules approach but are lower than the density of magnetite (5.18 g/cm³), due presumably to at least some of them being hollow, porous or containing internal vugs and cavities. The apparently solid larger particles have densities which are generally higher than magnetite but lower than metallic iron (7.9 g/cm³).

Size distribution. Size measurements were made on 2014 individual spherules from the Site 2 deep core samples and on 5232 individual spherules from the Camp Century firn samples. The diameter range of the Site 2 spherules measured extends from 5 to 100 μ (the Camp Century spherules extend in diameter from 5 to 230 μ); the mass ranges from 2.6×10^{-9} g to 2.6×10^{-6} g. A mean diameter of 16.4 μ is obtained for the Site 2 spherules using the number distribution of spherule occurrence; using the mass distribution for this calculation gives a mean diameter of 21.9 μ . The data grouped into 10- μ class intervals are given in Table XVIII, Columns 1-6 and Table XIX, Columns 1-6. Summary statistics are given in Table XX. The size distribution of the spherules for both locations is given in Figure 26 plotted as cumulative number frequency per kg of glacier material versus diameter. Figure 27 shows the total mass distribution of spherules plotted against the diameter.

Table XVI. Classification of spherules according to microscopic appearance.

Type	Color	Luster	Surface features	Other
1	Black or gray	Metallic	Sometimes pitted	Sometimes with protuberances
2	Black	Vitreous	Smooth	High reflectivity
3	Colored (clear, white, amber, etc.)	Vitreous to resinous	Smooth to slightly pitted	Transparent to translucent

Table XVII. Density measurements of composite groups of black metallic spherules and single larger metallic fragments from Camp Century, Greenland (from Langway and Marvin, 1964).

Sample	Mass (mg)	Density (g/cm ³)
1 (Spherules)	13.06	4.27
2 (Spherules)	27.51	4.65
3 (Spherules)	10.18	4.93
	Average	4.62
4 (Fragment)	42.91	5.43
5 (Fragment)	76.63	5.90

The size distributions and number concentrations are slightly different for each site, which is not accounted for by the different snow accumulation rates. Both curves in Figure 26 show concentrations essentially similar in the 10-20 μ diam class interval but the slope of the Site 2 curve decreases at a faster rate terminating at 100- μ diam. It is unlikely that any of the larger spherules were neglected in counting and, since the number concentrations in the smaller size ranges are similar, the differences found in the larger sizes are apparently real and suggest that the character of spherule accretion has changed. A difference is, of course, also noted between the two sites in the computed mass frequency distribution curves (Fig. 27).

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Table XVIII. Size (diameter), frequency, cumulative distribution and rate of deposition of black spherules from 300-m samples, Site 2.

(1) Size range d (μ)	(2) Mid- point d (μ)	(3) Number of spherules (n)	(4) Number of spherules (cumulative)	(5) Size frequency (%) (in range)	(6) Size frequency (%) (cumulative)	(7) Cumulative number spherules ($\times 10^5$) ($m^{-2} sec^{-1}$)	(8) Cumulative number spherules ($\times 10^5$) ($cm^{-2} yr^{-1}$)
5-15	10	1126	2014	55.91	100.00	49.9	1.57
15-25	20	628	888	31.18	44.09	22.0	.69
25-35	30	181	260	8.99	12.91	6.45	.20
35-45	40	51	79	2.53	3.92	1.96	.062
45-55	50	18	28	.89	1.39	.69	.022
55-65	60	4	10	.20	.50	.25	.008
65-75	70	3	6	.15	.30	.15	.005
75-85	80	0	3	.0	.15	.074	.002
85-95	90	1	3	.05	.15	.074	.002
95-105	100	2	2	0.10	0.10	0.050	0.001

 $N = 2014$

100.00

 $\bar{x}_d = 16.4\mu$

Table XIX. Size (diameter), frequency, cumulative distribution and rate of deposition of black spherules from 6 m deep samples, Camp Century.

(1) Size range d (μ)	(2) Mid- point d (μ)	(3) Number of spherules (n)	(4) Number of spherules (cumulative)	(5) Size frequency (%) (in range)	(6) Size frequency (%) (cumulative)	(7) Cumulative number spherules ($\times 10^5$) ($m^{-2} sec^{-1}$)	(8) Cumulative number spherules ($\times 10^5$) ($cm^{-2} yr^{-1}$)
5-15	10	2854	5232	54.55	100.00	42.9	1.35
15-25	20	1135	2378	21.69	45.45	19.5	.62
25-35	30	534	1243	10.21	23.76	10.2	.32
35-45	40	307	709	5.87	13.55	5.81	.18
45-55	50	168	402	3.21	7.68	3.30	.10
55-65	60	97	234	1.85	4.47	1.92	.060
65-75	70	61	137	1.16	2.62	1.12	.035
75-85	80	35	76	.67	1.46	.62	.020
85-95	90	12	41	.23	.79	.34	.011
95-105	100	9	29	.17	.56	.24	.0075
105-115	110	7	20	.13	.39	.16	.0052
115-125	120	4	13	.08	.26	.11	.0034
125-135	130	4	9	.08	.18	.074	.0023
135-145	140	1	5	.02	.10	.041	.0013
145-155	150	1	4	.02	.08	.033	.0010
155-165	160	1	3	.02	.06	.025	.0008
165-175	170	1	2	.02	.04	.016	.0005
225-235	230	1	1	0.02	0.02	0.008	0.0003

 $N = 5232$

100.00

 $\bar{x}_d = 20.2\mu$

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Table XX. Summary statistics for Greenland black spherules.

<u>Firn and ice samples:</u>	<u>Site 2</u>	<u>Camp Century</u>
No. melt water samples	40	120
Total volume melt water, l	45	120
Depth below surface, m	282 to 296	6.1 to 7.6
Year sample layers deposited, A. D.	C. 1250	1951-53
No. annual layers represented, yr	36.4	2.4
Avg accumulation rate, g/cm ²	35	31
Surface area of samples, cm ²	39.2	1600
<u>Spherule data:</u>		
Total number, N	2014	5232
Total volume, $V = \frac{\pi}{6} \sum (n_i d_i^3)$, cm ³	11.1×10^{-6}	103.0×10^{-6}
Total mass, ($\rho = 5 \text{ g/cm}^3$), $M = \rho \sum V_i$, g	0.55×10^{-4}	5.15×10^{-4}
Diameter range, μ	5 to 100	5 to 230
Mass range, g	2.6×10^{-9} to 2.6×10^{-6}	2.6×10^{-9} to 3.2×10^{-5}
Avg diam, $\bar{x}_d = \frac{\sum f_i n_i}{N}$, μ	16.4	20.2
Avg mass, $\bar{m} = \rho \frac{\pi}{6} \frac{\sum (n_i d_i^3)}{N}$, g	2.8×10^{-8}	9.8×10^{-8}
Avg diam (mass), $\bar{x}_m = \sqrt[3]{\frac{\bar{m}}{\rho \frac{\pi}{6}}}$, μ	21.9	33.5
Avg no. spherules/g snow	44.7×10^{-3}	43.6×10^{-3}
Avg mass spherules/g snow, $\frac{\sum n_i m_i}{N}$, g	1.21×10^{-9}	4.24×10^{-9}
Avg no. spherules/cm ² -yr	1.57	1.35
Avg mass spherules/cm ² -yr, g	0.40×10^{-7}	1.31×10^{-7}
Spherule influx per year for entire earth, metric tons	2.10×10^5	6.57×10^5

Figure 26. Size frequency distribution of spherules per kg of snow for Site 2 (S2) and Camp Century (CC).

Figure 27. Mass frequency distribution of spherules per kg of snow for Site 2 (S2) and Camp Century (CC).

Size can be an important criterion regarding the origin of the spherules. Because of settling velocities, particles larger than 10 to 20 μ diam, especially with densities greater than 4.6 g/cm³, would not be expected to remain airborne for appreciable lengths of time.* If particles larger than 20 μ are found in a sample of polar snow which also includes particles less than 20 μ having the same physical and chemical properties, it may be assumed with some confidence that both are of a similar genesis. With essentially no industrial society existing at the time the 300 m deep ice core samples fell as snow the only possible origins of the spherules found in the Greenland ice sheet are volcanic or extraterrestrial. Arguments supporting the extraterrestrial nature of this material will be presented later.

Chemical properties

Elemental composition. Of the 7246 spherules examined in detail from Site 2 and Camp Century, 115 spherules, in a size range between 10 and 150 μ , have been chemically analyzed by the electron probe microanalyzer. These include 94 spherules from Site 2 (Wright et al., 1963; Hodge et al., 1964); and 21 from Camp Century (Langway, 1963; Langway and Marvin, 1964). The chemistry results are reported accurate to $\pm 10\%$ of the elemental amount present, in weight percent, because of the non-ideal geometry of the particles. All analyses are for surface compositions but subsequent chemical analyses showed that broken and sectioned spherules did not differ significantly in composition from the outer surfaces on the same and other particles (Langway and Marvin, 1964; Hodge and Wright, 1965).

The elements most often detected in the Greenland spherules are Fe, Si and Mn. Fe is by far the most abundant constituent and is found in varying amounts up to 70% by weight. Mn is usually present in the Fe-rich spherules in amounts less than 1% and Si when present is variable between 0.5 and 5% by weight. Silicon is present in the Si-rich spherules in concentrations ranging from 15 to 55%; and with from 0 to 8% Fe, some Al, and traces of K, Ca, and Ti. Ni is rare in Greenland spherules, and has been found in only 3 of the 115 spherules analyzed.

Mineralogical composition. A mineralogical study was performed on about 30 spherules that had earlier been microprobe analyzed (Langway and Marvin, 1964). The X-ray diffraction patterns show that magnetite (FeFe_2O_4) or magnetite with minor amounts of hematite ($\alpha\text{Fe}_2\text{O}_3$) are the major constituents of the black spherules, although some α iron and wüstite (Fe_{1-x}O) were detected in other metallic dust samples. A serendipitous find by U. Marvin during a microscopic examination of some of the Camp Century material was an opaque, black, dull appearing, 65 μ diam spherule which gave an X-ray powder pattern of olivine. The beta index of refraction of this spherule is 1.675, thus the mineralogical composition is about 95% fosterite (Mg_2SiO_4), a common meteoritic mineral.

Figure 28 shows a micrograph of a 115 μ diam, hollow, black, shiny spherule taken before chemical analysis on filter paper (insert) and after electron probe analysis. Figure 29 shows various gray and black spherules mounted on beryllium substrates. Micrographs were taken after chemical analysis; straight lines on background are produced by the electron beam burning the mounting medium. Results of the chemical analyses and mineralogy of the spherules shown in Figures 24, 28 and 29 and other representative spherules are given in Table XXI.

*A 20 μ diam spherule with a density of about 5 g/cm³ in still air will fall from a height of 50 to 100 km in 8 to 16 days. A 100 μ diam spherule will fall the same distance in 0.3 to 0.7 days (Thiel and Schmidt, 1961).

Figure 28. A 115 μ diam hollow black spherule before chemical analysis (insert) and after electron probe analysis. Note hole in spherule (from Langway and Marvin, 1964).

Figure 29. Various black and gray spherules mounted on beryllium substrates. Straight lines on background are result of electron beam burning mounting medium (from Langway and Marvin, 1964).

Table XXI. Elemental composition and mineralogy of representative black, gray and glassy spherules from Greenland. (From Wright et al., 1963; Hodge et al., 1964; and Langway and Marvin, 1964).

