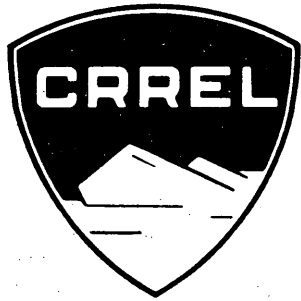


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CATIONIC ANALYSIS OF THE BYRD STATION, ANTARCTICA, ICE CORE

Stephen E. Ragone and Roland V. Finelli

August 1972

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

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CORPS OF ENGINEERS, U.S. ARMY
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PREFACE

This report was prepared by Captain S.E. Ragone and SP R.V. Finelli, formerly of the Snow and Ice Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory (USA CRREL).

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INTRODUCTION

The chemical constituents in Antarctic snow, firn, and ice have been studied considerably in recent years (Sugawara 1961, Brocas and Delwiche 1963, Matveev 1961, Angino et al. 1965, Wilson and House 1965, Hochstein and Risk 1967, Brocas and Picciotto 1967, Lorius et al. 1968, Hanappe et al. 1968, Murozumi et al. 1969, Matveev 1970). However, these studies have been limited to the upper several hundred meters of the ice sheet. In 1968 the ice sheet at Byrd Station (80° 01'S, 119° 31'W, elevation 1530 m) was penetrated to bedrock (Ueda and Garfield 1969) and an ice core was recovered (Gow et al. 1968) using an electromechanical drill (Ueda and Garfield 1968). For the first time a continuous record of Antarctic snow accumulation for 100,000 years before the present (BP) (Epstein 1970) was available for analysis.

This report presents concentrations of the major cationic constituents Na^+ , K^+ , Ca^{2+} , and Mg^{2+} in the ice core to establish their relative concentrations and variations with depth (time).

METHODS OF ANALYSIS

Sampling and cleaning procedures

Eighty-five 10-cm-long 4/5-segment samples from 168 to 2153-m depths of a 2164-m-long ice core were taken for analysis. Selection was based on transmitted light analysis; only unfractured pieces were used. No samples were taken between 518-920 m because the cores were highly fractured in this region.

The ice core contacted several different fluids required for drilling that were potential sources of contamination. Studies showed that contamination was limited to the surface of the ice core and could be successfully removed in three steps, by ultrasonically vibrating the water and rinsing the samples successively in distilled water (Ragone and Finelli 1970). Approximately half the core volume was consumed during washing. Samples were often melted in two or more sequential aliquots that were analyzed separately as a further check to ensure that the surfaces were properly cleaned.

Analytical procedures

Analyses were performed using a Perkin-Elmer Model 303 atomic absorption spectrophotometer with a DCR-1 digital readout accessory, according to procedures described by Ragone and Finelli (1971).

The low concentrations of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} observed in the samples made a definition of detection limits necessary. The limit of detection is generally defined as the smallest quantity of sample that can be measured with certainty. This definition in part covers a special case of sensitivity because it establishes a quantity of sample discernible from a blank.

The calibration curves for the standard solutions are linear from 2 to 100 $\mu\text{g}/\ell$ and show significant absorption differences in the standard solutions even at the lower concentrations studied.

Figure 1 shows the net absorption and least squares fit for 21 sets of standard solutions from 2 $\mu\text{g}/\ell$ to 20 $\mu\text{g}/\ell$.