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Fig	Sample	Diam (μ)	Fe	Mn	Si	Other	Mineralogy	Type and remarks
Black and gray metallic								
24	6-11-1a	120	63-65	0.3	4-6	Ca, 0.2		(1) Black
28	I, 4-1	115	45-50	<0.5	-			(2) Black, hollow
29a	7-5-1	150	69-71	-	-		a Fe and magnetite	(1) Gray
29b	6-25-1	65	66-68	0.3	2.3		Magnetite	(1) Black
29c	2-10	150	68-70	0.1	-		Magnetite & hematite	(1) Black, hollow
29d	2-10	110	66-68	1-2	-		Magnetite & hematite	(1) Black, hollow flask
Black with nickel								
	18-17b	20	70-75	-	-	Ni, 2-3		(1) Black
	5-11	12	1-2	-	6-7	Ni, ~5; Mg, 18-19; Ca, 19-20; Cu, 1-2; S, ~1; Ti, ~5		(2) Black
	4-10	20	~1	-	~5	Ni, 5-6; Ca, 3-4; Cr, ~1; S, (t); Al, ~7		(1) Black
Silicon rich								
	5-17	20	1-2	-	16-18	Ca, 1-2		(2)
	8-9	25	-	-	50-55	Al, 5-10; K, (t)		(2)
	11-4	35	6-8	-	35-40	Al, 16-18; Ca, (t); Ti, (t); K, (t)		(3) Light brown
	12-14	35	-	-	15-20	Al, 14-16; Fe, (t); K, 5-10		(3) White glassy

It is important to note that spherules collected from recent Antarctic snow deposits (Schmidt, 1963, 1964; Schmidt, Venkataraman, Jackson and Woollard, 1963), Paleozoic salt deposits (Mutch, 1964a, 1964b) and various airborne and isolated sites are essentially identical in chemical composition to those shown in Table XXI. (For detailed discussion of compositional data see Wright et al., 1963; Hodge et al., 1964.)

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The chemical data of the 115 spherules have been reevaluated in terms of the modified morphological classification given here (Table XVI) and, based on the predominant chemical constituents, the results summarized (Table XXII). The chemical analyses of the various types of spherules are not consistent with their microscopic appearance. For example, in chemical Group II, 76% of the Fe-rich w/o Ni spherules appear black or gray and have a metallic luster (Type 1), and 24%, with a similar composition, appear black and have a vitreous luster (Type 2). This points again to the caution one must take when drawing conclusions about spherules from only visual examinations, as was earlier demonstrated with the olivine spherule. Included in Group IV are the two spherules containing Ni but noticeably deficient in Fe (Table XXI).

As classified by appearance (Table XXIII) 80.8% of the spherules are black or gray and 19.2% are colored (glassy). In comparison, of the total spherule concentrations found in Antarctica samples, Schmidt (1964) finds 69.2% are black and 30.8% are glassy, and from air collections Buddhue (1950) finds 69% black and 29% glassy. From these Greenland data, once the spherule deposit rate is known, we can estimate the mass contribution of the various elemental constituents comprising this form of extraterrestrial dust.

Table XXII. Chemical classification of Greenland spherules.

Group	Chemistry	Spherules		Microscopic appearance	
		(No.)	(%)	(Type)	(No.)
I	Fe-rich w/Ni	1	0.9	1	1
II	Fe-rich w/o Ni	68	59.1	1	52
				2	16
III	Si-rich	10	8.7	1	1
				2	5
				3	4
IV	Other	36	31.3	1	14
				2	4
				3	18
Total		115	100.0		115

Table XXIII. Percentage of microscopically identified spherule types in Greenland glacier samples.

Type	Microscopic appearance	Spherules	
		(No.)	(%)
1	Black or gray, metallic	68	59.1
2	Black, vitreous	25	21.7
3	Colored	22	19.2
Total 115			100.0

Discussion of Results

Besides the fundamental interest in the physical and chemical characteristics of black spherules it is of glaciological importance to determine their relative concentrations and distributions in vertical profiles for possible use as a stratigraphic tool and for estimating the annual rate of spherule deposit.

Stratigraphic variability

It has been advanced by some (Bowen, 1953, 1956a, 1956b) that the accretion of extraterrestrial dust is influenced by meteor showers, while others suggest annual maximum peaks in dust concentrations for certain months of the year (Hasegawa, 1959; Crozier, 1962; Parkin, Hunter and Brownlow, 1962) or concentrations related to meteorological effects (Schmidt, 1963). Much study is currently being directed towards the relationships between lunar synodical phases and meteor showers (Adderley and Bowen, 1962; Bowen, 1963), extraterrestrial ice nuclei sources (Bigg and Miles, 1963, 1964) and other lunar influenced meteorological phenomena (Brierley and Davies, 1963; Brier and Bradley, 1964; Lund, 1965). Studies of particles collected by rockets from high altitude noctilucent clouds (Hemenway and Soberman, 1962; Chapman and Kendall, 1965), which normally only appear in the summer, show small diameter ($2\ \mu$) black spherules to be present.

The concentrations of black spherules, or, for that matter, any dust or debris in polar snows, are so low that it is impossible to microscopically observe this material suspended in the solid glacier samples. The Site 2 deep core was melted by piece numbers and unfortunately the piece height represents too long a time period for direct stratigraphic interpretation. The average vertical height (31 cm) of the core pieces melted for spherule studies gives time increments of 0.89 years. The spherule concentrations per core pieces (representing 0.57 to 1.25 years) were nevertheless converted into units of number/cm²-yr and number/liter for those particular time periods and plotted as a function of depth (Fig. 30).^{*} Although annual layers cannot be determined from the curves these data do show variability in the spherule concentrations and yield useful information. As shown in Figure 30 the concentrations/liter range between 12 and 102 and the concentrations/cm²-yr range between 0.4 and 3.3; the averages are 44.7 and 1.57, respectively. The spread of these values indicates a non-uniform rate of spherule deposit and suggests the possibility of some cyclic phenomena.

In Figure 31 an even more convincing periodic relationship is shown between the variations in spherule concentrations and seasonal snow accumulation. This figure shows the results from an analysis (Langway, 1963) of two adjacent firn profiles at Camp Century, each having a surface area of 200 cm², between the depths of 6.10 m and 7.60 m. The annual snow deposits (summer to summer) are delimited by the arrows given on the right of the figure. The data suggest a possible correlation of maximum peaks of spherule concentrations with summer snows, but because so few cycles are involved these encouraging results require further studies to establish general relationships.

No reliable correlation has yet been reported on the seasonal or periodic variations of spherules. A comprehensive study of black spherule concentrations performed in Antarctica by Schmidt (1963) was unfortunately made on calculated yearly increments from a series of eleven 10 m deep firn cores and does not permit seasonal interpretations. The cores were obtained at inland stations about 100 km apart during a 1961-62 oversnow traverse. Schmidt makes some

^{*}The number concentrations and size distribution data from a 3.15-m depth interval between 286.72 m and 289.87 m are from a microscopic examination by F. W. Wright conducted in relation to an earlier study (Wright *et al.*, 1963; Hodge *et al.*, 1964).

Figure 30. Depth distribution of black spherule concentrations in the Site 2 deep core.

Figure 31. Depth distribution of black spherule concentrations in the Camp Century firn. Stratigraphically determined annual layers are indicated by arrows at right (from Langway 1963).

interesting conclusions from his data. He finds that spherule concentrations are inversely related to the amount of snow accumulation at a station and suggests that spherule occurrence is controlled by snow accumulation. He states that the spherules are captured (washed-out) during heavy precipitation periods and observes in his data that smaller spherules are less concentrated at stations having low accumulation, which he attributes to the winds preferentially carrying away the smaller spherules during non-precipitating weather. These results are not consistent with findings in Greenland.

Composition studies of snow crystal nuclei at Site 2 (Kumai, 1965) have definitely shown that small sized black spherules (0.2 to 3.0μ diam) are present as snow crystal nuclei in number concentrations of about $2.4 \times 10^3 / g$ in summer snows. In addition, a size-frequency distribution plot using Kumai's small spherule data (0.2 to 3.0μ) and the size data from this study (5 to 230μ) shows near linear continuity on a log-log plot, by interpolating over the size gap. This study does not show the variability in the small spherule sizes as described in the Antarctic by Schmidt. The detailed spherule size data from both Site 2 and Camp Century do not show any noticeable presence or absence of the smaller spherule sizes with time of year or year A.D. Schmidt concludes from his study that no correlation exists between the concentrations of spherules in the computed yearly layer increments at adjacent or distant stations along the traverse route and reports (Schmidt, 1965, p. 9) that it is a "forlorn hope" to consider using particulate matter as a quantitative stratigraphic parameter as suggested by Marshall (1959, 1962). Be that as it may his statistics show that his correlations involved absolute yearly spherule concentrations that ranged from 0 to 14 per year; the average absolute yearly spherule concentrations for his eleven stations range between the extreme values of 1.4 spherules (for 26 years accumulation) and 8.2 spherules (for 11 years of accumulation). Small differences in extremely low concentrations must be viewed with caution when attempting detailed correlations of this type, especially when assuming a time constant average value for net snow accumulation. The variability in annual layers of polar snow accumulation can be 25% to 50% or more (Bader, 1955; Schytt, 1958; Langway, 1961).

Annual deposit

A common assumption often made in extraterrestrial dust studies is that the rate of deposit is essentially uniform over the earth's surface. The results obtained from a usually small isolated collecting area then can be extrapolated over the entire earth. This is convenient for comparative purposes but there are some indications that a polar magnetic effect may influence the deposit rate of metallic spherules (Schmidt and Cohen, 1964; Brownlow, Hunter and Parkin, 1965). Other factors to consider in dust deposits are particle density and size considerations. Particles entering the earth's upper atmosphere at the same time do not have the same fall velocity. In addition, it must be pointed out that reported estimates of dust accretion are not always based on similar type particles nor are the collecting methods and analytical procedures used always compatible.

When rates of snow accumulation are known it is possible to calculate spherule influx rates. To normalize the variable snow accumulation from different locations one may express the spherule influx data in terms of earth impacts per unit area per unit time interval. The computed rates of spherule deposit are listed in Table XVIII (Columns 7 and 8) for Site 2 and in Table XIX (Columns 7 and 8) for Camp Century; they were determined by using the mean net snow accumulation and the total mass of spherules incorporated in the annual snow deposits. For comparative purposes a density of $5 g/cm^3$ is used in the calculations and a uniform earth

deposit was extrapolated. The total mass influx is obtained by assuming a normal size distribution over the class intervals and numerically integrating the mass contribution of each class between the limits. The results give a spherule influx of 2.10×10^5 metric tons/yr for the Site 2 samples and 6.57×10^5 metric tons/yr for the Camp Century samples. These data are graphically shown in Figure 32 with the data of Crozier (NM) (1962); Thiel and Schmidt (A) (1961), and the theoretical distribution of Laevastu and Mellis (T) (1961) for comparison. Laevastu and Mellis (1961) investigated spherules from sea sediments and dust from satellite impact measurements and concluded that the mass of particles in equal diameter intervals remains constant.

Except for noticeable tailing off of the curves (Fig. 32) the data are in approximate agreement and closely approximate the straight line of the theoretical distribution curve. Since the Site 2 spherules are from deep ice layers which fell as snow over 700 years ago and the Camp Century deposit is about 12 years old the Greenland data suggest that the rate of influx of black spherules is 3 to 4 times greater today than it was in the past. Although unlikely because of the large number of spherules represented and the short distances involved, this amount of variability could possibly be accounted for by geographical variations or magnetic pole effects (Camp Century is closer to the geomagnetic pole). Schmidt (1963) found a wide variation, up to a factor of 6 difference, in rates of spherule deposit along his eleven stations (about 100-km spacings) in Antarctica and explains these variations as due to local surface morphology and meteorological differences. His station results are from an average of only 75 spherules each.

For completeness and assessment all previously published estimates of spherule accretion rates are given in Table XXIV.

Figure 32. Rate of spherule deposit at Camp Century (CC), Site 2 (S2), the Antarctic (A), New Mexico (NM) and theoretical distribution (T).

Table XXIV. Rate of accretion of spherules over the earth (modified after Wright, Hodge and Langway, 1963; and Schmidt, 1965).

Source of spherules	Diameter (μ)	Annual deposit (metric tons/yr)	Reference
Air, rain	-	8 to 1.29×10^5	Buddhue (1950)
Sea sediments	< 500	30	Bruun <i>et al.</i> (1955)
Sea sediments	> 10	125	Laevastu and Mellis (1955)
Sea sediments	< 250	2.4 to 5.0×10^3	Pettersson and Fredriksson (1958)
New Mexico air	> 5	9×10^4	Crozier (1961)
Antarctic firn	> 10	1.2×10^5	Schmidt (1963)
New Mexico air	> 5	1.6×10^5	Crozier (1962)
Antarctic firn	> 15	1.8×10^5	Thiel and Schmidt (1961)
Stratospheric air	> 3	2×10^5	Wright and Hodge (1962)
Greenland ice	> 5	2×10^5	Wright, Hodge and Langway (1963)
Arctic air	> 3	5×10^5	Hodge and Wildt (1958)
Greenland firn	> 5	9×10^5	Langway (1963)
Air	> 10	2×10^6	Thomsen (1953)
Air	-	3.1×10^6	Kreiken (1959)

A wide range in values is shown from pre-1960 study estimates. The most recent estimates in spherules are in better agreement and appear to average at a value close to 10^5 - 10^6 metric tons per year.

Total solids

The spherules are only one component of the extraterrestrial dust which reaches Earth. From a variety of studies performed in Greenland since 1961 we have compiled all available data on the total insoluble material found in Greenland ice (Table XXV) and present some simple calculations of average mass per unit volume of melt water.

The water well data from Camp Century contained in Table XXV are from a cooperative volume-dust collecting research program with the Smithsonian Astrophysical Observatory (Fireman *et al.*, 1965; Langway and Fireman, 1965; Fireman and Langway, 1965) and the Tuto ice tunnel data are from a cooperative radiocarbon dating of ice research program with the University of Bern, Switzerland (Langway, Oeschger, Alder and Renaud, 1965; Oeschger, Alder, Loosli and Langway, 1965).

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Table XXV. Insoluble material in the Greenland ice sheet.

Location, type and year sampled	Year snow deposited (AD)	Total quantity of melt water (liters)	Total insoluble material (mg)	Average insoluble material ($\mu\text{g/liter}$)
<u>Camp Century:</u>				
Pilot study: (Spherules, 1961)	1951-53	120	(calc) 0.515	4.3
Magnetic separation: (Spherules, 1962)	1950-54	1.25×10^5	(wt) 760	6.1
Aluminum tanks: (Total, 1962)	1810-1920	10^7	(wt) 5×10^5	50
Water well #3: (Total, 1962, 1963, 1964)	1810-1920	4×10^6	(before ashing) (after ashing)	300 50
(Total, only 1964)	1810-1920	2×10^6	(before ashing)	200
<u>Site 2:</u>				
Deep core study: (Spherules, 1957)	1250	45	(calc) 0.055	1.2
<u>Tuto ice tunnel:</u>				
Radiocarbon study: (Total, 1964)	3000 BP	825	514	623
	5000 BP	1745	904	516

Two basic types of insoluble dust samples are involved in the discussion of Table XXV: (1) only spherules which were microfiltered or magnetically separated (Langway, 1963), and (2) the total solids which were either swept from the bottom of an aluminum subsurface water storage tank, the filtrate collected during the volume-dust collecting program, or the filtrate of large blocks of melted ice in the Tuto tunnel from which the CO_2 gas was used for radiocarbon dating. The total weight of material in some cases was calculated (calc) from microscopic particle measurements and in other cases was acquired by direct weighing (wt) of the filtrate. From these data we may draw some important conclusions.

A most interesting aspect of the data is that they show an order of magnitude consistency regarding the mass concentrations of dust samples from different geographical locations and from different time periods. The spherule concentrations from the pilot study (calc 0.515 mg) and the magnetic separation (wt 760 mg) appear in approximate agreement even though there is three orders of magnitude difference between melt water sample sizes. The Site 2 spherules, as discussed earlier, are found in lesser concentrations than the Camp Century spherules.

The average mass concentration given for the aluminum water tank sludge collection (wt 500 g) is probably the least accurate of all, since water had been passing through the tank for nearly 2 years before the writer "swept" the bottom. Back surges in the water line could have added or subtracted from the total accumulated mass. The 1962, 1963 and 1964 water well samples (wt) that have been

investigated suggest that nearly 86% of the total debris filtered from the glacier ice is either organic contamination induced during collecting (polyethylene fibers, cloth fibers, etc.); terrestrial organic dusts (pollen, spores, etc.) and extraterrestrial organic dusts; or volatile inorganics which are lost on high temperature ignition. The residue is then nonvolatile inorganic terrestrial and extraterrestrial material. If we look at the Camp Century spherule concentrations we see that they would account for about 10% of the ignition residue from the water well samples.

The Tuto tunnel samples contain 2 or 3 times the concentration of total insoluble materials measured at inland stations. An explanation for this is found in a microscopic examination of the filter paper which shows quartz and other mineral fragments are present in the filtrate. The solid ice blocks used for the carbon dating samples had no visible included debris and great care was taken to clean the surface of the sample before melting in the vacuum vessel. In certain forward regions of the tunnel, however, visible layers of debris are present (Rausch, 1958), products of basal scouring by active shear bands (Bishop, 1957; Weertman, 1962). Mineral particles from the old ground moraine are carried from the subglacial floor toward the surface (Swinzow, 1962) and although not plentiful, individual particles must be distributed throughout the clean-looking ice at the rear of the tunnel. The scoured mineral particles contribute at least 60% of the total included insolubles in the tunnel samples.

In summary, Table XXV shows that the absolute concentration of insoluble material in the Greenland ice sheet is extremely low. The mass concentration of the total insoluble constituents is usually much less than the average total dissolved solids from the same sample location (see Table XIV); even in the tunnel ice the range in the insoluble concentrations, 0.5-0.6 mg/liter, is less than half of the average total dissolved solids (including SiO_2). From the Camp Century material it appears that 10% by weight of the total bulk material incorporated in the glacier consists of insoluble, non-volatile solids and that 10% of this is made up of the spherule component. In other words, 1% of the total insoluble content of the Greenland ice sheet consists of black spherules of which 1 out of every 100 are Ni-rich spherules (Table XXII).

Before concluding this section we would like to briefly point out that Kumai (1965) finds that 1.9% of the total solid, crystal nuclei in Greenland snows are black spherules and that several investigators have suggested that metallic black spherules represent about 10% of the total extraterrestrial particle influx (Dubin, 1963; McCracken and Alexander, 1961; Schmidt and Cohen, 1964). Both findings are in complete agreement with the preceding results, when the scale of samples used to construct Table XXV is considered.

We turn to an indirect measuring method to obtain some detailed information on the solids content in the submicroscopic size ranges. A study of a continuous sequence of the Site 2 deep core (Piece nos. 537 to 559) from between 117.4 m and 120.2 m (a 2.84-m profile) was recently accomplished by Hamilton (1965). The core pieces were cut into 89 3-cm thick increments, meticulously handled, melted and measured under clean room conditions for their total average solids content using the Coulter counter technique (Marshall, 1959, 1962; Bader, Hamilton and Brown, 1963; Taylor and Gliozzi, 1964). Hamilton's deep ice core results show that the average volume concentration of solid particulates to melt water is 2.12×10^{-8} , in the diameter size range 0.6 to 3.0 μ , inclusively. The Coulter counter does not differentiate the materials, so little is known about the composition of the particles but maximum and minimum volume concentrations are observed in a depth plot of the data.

For the six cycles recognized over the profile Hamilton finds an average period equivalent to 45 cm of ice and concludes that if the concentrations are related to annual cycles, the data give an annual snow accumulation rate of 40.3 g/cm^2 . This is less than 20% higher than other indirect and direct accumulation measurements given in this report for near the 100-m depth and, considering the variability of net snow accumulation, in acceptable stratigraphic agreement with our results.

From Hamilton's (1965) study the average volume concentration of solids for Greenland is shown to be about a factor 3 to 5 higher than that given for Antarctica (Bader et al., 1963; Taylor and Gliozzi, 1964). These data show the same trend as the black spherule concentrations for both places. In Greenland, it is shown here, the spherule influx rate ranges between 2.10 and 6.57×10^5 metric tons and in Antarctica it ranges between 0.4 and 2.4×10^5 metric tons (Thiel and Schmidt, 1961; Schmidt, 1963). Another quite important observation made by Hamilton on the Greenland core samples is that the volume concentrations are comparatively higher in the winter layers than in the summer layers. These results are supported by similar seasonal maximum concentrations in the dissolved constituents of the deep core (see Chapter VI).

The data from a Coulter counter study made on a limited number of samples (4) covering a 10.5-cm core profile from the 21-m depth at Byrd Station, Antarctica (Marshall, 1962) yield opposite results from those given by Hamilton in Greenland. Marshall reports that greater concentrations of solids (between 0.7 and about 15μ diam) are found in the summer snows in the Southern Hemisphere (our winter). If true, these Coulter counter data from Greenland and Antarctica suggest a global seasonal effect, at least in the smaller solid particle sizes, that might very well be extraterrestrial in origin.

In this light it might be interesting to speculate regarding the high dissolved SiO_2 concentrations found in the Greenland samples discussed in Chapter VI. The conclusion reached there was that only about 38% of the dissolved SiO_2 could be accounted for by the complete dissolution of the siliceous clay nuclei and that terrestrial dry fallout contributes the remaining material. We now consider the possibility of the excess siliceous material being of stony extraterrestrial origin. Little is known of the characteristics of stony micrometeorites. Reliable estimates for siliceous dust accretion are scarce. Hodge et al. (1964) gives a value of 4.4×10^5 metric tons/year for all Si-rich particles (spherules and irregular shapes). In terms of the spherical forms we show (Table XXIII) that type 3 spherules (glassy) compose about 20% of the total spherule concentration and Schmidt (1964) reports that 30% of the total Antarctic spherules are glassy. A closer estimate of siliceous dust accretion may possibly be obtained by considering the fall ratios of meteorites. If the fall ratio of extraterrestrial siliceous dust to metallic dust is roughly proportional to the fall ratio of stony meteorites to metallic meteorites, then we should receive on earth approximately nine times more stony dust by number (of an unknown particle composition and shape) than metallic dust; but in approximately equal weight ratios (Fireman, personal communication). For an equivalent value we use the data obtained in this study for black spherules (the lower limit of total metallic dust) as the estimate. Accordingly we obtain 4.1×10^5 metric tons/year as the weighted average stony dust influx, in good agreement with Hodge et al. (1964). If half the stony dust is SiO_2 , equivalent to a SiO_2 deposit of $4 \times 10^{-8} \text{ g/cm}^2$ -yr for the earth we calculate a value of about 10^{-3} mg/liter as the maximum contribution of silica in the Greenland snows from extraterrestrial sources. Only if the stony dust accretion were approximately 100 times more than the black spherule concentrations, and all the SiO_2 went into solution, could we account for the SiO_2 concentrations in the Greenland samples on the basis of extraterrestrial deposits.