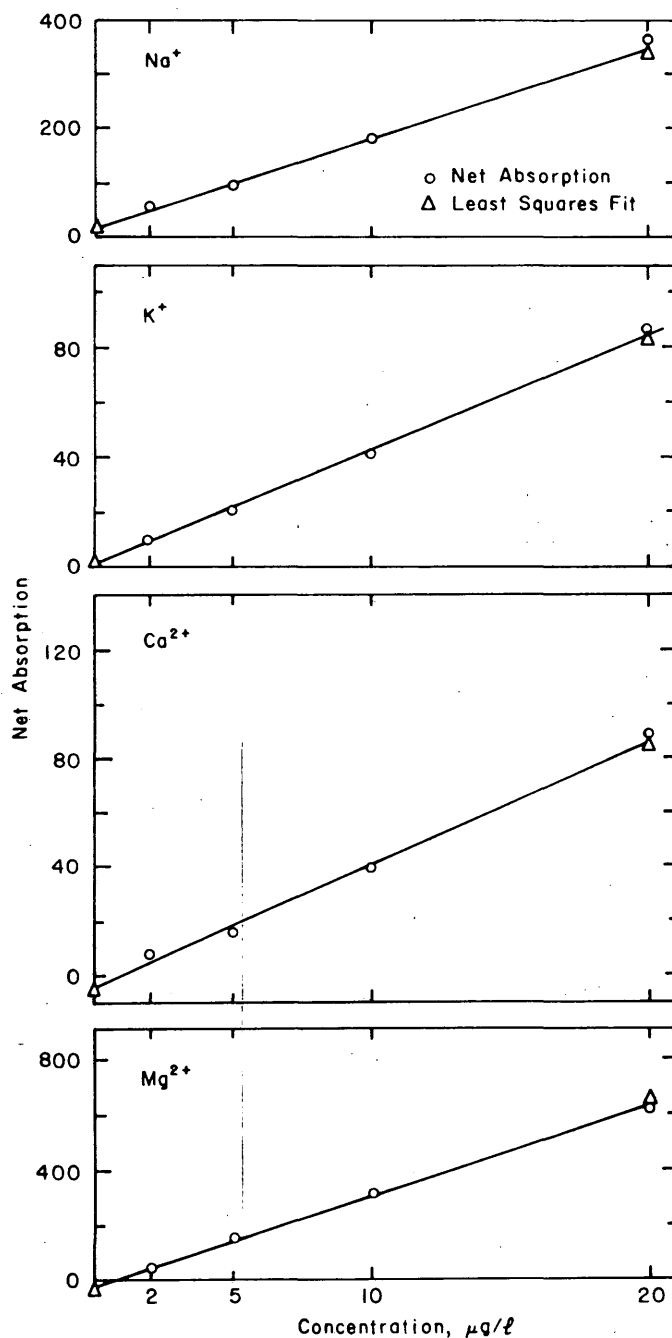


Figure 1. Least squares fitted calibration curves for Na^+ , K^+ , Ca^{2+} and Mg^{2+} .

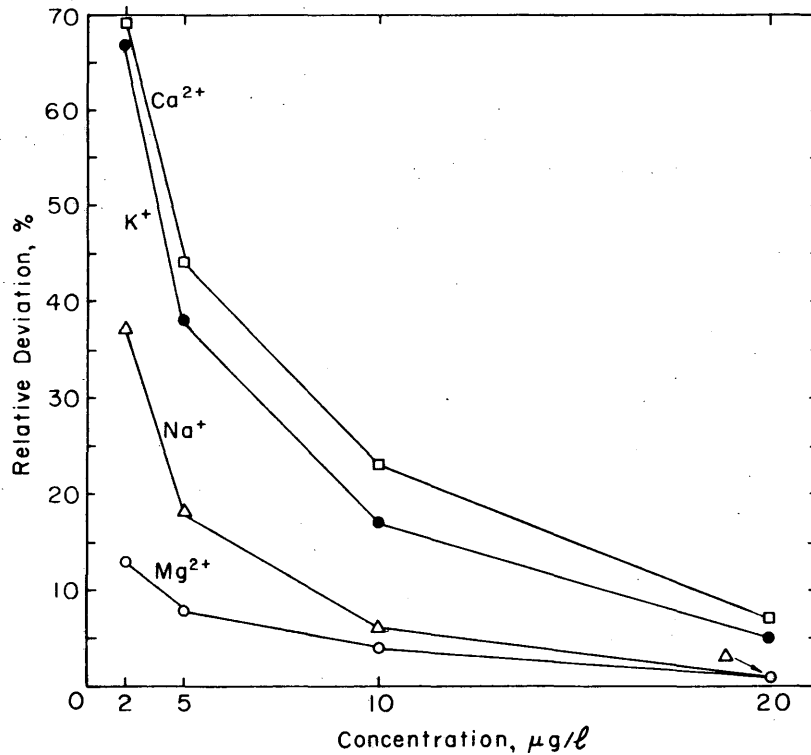


Figure 2. Variation in the relative deviation of the net absorption with concentration for Na^+ , K^+ , Ca^{2+} and Mg^{2+} .

The second aspect of the definition includes a statistical certainty for detection. A cation is defined as being detected if its signal is precise to \pm one standard deviation ($\pm 100\%$ relative deviation). The relative deviation of a replicate set of determinations increases significantly from $20 \mu\text{g/l}$ to $2 \mu\text{g/l}$ but remains less than 100% at $2 \mu\text{g/l}$ for all the cations studied (Fig. 2). Consequently, all the cations are detected to at least $2 \mu\text{g/l}$.