Summary and Conclusions

The morphological, physical and chemical characteristics of spherules collected from Site 2 and Camp Century are similar. The Site 2 sample consists of 2014 spherules from a 36.4-year snow accumulation profile deposited about 1250 A.D., and the Camp Century sample consists of 5232 spherules from a 2.4-year snow accumulation profile deposited between 1951 and 1953. Three microscopic types of spherules are identified. The average number-frequency diameter of the Site 2 spherules is $16.4\ \mu$ and the average mass-frequency diameter is $21.9\ \mu$; for the Camp Century samples they are 20.2 and $33.5\ \mu$, respectively. The average number of spherules per liter of melt water is, however, comparable: 44.7 at Site 2 and 43.6 at Camp Century. The maximum size range and frequency of occurrence differ, which may possibly be related to a gross time rate change in spherule deposit, or a magnetic field effect. The vertical variations in the concentrations of black spherules at Camp Century are suggestive of a maximum occurrence in summer snows. The annual global mass deposit of black spherules is 2.10×10^5 metric tons from the Site 2 data and 6.57×10^5 metric tons from the Camp Century data.

Elemental chemical and X-ray analyses identify the composition of particles, but it is extremely difficult to prove that particles without nickel are of extraterrestrial origin, although one has actually no a priori knowledge of the composition of extraterrestrial dust. Electron probe microanalyses show the metallic spherules (Types 1 and 2) to be mainly Fe-rich with some Si and traces of Mn; and the glassy spherules (Type 3) to be mainly Si-rich with some Al and Fe and traces of Ca and K. X-ray diffraction patterns show that magnetite is the major mineralogical constituent of the metallic spherules, but an olivine spherule was also identified. One percent of the black spherules contain Ni with a Ni/Fe ratio of 0.043. Density measurements on the metallic spherules indicate a bulk value of $4.6\ \text{g/cm}^3$.

This study of the occurrence of spherules and of multiple analyses performed on the same particle shows that it is very difficult to definitively establish the extraterrestrial nature of particles by standard physical and chemical criteria. By using bulk samples of dust from Greenland (Langway and Fireman, 1965; Fireman et al., 1965; Fireman and Langway, 1965) advances are being made in this direction by attempting to detect cosmic-ray produced radioactivities.

Although particles similar in composition and form to the Greenland black spherules have been collected over the earth's surface and at the site of the Siberian Sikhote-Alin meteorite fall (Krinov, 1960), some maintain they are of terrestrial origin. The main current thinking regarding the origin of spherules is that they are either volcanic (e.g., Fredriksson and Martin, 1963; Fredriksson and Gowdy, 1963; Giovinetto and Schmidt, 1965), or extraterrestrial (e.g., Pettersson and Fredriksson, 1958; Parkin and Hunter, 1960; Skolnick, 1961; Schmidt, 1963, 1964; Langway, 1963; Hodge et al., 1964; Wright et al., 1965; Mutch, 1964a, 1964b). Some authors take both viewpoints. Although certain characteristics of industrial or other terrestrial particles and extraterrestrial spherules are held in common, earlier studies have demonstrated that industrial fly ash (Handy and Davidson, 1953); weld spatter (Hoppe and Zimmerman, 1954; Langway and Marvin, 1964), and products of nuclear explosion (Adams, Farlow and Schell, 1960; Mamuro, Seiyama, Matsunami, Fujita and Yoshikawa, 1963) do not have either the chemical characteristics, the physical nature or the generally accepted distribution and influx of the Greenland spherules. The possibility of welding or other industrial activities providing a source of contamination is precluded in the 725 year old ice core samples. Interestingly enough, however, a study of weld-spatter spherules (Langway and Marvin, 1964) has shown that many contain a Ni/Fe ratio that would be mistaken as a definite indication of extraterrestrial origin if one did not know

the true source. In addition the results of atmospheric aerosol studies in Greenland (Junge, 1960; Kumai and Francis, 1962a; Fenn and Weickmann, 1959; Fenn, 1960) show that industrial pollutants or combustion products from North America are not found on the inland ice sheet.

Chemical analyses of actual volcanic dust (Hodge and Wright, 1964; Wright and Hodge, 1965; Mutch, 1964a, 1964b) indicate the great difference between this material and the spherically shaped Greenland spherules, particularly in regard to the high concentrations of Al, Si, Ca, Cr and the low concentrations of Fe and Mn in the mainly solid, sub-spherically shaped volcanic dust. A real question arises about the ability of volcanoes to even produce spherical metallic oxides with a 60-70% Fe content. In the Greenland samples some spherules are found to be hollow and suggestions are that this is a criterion of volcanic dust (Fredriksson and Martin, 1963; Fredriksson and Gowdy, 1963; Schmidt, 1964). Hollow black spherules of magnetite composition are reported to have been picked off fallen meteorites (Krinov, 1960) and nearly all the magnetite rich (some with Ni) extra-terrestrial spherules collected from a sea sediment study are reported to have spherical cavities (Bruun et al., 1955). Analysis on the Greenland spherules by the electron probe microanalyzer has provided overwhelming evidence that the interiors are similar to the external surfaces of the same particles (Hodge and Wright, 1965), even when the inner material appears microscopically different (Langway and Marvin, 1964). Chemically then the Greenland spherules are dissimilar to the reported terrestrial source materials.

The volcanic hypothesis is also an unsatisfactory explanation of the sizes of spherules found in Greenland, on several counts. Not only because of the airborne residence times and fall velocities for high density ($> 4.6 \text{ g/cm}^3$) large diameter ($> 20 \mu$) particles, but also because no known active volcanoes are favorably situated for direct wind transport of material to the 2000 m plus elevations of the North Greenland ice sheet. Iceland does have active volcanoes but it lies 2400 km (1500 mi) to the southeast. The closest active volcano in the Northern Hemisphere that might contribute ejecta to the ice sheet under ideal wind conditions is Mt. Katmai, Alaska. A great circle route to Site 2 from Mt. Katmai is approximately 4500 km. According to studies made by Fisher (1964) on tephra (pyroclastic fragments), median diameters of ejecta vary with distance from the source according to particle density, force of explosion and wind velocity (strength and direction at progressively higher velocities are also important). Plots made by Fisher of median diameters versus distance from the source for all published data (114 investigations) show a non-linear decrease in size to a $2\text{-}\mu$ minimum limit. Using his distance-diameter curve (Fig. 9, p. 350) we find that for any tephra reaching Site 2 from Mt. Katmai, a maximum size diameter of $4\text{-}8 \mu$ is to be expected. This is considerably smaller than the average diameters of the Greenland spherules (Tables XVIII, XIX).

In the opinion of the writer, most evidence points to an extraterrestrial origin for the Greenland spherules. From this study the weighted average annual deposit of metallic spherules on the earth's surface is 4.1×10^5 metric tons. Taking into consideration the percentages of the spherule types (Table XXIII) and the average chemical compositions of representative spherules (Table XXI) we can compute the earth's accretion of the major extraterrestrial elemental constituents from the total spherule deposit. For the metallic spherules (Types 1 and 2) we take an average Fe content of 50% by weight and an average Ni content of 6% by weight (of 1% of the metallic spherules) and calculate that the earth annually receives on its surface 2.05×10^5 metric tons of Fe and 2.46×10^2 metric tons of Ni from the metallic spherules. Since the glassy spherule occurrence (Type 3) is about $\frac{1}{4}$ that

of the metallic spherules, if we take an average Si content of 40%, by weight, we calculate that 4×10^4 tons of Si from glassy spherules is deposited on earth per year. These values, in mg/cm^2 -yr units are: Fe, 4×10^{-5} ; Ni, 5×10^{-8} and Si, 8×10^{-6} . If the earth has been accreting black spherules at its present rate of 1.12×10^3 tons/day since its formation (5×10^9 years) a layer about 80 cm thick would blanket the globe.

VIII. CLIMATOLOGICAL IMPLICATIONS

General Background

The Greenland ice sheet is conditioned by climatic factors (Hare, 1951; Ahlmann, 1953) and is subject to fluctuations and changes over long and short periods (Flint, 1957; Sharp, 1956a). The relations between glaciers and climate are very complex and far from clear (Lamb, 1963; Meier and Tangborn, 1965; Nye, 1965a, 1965b) but it is well recognized that snow is extremely sensitive to temperature changes, especially around the melting point (Bader, *et al.*, 1939).

The precipitation record contained in the deep ice core is unequalled on the earth's surface. But one must remember for climatological evaluation that the core is a narrow profile of Arctic history, an infinitesimal fraction, 4×10^{-15} , of the total area of the ice sheet. Although evidence is available to show that prime meteorological events, such as a pronounced temperature rise, are continuous over extensive inland areas there are many exceptions which must be considered when projecting trends to distant geographical areas. Observations indicate that the greatest source of misinterpretation of the core data lies in local variations in surface melt conditions (sometimes completely omitting a feature in core profile) and the multi-occurrence of a single event (i. e., percolation). As explained earlier it was not possible to investigate the entire core in continuous detail, but all the core was examined thoroughly enough to allow certain deductions to be made.

As applied to the deep ice core the gross climatic indicators may be restricted to mean variations in the rates of net accumulation and the presence or absence of melt layers. These criteria represent, in the first case, the sum total of the yearly weather and in the second case the response to the maximum temperatures of the warmest summer periods. By simple deduction a layered ice feature deep within the glacier mass is positive evidence of elevated surface temperatures, hence a climatic guide. As aptly pointed out by Hattersley-Smith (1963) the thickness and frequency of ice layers are not necessarily measures of the general summer temperature of a particular year, but their scarcity over a period is a definite indication of a comparatively cold summer.

To aid us in reconstructing the past history from the deep core it will first be helpful to establish a foundation by discussing the present meteorological conditions, recent pit studies and stake measurements.

Recent History of the Inland Ice

Present meteorological conditions

Prior to 1930 no meteorological data are available from the inland ice sheet. That year the British Arctic Air Route Expedition at Camp Watkins ($67^{\circ}03'N$, $41^{\circ}49'W$, 2440-m elevation) collected 8 months of data and the Deutschen Grönland

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Expedition Alfred Wegener at Eismitte (70°54'N, 40°42'W, 3000-m elevation) gathered detailed meteorological data nearly every hour for 1 year.* Climatological summaries of these data and the succeeding meteorological stations established for more than 3 months on the inland ice are contained in reports by Diamond (1965), Diamond and Gerdel (1957), Hamilton and Rollitt (1957), Diamond (1958) and Haywood and Holleyman (1961).

Site 2 was a U.S. Air Force station between July 1953 and May 1957, and continuous data were taken by trained observers at 3-hour intervals during fair weather and hourly during storms. A condensed summary of these meteorological conditions is given in Table XXVI.

Table XXVI. Summary of meteorological data from Site 2 (from Hayward and Holleyman, 1961).

<u>Period of record:</u>	July 1953 to May 1957								
<u>Temperature data (surface):</u>	Mean annual	-24.4 C							
	Mean maximum	-20.2 C							
	Mean minimum	-28.4 C							
	Absolute maximum	+2.2 C							
	Absolute minimum	-56.1 C							
<u>Wind (direction and frequency distribution, %):</u>									
	N	NE	E	SE	S	SW	W	NW	Calm
	0	2	28.5	41.5	23	3	0	0	2
<u>Precipitation:</u>	(measurements not made)								

As shown in Table XXVI wind blows predominantly from the fourth quadrant. Wind speeds ranged from 6 to 20 knots for 86% of the observations. Although snow gauge precipitation measurements on the ice sheet have been reported faulty (Hamilton, 1958a, 1958b; Diamond, 1958; Benson, 1962) it is unfortunate that gauge measurements were not taken during this long recording period at Site 2 for comparative purposes.

Recent surface investigations

Two approaches may be used to determine the material balance of an ice sheet. On one hand there is the shallow pit study technique which utilizes the principle of covering an extensive geographical area and studying the current rates of accumulation from near surface layers. On the other hand there is the deep core investigation which limits the study to a point, but, by probing deeper into the body of the glacier, exposes a longer time interval. Both methods of investigation are valuable in reconstructing the history of the ice sheet.

*The German expedition was in part formed to investigate the validity of Hobbs' "glacial anticyclone theory" (Hobbs, 1911, 1926, 1943; Matthes, 1946; Matthes and Belmont, 1950).

The present-day material balance for the Greenland ice sheet has been established mainly due to an exhaustive 4-year field study by Benson (1959, 1962) and other contributions (Langway, 1959, 1961; Ragle and Davis, 1962; Davis, 1964; Mock, 1965 and others). A detailed compilation and evaluation by Bader (1961) using most of these results indicates that the present net average snow accumulation for all Greenland is 36.7 g/cm^2 . It should be pointed out that an indiscriminate comparison of average surface accumulation measurements from different time periods (e.g. present day multi-year measurements with the single year measurements from expeditions of 50 years ago) is not warranted but for general considerations. It is not likely that precipitation occurs uniformly over an area as extensive as the ice sheet, or even a large part of it.

Stake measurements. Net snow accumulation has been measured by USA SIPRE and USA CRREL personnel at Site 2 for several years by use of an established stake farm (i.e., bamboo poles covering a rectangular area $1.0 \text{ km} \times 0.7 \text{ km}$). A shallow pit is excavated near a different stake each year for the density measurements necessary to calculate the annual water equivalent. Table XXVII presents these data. No readings were taken in 1964. The 1963-65 accumulation totaled 88.1 g/cm^2 with an average density for the 2 years of 0.380 g/cm^3 . Data are not available for 1954-55 and 1958-60.

Table XXVII. Snow accumulation at Site 2 from stake measurements.

Year measured	Average net accumulation (g/cm^2)	Average density of annual layer with no overburden (g/cm^3)
1964-65	42.1	0.356
1963-64	46.0	-
1962-63	47.8	0.344
1961-62	22.4	0.350
1960-61	36.3	0.356
1957-58	30.9	0.332
1956-57	36.0*	0.346
1955-56	45.0†	-
1953-54	37.5*	0.358
1952-53	39 *	0.36

*Top layer measurement from pit study.

†Only depth recorded; accumulation calculated assuming density of 0.35 g/cm^3 .

Pit studies. Near surface and deeper pit investigations performed at Site 2 provide the net accumulation results which are given in Table XXVIII.

The most extensive study was done by Bader et al. (1955) over a 47-m profile (30 m of pit wall, 17 m of hand-augered core). Benson (1959, 1962) reports on a pit (3 m) and hand-augered core (11 m) study to a depth of 14 m. For purposes of this table the writer's investigation includes only the data from the exposed 3-m wall of the pit.

Table XXVIII. Snow accumulation at Site 2 from pit studies (from Langway, 1959).

Observer	Years measured (A. D.)	Number of years (n)	Average net accumulation (g/cm ²)	Standard deviation (g/cm ²)	(%)
C. Langway	1954-1957	3	42.3	7.8	18.5
C. Benson (1962)	1933-1955	22	40	-	-
H. Bader (1955)	1884-1954	70	40.6	12.5	30.8

Meteorological index horizons

As discussed earlier, effects of elevated air temperatures are manifested as melt features in the inland polar snow pack. These features form in thicknesses and depths that are proportional to the degree and length of the melt conditions. No quantitative data are available but satisfactory correlations of inland melt features and above average air temperatures (as recorded at coastal weather stations at Thule and Upernivik, Greenland) have been made by Benson (1959) on the Greenland ice sheet and Hattersley-Smith (1963) on Ellesmere Island. From inland pit studies covering most of inland Greenland it is evident that no true dry-snow zone exists today. Firn profiles 10 to 15 m deep from north to south at elevations of up to 3000 m all exhibit some melt features.

An unusually warm period was spectacularly recorded at the time of its occurrence, 12-14 July 1954, by three separate groups working on the North Greenland inland ice (Bader, 1955, p. 14; Bull, 1958, p. 241; and Benson, 1959, p. 53). This melt horizon was clearly recognized in pit walls during field investigations 5 years after its occurrence (Langway, 1961; Ragle and Davis, 1962). Bader reported this period as the warmest at Site 2 for 68 years.

In the pit study done at Site 2 in the summer of 1957 about 1 km from the mechanical bore hole the 1954 summer layer was reflected as a 40 cm thick icy firn layer between 3.02 m and 3.42 m with a 3 mm thick ice layer at 3.23 m. No percolation was noticed below this depth in the Site 2 pit study although other investigators (Benson, 1959) reported up to 2 m percolation from this July melt, at slightly lower elevations. North of Site 2, at about the same or higher elevations above sea level, all but one of a series of pits (Langway, 1961, Fig. 9, Pit nos. 2, 3, 4, 5, 9, 10 and 11) showed the effects of the 1954 melt as icy firn and other ice features over a 20 to 60 cm thickness in the exposed pit walls. The July 1954 surface is, consequently, a prime index horizon for the North Greenland ice sheet. Recently rain was reported falling in November at an elevation of 2330 m on the South Greenland inland ice (Havens, 1964). These are the only reported direct records of unusual meteorological conditions on the inland ice.

Past History From the Deep Core

Accumulation rates

All of the pit and stake data discussed above provide us with a good picture of the snow accumulation back to 1884. A yearly count of the upper 100 m of the deep core yields 174 years (A. D. 1783) of net accumulation. The O-isotope determined accumulation rates at 100 m, 300 m and 411 m (Table V) give annual averages of 32.6, 34.8 and 33.0 g/cm²-yr, respectively (mean of columns 10 and 12). Table XXIX summarizes the results of the depth-accumulation data.

Table XXIX. Depth-accumulation rates from the deep core.

Depth (m)	Average density (g/cm ³)	At (kg/cm ²)	Mean snow accumulation (g/cm ² -yr)
0-3	0.38	0.12	42.3
50	.73	3.13	
100	.89	7.31	32.6
150	.912	11.70	
200	.914	16.30	(33.7)
250	.915	20.90	
300	.916	25.50	34.8
350	.916	30.08	
411	.917	35.65	33.0

To interpret properly the measured accumulation data obtained from a deep ice core one must consider the effects of vertical plastic compression due to the overlying load (Nye, 1963; Bader, 1962). With increasing depth a layer undergoes increasing deformation which causes a thinning of layers in the vertical direction and an extension of layers in the horizontal direction. Therefore, a correction factor must be applied to the accumulation values obtained by any direct measurement (see Appendix B).

A depth-age relation is constructed for the core profile on the basis of the data given in Table XXIX, with a correction for thinning of beds. As shown in Table XXX, the thinning of beds corrections (Column 3) are sizable for deep ice, amounting to 26% at 411 m. The intermediate ages given in the table are estimated by linear interpolation using

$$At = \int_0^h \gamma dh \quad (1)$$

for $A = 39.7 \text{ g/cm}^2 \text{ -yr}$ over the upper 100 m (the accumulation mean of the surface studies and the O-isotope measurements at 100 m) and the mean of the two neighboring values for the other depths. For any depth the numerical value of At is the sum of the overlying load (σ_h , see Appendix A and D). Using eq 1 we obtain 184 years (A. D. 1773) of accumulation at $t_{100 \text{ m}}$.

The 411 m of core includes 10 centuries of net precipitation. A plot of the average accumulation (Table XXX, Column 4) versus depth shows that snow accumulation decreased slightly from A. D. 934 to A. D. 1233 and then more rapidly to A. D. 1773. A general marked increase is noted from A. D. 1773 to 1957. Stake measurements since 1957 (Table XXVII) show variability but the last 3 years are generally high. There is an average increase in snow accumulation of about 20% between 1773 and 1884 and a rate averaging about $41 \text{ g/cm}^2 \text{ -yr}$ (Table XXVIII) during the last 81 years. For the lower 300 m of the core profile one must bear in mind that the accumulation rates are based on direct measurements covering less than 3% of the depth interval.

Table XXX. Corrected depth-accumulation rates for the deep core.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
Depth (m)	Meas accum (g/cm ² -yr)	Corr factor ($\frac{H}{\bar{h}}$)	Corr accum (g/cm ² -yr)	Yrs from 1957 surface (yr)	Year deposited (A. D.)	No. yrs accum/m core (yr)
0-3	42.3	1.00	42.3	-	1957-54	0.9
100	32.6	1.05	34.2	184	c. 1773	2.7
200	(33.7)	1.11	37.4	444	c. 1513	2.7
300	34.8	1.18	41.1	724	c. 1233	2.6
411	33.0	1.26	41.6	1023	c. 934	2.8

Melt features

The structural features observed in the detailed study section at 100 m (Fig. 16) include one peculiar feature: a 4 mm thick DIM structure at 98.12 m (core piece no. 478). It is unusual in that it is the only structural melt feature seen both in transmitted light in the core piece and also between crossed polaroids in thin section (Fig. 12) in the nearly 100 vertical thin sections studied. This rare and interesting layer is just below the summer O-isotope peak at 98.10.

The complete data on all the melt features found in the 214 m of core profile that was in good enough physical condition to allow stratigraphic observation are listed in Table XXXI. The upper 100 m is arbitrarily divided into 10-m depth intervals for ease in determining trends. Core recovery below 100 m is not continuous enough to compare directly with the continuous upper 100-m profile. Due to compaction and thinning the 10-m depth intervals represent circa 11 years at the surface and circa 25 years at 100 m. The years are approximate to an estimated $\pm 10\%$. Thicknesses in Table XXXI are read as the number of features in the class interval equal to or less than the thickness listed at the head of the column. The most frequent thicknesses are 1 mm and 2 mm. They occur four times as often as all other melt features combined. In the upper 100 m one out of 20 observations is greater than 5 mm thick. The rate is doubled in the lower 124 m of core, with fewer total observations.

The depth spacing of melt features 5 mm thick and greater is given in Table XXXII. The 5-mm and 1-mm units shown for the 1953 layer are interpreted as percolation from the 11-14 July 1954 period. We may use this exceptionally warm, but short, period as a measure to guide our interpretation of the other melt features observed in the core. Listed in order of depth are the major ice features which are taken to represent periods of air temperature equal to or greater than that recorded for July 1954. The year column gives the approximate age, $\pm 10\%$, of the layer in which the ice feature is found; the depth interval is the inclusive range over which they are contained. The number in parenthesis before the thickness in mm represents the concentration of features when more than one is present. In Table XXXII we see that the upper 100 m contains evidence of many extraordinary periods of elevated air temperatures with irregular spacing in time. The most pronounced melt events are found in the snow layers deposited c. 1715, c. 1824, c. 1921 and c. 1940-41 A. D.

Table XXXI. Summary data of all ice layer, ice crust and ice wedge features observed in the core.

Depth interval (m)	Year top layer formed (A. D.)	Thickness (mm)						Total
		≤1	≤2	≤3 (Number frequency)	≤4	≤5	>5	
0-10	1957	7	5	2	1	1	0	16
10-20	c. 1945	9	5	3	1	1	1	20
20-30	c. 1930	8	2	2	2	1	4	19
30-40	c. 1915	16	4	2	2	0	0	24
40-50	c. 1900	23	6	1	0	2	0	32
50-60	c. 1880	23	4	1	2	0	2	32
60-70	c. 1860	19	1	0	1	2	0	23
70-80	c. 1840	12	6	1	4	2	5	30
80-90	c. 1820	21	7	2	1	0	0	31
90-100	c. 1795	33	4	1	0	2	0	40
Subtotal		171	44	15	14	11	12	267
%		64.0	16.5	5.6	5.2	4.1	4.5	99.9
110-120	c. 1750	11	6	0	0	1	0	18
121-214	c. 1725 to c. 1515	23	11	12	1	1	7	55
Subtotal		34	17	12	1	2	7	73
%		46.6	23.2	16.4	1.4	2.7	9.6	99.9
Total		205	61	27	15	13	19	340
%		60.3	18.0	7.9	4.4	3.8	5.6	100.0

Table XXXII. Pronounced melt features observed in the core.