RESULTS

Figure 3 summarizes the findings. The complete data are given in the Appendix. The broken lines indicate points that fall below the detection limit. While the cationic concentrations of the samples vary substantially over the entire core profile studied, the mean concentrations of all the cations definitely increase from about 1264 to 2090-m depths. From 168 to 1243-m depths the average Na^+ , K^+ , Ca^{2+} and Mg^{2+} concentrations are 21, 3, 2 and $3 \mu\text{g/l}$ respectively. The average concentrations increase to 37, 5, 5 and $7 \mu\text{g/l}$ respectively in the 1264 to 2090-m region, then decrease to 19, 4, 2 and $2 \mu\text{g/l}$ respectively from 2100 to 2153-m depths (Table I).

DISCUSSION

The 1264-2090-m region represents snow accumulations deposited over the last 13,000 to 60,000 years (Epstein, et al. 1970). The Wisconsin stage occurred from 11,000 to 25,000 years BP (Epstein, et al.). The increased mean cationic concentration from 1264 to 2090 m and the coincidence of this region with the Wisconsin stage cold interval suggest that there is a correlation between

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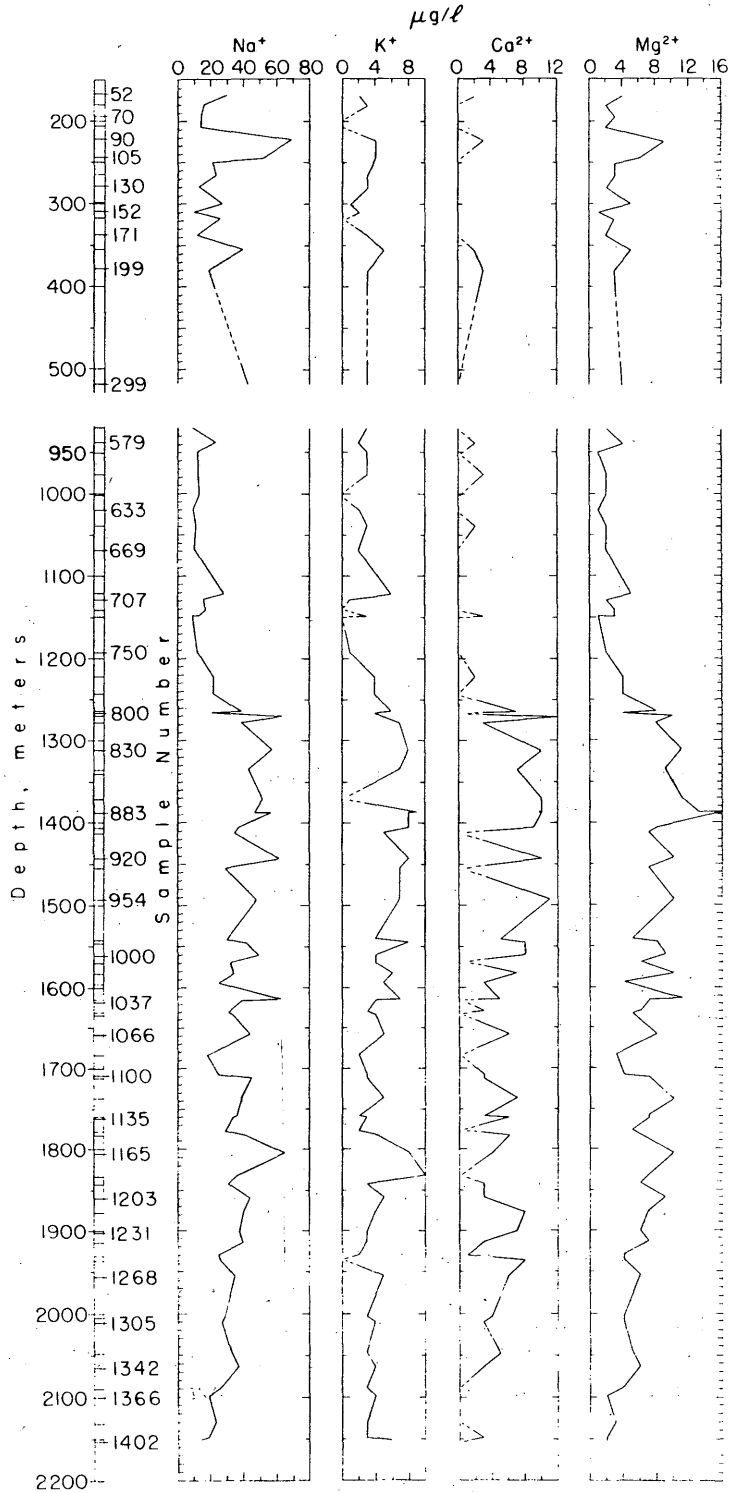


Figure 3. Variation in the cationic constituents with depth.