Year (A. D.)	Depth interval (m)	Features, thickness and remarks
1953	4.00- 4.13	1 mm I. L. *, 5 mm lens (percolation from summer 1954)
1941	13.21- 13.26	2 mm I. L., 3 mm I. L., 4 mm I. L., 5 mm I. L.
1940	13.83	16 mm I. L.
c. 1930	20.36- 20.49	1 mm I. L., 2 mm I. L., 3-6 mm I. L., (2) 4 mm I. W. †
c. 1925	23.79	2-5 mm I. L.
c. 1921	25.33	45 mm I. L. (interbedded with lens)
c. 1919	27.63- 27.74	(2) 10 mm I. L.
c. 1881	43.97- 44.04	(2) 1 mm I. L., 2 mm I. L., 5 mm I. L.
c. 1880	44.76	5 mm I. L.
c. 1864	58.28- 58.42	1 mm I. L. (inclined), 1 mm lens, 2-3 mm I. L., 4-8 mm I. L., 4 mm I. W., 8 mm I. W.
c. 1845	67.00	5 mm I. L.
c. 1839	69.52	3-5 mm I. L.
c. 1829	74.55- 74.58	(2) 2 mm I. L., 0-5 mm I. W.
c. 1824	76.31- 76.48	3 mm I. L., (2) 4 mm I. L., 5 mm I. L., 6 mm I. L., 3-7 mm I. W., 30 mm I. W., 3-12 mm I. W., 5-40 mm I. W.
c. 1776	96.33- 98.49	(3) 1 mm I. L., 2-5 mm I. L., 4-5 mm I. L.
c. 1727	119.99-120.02	2 mm I. L., 1-5 I. W.
c. 1719	124.43	5-7 mm I. L.
c. 1715	125.43-126.35	1 mm I. L., 2 mm I. L., (5) 3 mm I. L., 5-7 mm I. L., 10 mm I. W., 12 mm I. W., 15 mm I. W., 16 mm I. W.
c. 1660	149.40-149.42	10 mm lens, 5 mm lens

*I. L. = ice layer

†I. W. = ice wedge.

As revealed in the ice core record it was warm on the inland ice in the mid-17th century and the first third of the 18th century. This was followed by about 50 years of normal or colder summer temperatures, a single warm event (c. 1776), and then about 50 more years of normal or colder summer temperatures. A pronounced rise in temperature is registered c. 1824 and continues to a lesser extent throughout the mid- and late 19th century. Between c. 1881 and c. 1919 the summers were apparently colder on the inland ice. Starting in 1919 we see a generally warmer period evolving that continues to today. The portion of the deep core covering the same 1884-1954 interval as studied by Bader at Site 2 (Bader et al., 1955) is in good comparative agreement.

Apparently the effects of the general warming trend that started in the early 20th century (Ahlmann, 1953; Weidick, 1959) brought an increasing amount of accumulation to Site 2. If this is a general relationship for the inland ice we read the record in the deep core as meaning that the temperature as well as the accumulation in A.D. 934 were similar to those of today. From A.D. 934 a slow decrease in temperature and accumulation appears to have begun which reached a minimum around the late 18th century; thereafter a gradual warming and increase in precipitation occurred that are still in effect today.

In terms of the dissolved chemical constituents in the deep core (Table XIII) the general tendency seems to be one of a gradual average decrease in total concentrations from A.D. 934 to about A.D. 1400 and a general increase to the present, with wide variability. The generally larger concentrations in older ice (411 m) might be a lingering result of the optimum climate reported (Ahlmann, 1953; Lamb, 1963) for the Roman era, from A.D. 0-400. Presumably the Arctic Ocean was more ice free then than during the preceding and following colder periods. The effect of the post-Wisconsin climatic optimum, about 5000 to 1000 B.C., is not directly detectable in our deep core record, but in ice samples of approximately the same age from the Tuto tunnel (3000 to 5000 BP) we also find a relatively higher concentration of chemical constituents.

This climatological evaluation of the core profile lets us form a new perspective on the O-isotope data (Chapter V). Table V, Column 7 (p. 40) shows that the average O-isotope value, δ , varies unsystematically with depth. It was postulated in the discussion regarding the erratic displacement of the 300-m value (p. 39) that it could possibly represent a climatic change. A plot of the values from the surface to the 411-m depth is now meaningful in light of the climatic inferences made on the core. Starting at the bottom, the 411-m δ value (-30.0) is relatively less negative (but in exact agreement with the present estimated surface value of $\delta = -29.8$, after adding the -0.2δ correction for the temperature conditions existing at the 15 km upstream location of its origin) corresponding to the warmer period and greater snow accumulation envisioned for A.D. 934 and comparable to today's climate. At 300 m the δ value (-30.7) is more negative, corresponding to the general decreasing accumulation rate and colder weather. Unfortunately the 200-m δ values are not yet available but the 100-m δ value (-30.4) and the surface δ value (-29.8) have exactly the same increasing trend as accumulation and temperature for the same time interval. In short, the O-isotope data, the snow accumulation rates, the bulk concentrations of dissolved solids and the stratigraphic melt features are all in climatological agreement (Fig. 33).

Figure 33. Depth-age and physical-chemical relations over 411-m Site 2 profile.

Summary and Conclusions

Four years of continuous surface meteorological records are available for Site 2. In addition, direct measurements have been made on snow accumulation for the past 12 years by stakes, and three separate pit studies extend our detailed information on net snow accumulation back to 1884. The deep ice core contains 1023 years of annual accumulation data. Melt features in the deep ice are reflections of elevated air temperatures of the same age (or slightly older when melt water percolation occurs) as the snow layer in which they are found. Precipitation rates are found to vary with temperature changes and correspond closely to historical evidence. The inland Greenland ice sheet appears to have received more accumulation during historically warmer periods and less during colder periods. The record of the net budget and melt features in the deep ice core indicates a temperature similar to today's in A.D. 934 with a gradual lowering of accumulation from A.D. 934 to a minimum in A.D. 1773. This minimum occurs on the inland ice at the time of historically documented advances of the Greenland marginal ice and the maximum extent of European and Alaskan glaciers in the late 18th century. A warming trend started after A.D. 1773 with a general increase in both the accumulation and temperature during the 19th and 20th centuries, a time of general Northern Hemispheric glacier retreat.

IX. SUMMARY AND CONCLUSIONS

Discussion

The deep rotary core-drilling project conducted on the inland Greenland ice sheet in 1957 provided for the first time continuous ice cores from the surface to deep within the body of a polar glacier. Core recovery (10 cm diam) was continuous down to 110 m, and about 80% to 300 m; the remainder consisted of two 5-m lengths from 360 and 411 m.

Two general problems related to the ice core are considered in detail in this report: (1) developing techniques for the stratigraphic analysis of the deep ice, and (2) the interpretation of the net accumulation and climatological inferences contained in these data. The core provides an opportunity to investigate in detail the structure and composition of a polar glacier in three dimensions and to determine its past glaciological and climatological history which one may project to other areas of the world. An understanding of the past climate, its effects, changes and trends may be helpful to predict and perhaps prevent or make use of future climatic variations.

A chief interest in the techniques of the ice core analysis program was developing and establishing new methods of delineating seasonal accumulation from the polar regions. This was particularly important for the deep ice where the tree-ring or lake varve couplet techniques used in classical surface stratigraphic interpretation were no longer applicable. A stratigraphic study of snow, firn or ice is essentially an investigation of the time variations in the variable physical and chemical properties of the material. The problem of interpreting an ice core is magnified because of the sparse quantities of any extraneous materials contained within the necessarily small sample increments used for analysis. From this study it is shown possible to interpret annual layers from the top 100 m of the polar glacier by employing classical stratigraphic criteria, but that no single criterion can by itself be used to determine accumulation cycles. A variety of methods and experimental techniques were tested for analyzing the deep ice. Some approaches were discounted after it became obvious that they would shed no light on direct stratigraphic analysis (e.g., grain size, crystal size, crystal orientation, air bubbles and bubble pressures), but these studies provided insight to the overall ice core analysis program. The analytical laboratory studies performed on pie-shaped segments from the same horizon show that it is possible to correlate meaningfully the slight physical and chemical variations found in polar glacier ice.

Just below 100 m the macroscopic and physical variations in the polar profile dampen to nearly imperceptible differences, and it is necessary to revert to indirect physical and chemical measurements and careful handling procedures to investigate the core. During the field studies it was found extremely important to keep core orientation known and to register in meticulous detail all visible stratigraphic features, using a light table and a full scale log of the core. A photographic record of the physical condition is useful. The most important field stratigraphic studies made on the core are the megascopic observations of melt features and light transmissivity and the bulk density measurements. Density variations are still reliable seasonal indicators at 100 m. We may briefly summarize the significant results of the detailed laboratory studies as follows: An investigation of the O-isotope ratio variations over the profile shows that original seasonal variations established when the snow was first deposited are still preserved at depth. A direct comparison of O-isotope variations with proven

classical stratigraphic indicators at 100 m has established the usefulness of the O-isotope ratio variations in deep polar ice, at least to 411 m. It appears that, with carefully prepared samples, the O-isotope technique is presently the best method available for detailed deep core stratigraphic analysis. An investigation of the dissolved solids content in surface snows and deep ice shows that low level non-uniform depth variations exist in the constituent concentrations that are related to seasonal factors such as moisture supply, composition of snow crystal nuclei and concentrations of dry fallout. Higher concentrations of total dissolved solids are found in winter snow deposits and lower concentrations are found in summer snow deposits. The average total ionic concentration of samples of the Greenland ice sheet is 0.76 mg/liter. The average specific conductance ranges from 1.78 to 3.85 micromhos/cm. It appears that aerosol and particulate pollutants from industrial North America do not reach inland Greenland in quantity. A study of the Fe-rich black spherule (extraterrestrial dust) concentrations in vertical firn profiles suggests that a maximum concentration of these particles occurs in summer snows. One percent of the black spherules contain nickel. The annual global mass deposit of black spherules calculated from glacier samples varies from 2.10×10^5 metric tons based on 700 year old ice from Site 2 to 6.57×10^5 metric tons based on 12 year old firn at Camp Century.

An evaluation of the accumulation data obtained from the field and laboratory analyses of the core indicates that the ice at 411 m fell as snow in the 10th century. A climatological analysis is made over the entire profile, based on stratigraphic melt features and accumulation data from the continuous upper 100 m and the discontinuous lower 300 m, and on detailed O-isotope and chemistry data from 1.3-m to 3.9-m vertical sections at 100-m, 300-m and 411-m depths (each with 3 to 10 years of precipitation record). The lower sectional profiles are short time periods and may not be fully representative of the extremes but on the average the results obtained are consistent and indicate a close relation to the historically documented advances and retreats of temperate regions glaciers. The effect on the inland ice sheet seems to be, however, in reverse to the response of temperate climate glaciers; that is, when temperate region glaciers are retreating the inland ice sheet, with higher summer temperatures, is building up, and when temperate region glaciers are advancing the inland ice sheet, with colder summer temperatures, is receiving a minimum amount of precipitation. Here we may have an answer to the old riddle regarding what causes the onset of glacial climates: an increase or a decrease in secular temperatures? The evidence observed in the core suggests that precipitation on the ice sheet is less during a general glacial maximum. In other words, increased secular temperature causes more evaporation from the ocean and provides more high latitude precipitation which builds up the ice sheet. A decrease in secular temperature decreases the evaporation from the ocean and provides a minimum of precipitation to the high latitudes. Further development and discussion of these interesting relations will require more detailed study.

In view of the results presented here it is seen that the value of investigating deep ice cores is almost limitless. It is hoped that the results of the studies given in this report will stimulate further interest in researchers from various scientific disciplines, and reveal to them the huge potential available in the study of glacier ice.

Post Site 2 Deep Drilling Programs

A great deal of work has been accomplished in polar deep drilling and core analysis since the initial Site 2 program, both in Greenland and Antarctica, by

USA SIPRE, USA CRREL and foreign countries. In all, USA SIPRE-USA CRREL has conducted four deep rotary drilling projects: the two at Site 2 in 1956 (305-m depth penetration; Lange, Langway and Hansen, 1959) and in 1957 (411 m; Langway, 1962; Lange, 1966), one at Byrd Station, Antarctica, in 1957-58 (308 m; Patenaude, Marshall and Gow, 1959; Gow, 1961) and another at Little America V, Antarctica, in 1958-59 (254 m; Ragle, Hansen, Gow and Patenaude, 1960; Bender and Gow, 1960; Gow, 1963). These four operations were all done in conjunction with IGY glaciological activities (Bader, 1958; Crary, Field and Meier, 1962) and the success and results of the overall program were interesting enough to justify post-IGY continuation with NSF support (Bader, 1962).

Although the rotary drilling method and core recovery was satisfactory it was realized that because of high drilling costs and logistical problems (primarily weight) it would not be feasible to attempt a complete penetration of a thick ice sheet using this system. In 1961 a new innovation was introduced to the polar drilling program: a thermal coring device. Hot point bore holes had been used in temperate glaciers of Europe and the United States (recently to recover small diameter cores - Kamb and Schreve, 1963a, 1963b) but never for polar ice core recovery. The thermal coring device was designed, developed and constructed by USA CRREL (L. B. Hansen, Chief, Technical Services Division), with some U.S. National Science Foundation financial aid. The unit was tested at Camp Century, Greenland, in the summer of 1961. The thermal boring device recovered good quality 12.7 cm (5 in.) diam core to 186 m during these trials. A new improved thermal tool was used in 1962 and a new hole was bored to a depth of 246 m. A third bore hole started at Camp Century in 1963 using a further modified boring tool reached a depth of 535 m by the summer of 1965. The principal advantage of the thermal rig is that the boring tool, which is hoist-operated and cable-suspended (used to transmit power as well as to lower and raise the tool), is much faster than conventional drilling. It also recovers a larger diameter ice core than the rotary rig. In turn, certain disadvantages are also present. There is great danger in allowing any melt water to remain in the bore hole where it may freeze-in the tool. The thermal process also structurally alters the porous upper firn layers (Langway, 1966b). This effect disappears at about 60 m where the firn is denser. In addition the deeper ice core (below 350 m) tends to be recovered in a fractured state, due in part to the thermal shock, but stress release from deep core obtained with the rotary drill also displayed considerable fracturing around 300 m and deeper.

The theoretical limiting factor on depth of penetration with a thermal boring tool is, of course, the ice-rock interface, although any appreciable moraine material suspended above the bottom might also prevent further penetration. This situation has been anticipated (B. L. Hansen, personal communication) and at present a down-hole electromechanical boring tool is being developed to be used on the thermal rig tower with the cable-hoist equipment. This apparatus recovers a 9.1-cm (3 5/8-in.) core and is capable of rock as well as ice boring. The electromechanical drill was inserted into the 547-m bore hole started by the thermal tool in late 1965, and penetrated between the 547-m and 1002-m depth at Camp Century in 6 weeks (Hansen and Ueda, personal communication). Continuous core recovery was excellent. The ice was slightly fractured near the beginning but the physical condition improves with depth. In the summer of 1966 the electromechanical drill penetrated completely through the Greenland ice sheet at Camp Century at the 1387 m depth and into 3.6 m of sub-ice material (frozen till), recovering perfect unbroken cores, some 5 m long (Hansen and Langway, 1966).

Over the past few years the USA SIPRE-USA CRREL drilling program on the Greenland ice sheet has provided about 2450m (8000 ft) of ice core from five different bore holes at two different locations, and 562 m (1840 ft) of ice core from

two different bore hole locations in Antarctica. In part sparked by USA SIPRE-USA CRREL's success in their drilling programs, several other countries have actively entered the field. The Canadians, with a USA CRREL built shallow-depth thermal boring rig, are currently core drilling in the small ice caps in the Arctic Archipelago, and a similar rig will be used by the Australians in their 1966-1967 Antarctic program. The Russians started a rotary core drilling program at Station Mirnyy, Antarctica, during IGY and penetrated a reported depth of 370 m. Very little information is available about the drilling and nothing to my knowledge about core quality or core analysis. Later Russian attempts at thermal-core drilling at Vostok met with only limited success (40-m to 50-m depth). In 1961 at Base Roi Baudouin, Antarctica, the Belgians modified a USA CRREL 7.6-cm (3-in.) hand operated coring auger with a mechanical attachment and reached a depth of 43.7 m. From 43.7 m to 115.7 m a Swedish Craelus rig was used to obtain a 4.8 diam core (Tongiorgi, Picciotto, De Breuck, Norling, Giot and Pantaneti, 1962).

The recovered deep cores mentioned above have been analyzed to some extent, mainly by the classical stratigraphic procedures (Gow, 1961, 1963; Bender and Gow, 1961; Tongiorgi, Picciotto, De Breuck, Norling, Giot and Pantaneti, 1962) and O-isotope ratio studies (Epstein, Sharp and Goddard, 1963; Gonfiantini, 1965). However, of late, great advances are being made in deep core stratigraphic analyses and age determinations by use of natural and artificial radioactive isotopes (Picciotto, 1962; Vickers, 1963; Lorius, 1964). Studies of Pb-210 (Goldberg, 1963; Crozaz, Picciotto and De Breuck, 1964; Crozaz and Langway, 1966), Sr-90 (mainly nuclear fission product fall-out) (Picciotto and Wilgain, 1963; Picciotto, Crozaz and De Breuck, 1964; Crozaz, Langway and Picciotto, 1965; Wilgain, Picciotto and De Breuck, 1965) and C-14 (Langway *et al.*, 1965; Oeschger *et al.*, 1965) have all been shown to be valuable tools in estimating rates of snow accumulation or in age dating glacier ice. Future studies on all aspects of deep ice core analyses promise to be extremely valuable and scientifically rewarding.

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APPENDIX A. SORGE'S LAW

In earlier papers Bader (1953, 1955) analyzed the density data of Sorge (1935) and developed what is known as Sorge's Law of Densification. This law is a mathematical expression of the concept that for polar conditions density is a function of depth below the surface, $\gamma = \gamma(h)$, and the form of the curve does not change with time. The practical glaciological significance of this expression is that it can be used to deduce the amount of annual accumulation where annual layers are difficult or impossible to determine.

The law is valid when two assumptions are made: (1) the glacier is stationary (no climatic change) and (2) melting is insignificant. The Site 2 location is considered to satisfy these conditions and, using the depth-density data from the 1957 deep ice core, Bader (1960, 1962) has expanded and refined certain aspects of Sorge's Law. For our purposes the following useful relationships from Bader's analysis are of interest and are briefly presented.

The term definitions are as follows:

- h = depth below the surface, cm
- γ_h = density of the sample at depth h , g/cm³
- t_h = time since deposition on the surface, yr
- σ_h = load pressure at depth h , g/cm²
- V_h = vertical velocity of a snow particle downward in relation to snow surface, cm/yr
- v_h = specific velocity of densification, yr⁻¹
- A = accumulation rate of snow, g/cm²
- $\dot{\epsilon}_h$ = the vertical strain rate, yr⁻¹.

If γ is the density at a depth h below the surface then

$$\gamma = \gamma(h). \quad (A1)$$

At any depth below the surface h , the vertical stress (load pressure) σ_h caused by the overlying snow is equal to the weight of the column above it in water equivalent which also is equivalent to the product of the accumulation rate and the elapsed time and is written as

$$\sigma_h = \int_0^h \gamma \, dh = A t_h. \quad (A2)$$

If an accumulation layer (load increment) $d\sigma$ falls to the surface in a time dt , and the density curve is invariant with time, a volume of snow at h will sink by dh and it follows that

$$d\sigma = A \, dt = \gamma_h \, dh. \quad (A3)$$

The vertical velocity dh/dt of any point h relative to the snow surface is given by

$$V_h = \frac{dh}{dt} = \frac{A}{\gamma_h} \quad (\text{A4})$$

and by differentiating eq A4 we have

$$dV = -\frac{A}{\gamma^2} \cdot d\gamma \quad (\text{A5})$$

and the specific velocity of densification (vertical strain rate)

$$v = \dot{\epsilon}_h = \frac{dV}{dh} = -\frac{A}{\gamma^2} \frac{d\gamma}{dh} \quad (\text{A6})$$

where $d\gamma/dh$ is the slope of the depth density curve in $\text{g/cm}^3\text{-cm}$.

Using additional assumptions, a viscosity factor, an empirical temperature cycle correction function and other substitutions, Bader (1960, 1962) has formulated an equation for the depth-density curve for Site 2. He treats the density curve in two increments covering the density ranges from the surface (0.36 g/cm^3) to about the 20-m depth (0.60 g/cm^3) and greater than 0.60 g/cm^3 and gives complex equations which fit the data. For the upper zone he uses an exponential relationship and for the deeper, denser material a hyperbolic sine function.

APPENDIX B. THINNING OF LAYERS

Nye (1964) and Bader (1963) have both studied the problem of the thinning of layers and have arrived at similar solutions using slightly different assumptions. A condensation of Nye's treatment and its application to the deep ice core follows.

Two simple assumptions are all that Nye found necessary to develop the correction factor: (1) negligible bottom melting is occurring and (2) the vertical plastic strain rate along any vertical line in the ice is uniform at any given instant. From these assumptions it follows that the vertical plastic strain rate of a layer is equal to the vertical plastic strain rate of the ice which lies between it and the subsurface. Thus, if ℓ is the thickness of a layer, in ice-equivalent, and h is the height of a layer, in ice-equivalent, above the subsurface we have

$$\frac{1}{\ell} \frac{d\ell}{dt} = \frac{1}{h} \frac{dh}{dt}$$

and

$$\int_L^\ell \frac{d\ell}{\ell} = \int_H^h \frac{dh}{h}$$

where L is the original layer thickness in ice-equivalent, and H is the height above the bed, in ice-equivalent, at which the layer first formed. Integrating we have

$$\frac{\ell}{L} = \frac{h}{H} \quad (B1)$$

which states that the total plastic strain of a layer is always equal to the total vertical plastic strain of ice lying between it and the bed. Time drops out of the expression.

For application of eq B1 to the deep core

ℓ = thickness of an annual layer measured from the core, g/cm²

L = original thickness of layer (corrected value), g/cm²

h = height of layer above the bed, measured at bore hole, cm

H = height of layer above the bed where layer formed, cm.

The terms ℓ and h are directly measurable but H must be approximated. For the Site 2 area, with a surface velocity of about 10 m to 20 m per year, the point of origin of the deepest ice at 411 m (assuming it is 1000 years old) would be about 10 to 20 km upstream; within this area the difference in ice thickness is negligible for this purpose.

The table below presents the correction factors to be multiplied by the accumulation values obtained from the deep core at Site 2, where $H = 2000$ m.

Depth below surface (m)	0	100	200	300	400	411
Correction factors (H/h)	1.000	1.053	1.111	1.176	1.250	1.265

APPENDIX C. STATISTICAL TERMS

n = number

d = diameter

N, total number = $\sum n_i$

$$\bar{x}_d, \text{ arithmetic mean} = \frac{1}{N} \sum_{n=i}^N f_i x_i$$

$$\bar{x}_m, \text{ arithmetic mean, mass frequency} = 3 \sqrt{\frac{\bar{m}}{\rho \frac{\pi}{6}}}$$

$$\bar{m}, \text{ average diameter mass} = \rho \frac{\pi}{6} \frac{\sum (n_i d_i^3)}{N}$$

$$s, \text{ standard deviation} = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N-1}}$$

 s_p^2 , pooled variance (i.e., mean of standard deviations) =

$$\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2 + \dots + (n_k - 1)s_k^2}{n_1 + n_2 + \dots + n_k - k}$$

where n_i is the number of observations in each sample s_i^2 is the sample variance

k is the number of different groups of observations.

$$r, \text{ correlation coefficient} = \frac{\sum xy - n\bar{x}\bar{y}}{\sqrt{[\sum (x^2) - n(\bar{x})^2][\sum (y^2) - n(\bar{y})^2]}}$$

$$\text{Student's t-test} = \sqrt{\frac{r^2 (n-2)}{1-r^2}}, \text{ where } n-2 = \text{degrees of freedom.}$$

For some of the chemical data a chemical equivalents per million (epm) calculation was made. By definition a milliequivalent (m.e.) is the ratio of the atomic weight of the ion to its valence and epm is numerically equal to m.e./liter. To compute epm, the concentration of individual ions in milligrams/liter (mg/l) is multiplied by the reciprocal of the combining weight.

APPENDIX D. AVERAGE DENSITY DETERMINATIONS FOR METER INCREMENTS FROM THE SURFACE TO 411.21 METERS, SITE 2, GREENLAND

Depth interval, Δh (m)	No. measurements (n)	Average density, $\bar{\rho}$ (g/cm ³)	Cumulative load pressure, Σp (kg/cm ²)	Depth interval, Δh (m)	No. measurements (n)	Average density, $\bar{\rho}$ (g/cm ³)	Cumulative load pressure, Σp (kg/cm ²)
Table 1				Table 4 (Cont'd)			
0 - 1	17	0.347	0.035	37 - 38	4	0.693	2.19
1 - 2	19	.394	.074	38 - 39	8	.696	2.26
2 - 3	16	.411	.115	39 - 40	6	.704	2.33
3 - 3.27	5	0.378	0.125	40 - 41	6	.724	2.40
Total:	57			41 - 42	5	.707	2.47
Table 2				42 - 43	7	.721	2.54
2.85 - 4	8	0.406	0.156	43 - 44	9	.734	2.62
4 - 5	8	.477	.200	44 - 45	8	.727	2.69
5 - 6	7	.446	.245	45 - 46	5	.721	2.76
6 - 7	7	.474	.292	46 - 47	6	.730	2.84
7 - 8	9	.492	.341	47 - 48	6	.735	2.91
8 - 9	7	.505	.392	48 - 49	4	.732	2.98
9 - 10.65	4	0.530	0.479	49 - 50	5	.744	3.06
Total:	50			50 - 51	2	.730	3.13
Table 3				51 - 52	4	.750	3.20
3.00 - 4	6	0.436	0.159	52 - 53	8	.758	3.28
4 - 5	10	.460	.205	53 - 54	7	.760	3.36
5 - 6	6	.469	.252	54 - 55	7	.760	3.43
6 - 7	7	.485	.300	55 - 56	6	.766	3.50
7 - 8	9	.502	.350	56 - 57	5	.769	3.59
8 - 9	5	.513	.401	57 - 58	6	.774	3.66
9 - 10	7	.532	.455	58 - 59	4	.787	3.74
10 - 11	9	.522	.507	59 - 60	6	.775	3.82
11 - 12	8	.554	.562	60 - 61	5	.785	3.90
12 - 13	7	.563	.619	61 - 62	6	.792	3.98
13 - 14	8	.571	.676	62 - 63	7	.789	4.06
14 - 15	7	.578	.734	63 - 64	4	.799	4.14
15 - 16	6	.586	.792	64 - 65	6	.803	4.22
16 - 17	6	.603	.852	65 - 66.12	5	0.810	4.31
17 - 18	7	.598	.912	Total:	252		
18 - 19	2	.592	.972	Table 5*			
19 - 20	4	.620	1.03	66.21 - 67	7	0.8346	4.46
20 - 21	5	.637	1.10	67 - 68	7	.8406	4.55
21 - 22	5	.617	1.16	68 - 69	7	.8344	4.63
22 - 23	5	.611	1.22	69 - 70	7	.8384	4.71
23 - 24.31	7	0.632	1.30	70 - 71	7	.8442	4.80
Total:	136			71 - 72	7	.8373	4.88
Table 4				72 - 73	5	.8382	4.97
19.62 - 20	3	0.604	1.03	73 - 74	4	.8347	5.05
20 - 21	5	.594	1.09	74 - 75	6	.8363	5.13
21 - 22	7	.604	1.15	75 - 76	5	.8472	5.22
22 - 24	7	.621	1.27	76 - 77	6	.8499	5.30
24 - 25	6	.623	1.34	77 - 78	7	.8491	5.39
25 - 26	5	.625	1.40	78 - 79	7	.8485	5.47
26 - 27	5	.624	1.46	79 - 80	5	.8578	5.56
27 - 28	5	.641	1.52	80 - 81	7	.8536	5.64
28 - 29	7	.647	1.59	81 - 82	7	.8664	5.73
29 - 30	6	.651	1.65	82 - 83	6	.8672	5.82
31 - 33	7	.664	1.85	83 - 84	8	.8667	5.90
33 - 34	7	.668	1.92	84 - 85	6	.8726	5.99
34 - 35	4	.677	1.98	85 - 86	7	.8668	6.08
35 - 36	4	.668	2.05	86 - 87	6	.8735	6.17
36 - 37	7	0.696	2.12	87 - 88	6	.8746	6.25
				88 - 89	9	.8770	6.34
				89 - 90	8	.8792	6.43
				90 - 91	7	0.8778	6.52

*Density values temperature corrected to -25.0C. Density of pure bubble free ice at corrected temperature, 0.92002 g/cm³.

Depth interval, Δh (m)	No. measurements (n)	Average density, $\bar{\gamma}$ (g/cm ³)	Cumulative load pressure, $\Sigma\sigma$ (kg/cm ²)	Depth interval, Δh (m)	No. measurements (n)	Average density, $\bar{\gamma}$ (g/cm ³)	Cumulative load pressure, $\Sigma\sigma$ (kg/cm ²)
Table 5 (Cont'd)*				Table 5 (Cont'd)*			
91 - 92	7	0.8807	6.61	231 - 232	1	0.9157	19.24
92 - 93	7	.8787	6.69	234 - 235	1	.9158	19.51
93 - 94	5	.8836	6.78	238 - 239	1	.9162	19.88
94 - 95	5	.8838	6.87	248 - 249	1	.9156	20.80
95 - 96	5	.8882	6.96	255 - 256	2	.9168	21.44
96 - 97	8	.8810	7.05	259 - 260	1	.9163	21.80
97 - 98	7	.8874	7.14	270 - 271	1	.9165	22.81
98 - 99	7	.8860	7.22	282 - 283	1	.9168	23.91
99 - 100	5	.8929	7.31	288 - 288.29	1	0.9168	24.40
103 - 104	2	.8864	7.67	Total:	313		
105 - 106	3	.8950	7.85				
108 - 109	1	.8903	8.12				
109 - 110	6	.8954	8.20				
110 - 111	7	.8962	8.30				
111 - 112	1	.9007	8.38				
112 - 113	1	.8991	8.48				
113 - 114	3	.8948	8.56				
114 - 115	6	.9006	8.65				
115 - 116	7	.9007	8.74				
116 - 117	4	.9028	8.84				
117 - 118	5	.9016	8.92				
120 - 121	1	.9025	9.20				
123 - 124	1	.9051	9.47				
126 - 127	1	.9077	9.74				
130 - 131	1	.9122	10.10				
132 - 133	1	.9083	10.28				
133 - 134	1	.9098	10.38				
135 - 136	1	.9095	10.56				
136 - 137	1	.9077	10.65				
139 - 140	1	.9084	10.92				
141 - 142	1	.9110	11.10				
150 - 151	1	.9117	11.83				
151 - 152	1	.9120	11.92				
153 - 154	1	.9123	12.10				
154 - 155	1	.9117	12.20				
161 - 162	1	.9139	12.84				
162 - 163	1	.9121	12.93				
166 - 167	1	.9139	13.29				
167 - 168	1	.9141	13.38				
180 - 181	1	.9144	14.57				
181 - 182	1	.9140	14.66				
184 - 185	1	.9144	14.94				
187 - 188	1	.9144	15.21				
192 - 193	2	.9147	15.67				
197 - 198	1	.9149	16.13				
213 - 214	1	.9151	17.59				
214 - 215	2	.9151	17.68				
215 - 216	2	.9156	17.77				
216 - 217	1	.9157	17.86				
218 - 219	1	.9154	18.05				
221 - 222	1	.9152	18.32				
226 - 227	1	.9155	18.78				
227 - 228	1	.9156	18.87				
228 - 229	1	.9161	18.96				
229 - 230	1	0.9157	19.06				
				Table 6†			
				Depth below 1957 surface (m)	Density γ (g/cm ³)	Depth below 1957 surface (m)	Density γ (g/cm ³)
				72.5	0.84541	198.0	0.91440
				74.5	.85671	203.1	.91458
				79.5	.86954	213.7	.91491
				83.0	.87557	220.3	.91480
				95.0	.88068	224.5	.91464
				99.6	.87916	230.8	.91516
				99.8	.88465	240.0	.91551
				108.0	.89380	245.0	.91552
				117.3	.89656	248.6	.91602
				127.3	.90657	256.6	.91592
				131.3	.90438	261.7	.91620
				135.2	.90952	265.0	.91606
				142.1	.90939	272.0	.91601
				150.0	.91207	279.1	.91637
				154.6	.91151	284.3	.91622
				161.5	.91283	290.2	.91625
				166.0	.91292	299.2	.91664
				180.1	.91428	300.1	.91628
				184.1	.91390	305.8	.91644
				188.1	0.91405	310.7	.91635
						360.4**	0.91719

*Density values temperature corrected to -25.0°C. Density of pure bubble free ice at corrected temperature, 0.92002 g/cm³.

†Precise individual density determinations measured for bubble pressure experiments (Langway, 1958).

**Assuming an extrapolated density of 0.917 g/cm³ over the interval 360 m to 411 m the cumulative load pressure at the bottom of the bore hole (411 m) is 35.65 kg/cm².

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13. ABSTRACT A deep rotary core drilling project in 1957 at Site 2 on the Greenland ice sheet (76°59'N, 56°04'W) provided ice core to a depth of 411 m. The vertical variation in bulk density, macroscopic structure, oxygen isotope ratios, ionic constituents, and extraterrestrial dust (black spherules) were analyzed using both field and laboratory techniques. These data permit the direct estimate of annual accumulation layers in the core. Continuous stratigraphic measurements and observations were made over the upper 110 m of the profile and detailed physical and chemical analyses were made on continuous 1.3 to 3.9-m core increments at 100, 200, 300 and 411-m depths. The average total ionic concentration in the ice sheet ranges between 0.65 and 1.35 mg/liter. The annual global mass deposit of black spherules as calculated from these studies varies from 2.10×10^5 metric tons in 700 year old ice to 6.57×10^5 metric tons in 12 year old firn. The oxygen isotope ratio variation provides the best means of estimating accumulation at depth. Results of the investigations indicate rates of net snow accumulation of 42.3, 34.2, 37.4, 41.1 and 41.6 g/cm ² -yr at the surface, A.D. c. 1773, c. 1513, c. 1233 and c. 934, respectively. Accumulation data and other physical and chemical evidence allow climatological inferences to be made over the 10-century profile. The ice core record shows that snow accumulation and temperature in A.D. 934 were similar to today, followed by a gradual decrease in accumulation to a minimum around the late 18th century and an increase in both accumulation and temperature from A.D. 1773 to 1957 and following.		

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