Table I. The mean concentrations of Na⁺, K⁺, Ca²⁺ and Mg²⁺ over different regions of the ice core.

Core tube no. (depth)	No. samples spanning interval	Na ⁺ (μg/l)	K ⁺ (μg/l)	Ca ²⁺ (μg/l)	Mg ²⁺ (μg/l)
52-784 (168-1243 m)	32	21 (8-69)*	3 (2-6)	2 (2-3)	3 (1-9)
798-1359 (1264-2090 m)	49	37 (12-66)	5 (2-9)	5 (2-12)	7 (2-16)
1366-1402 (2100-2153 m)	4	19 (13-23)	4 (3-6)	2 (2-3)	2 (2-3)
Avg		31	4	4	5

* Indicates range of values observed.

the two events. It may be speculated that the colder conditions during this period resulted in an increased flow of temperature air masses carrying dust, water vapor and water soluble salts into the Antarctic, as described by Hamilton (1969).

A more probable explanation in light of existing data is that the concentration increases resulted from local volcanic activity. Gow (personal communication 1970) has found bands of volcanic dust in the Antarctic core with maximum frequency of occurrence between about 1300-1600 m; these are tentatively attributed to volcanic sources within 400 km of Byrd Station.

Banding was observed in many of the samples used in this study, but occurred more frequently between 1264-1406 m depth (see Appendix). These band samples had cationic concentrations above the mean for the 1264 to 2090-m region. Since bands were observed in a few samples having low cationic concentrations, and relatively high cationic concentrations have been observed in samples showing no apparent banding, no specific correlation between the occurrence of bands and high cationic concentration can be made at this time.

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**APPENDIX: THE CONCENTRATIONS OF Na⁺, K⁺, Ca²⁺ and Mg²⁺
IN THE SAMPLES TAKEN FOR ANALYSIS**

Core tube no.	Depth* (m)	Na ⁺ (μg/l)	K ⁺ (μg/l)	Ca ²⁺ (μg/l)	Mg ²⁺ (μg/l)
52	168	30±0	2±1	2±1	4±0
61	180	16±0	3±2	BD†	2±0
70	194	14±1	BD	BD	3±1
79	206	14±0	BD	BD	2±0
90	222	69±0	4±1	3±2	9±0
105	244	52±2	4±0	BD	6±1
109	250	21±1	BD	BD	3±0
120	265	23±0	3±2	BD	3±0
130	279	13±1	3±2	BD	2±0
144	299	27±0	1±1	BD	5±0
152	309	10±1	2±1	BD	1±1
158	317	26±1	BD	BD	3±1
171	337	12±0	3±1	BD	2±1
184	355	40±1	5±1	2±2	5±1
199	378	19±1	3±2	3±2	3±1
299 (B)**	518	43±0	3±2	BD	5±0
567	920	8±0	3±2	BD	2±0
579	938	23±1	2±0	2±1	4±0
587	950	12±0	3±2	BD	1±0
605	977	12±2	3±2	3±2	2±0
621	1002	13±0	BD	BD	2±0
633	1020	9±1	2±1	BD	1±0
649	1044	11±1	3±2	2±2	2±1
669	1073	10±0	2±1	BD	2±1
701	1121	28±1	6±1	BD	5±1
707	1129	16±0	1±0	BD	2±0
715	1141	17±1	BD	BD	3±0
720A (B)	1149	13±1	3±0	3±2	3±1
720B		9±0	BD	BD	2±1
750	1193	12±0	1±1	BD	2±1
770	1222	22±0	4±2	2±2	4±1
784	1243	22±0	4±2	BD	4±0
798 (B)	1264	39±2	6±2	7±2	8±0
800	1266	21±1	4±0	BD	4±0
823 (B)	1300	64±1	5±1	12±2	10±0
828 (B)	1308	39±2	7±1	3±2	10±0
830 (B)	1311	58±0	8±1	10±2	11±0
847 (B)	1335	43±0	7±1	7±0	9±0
851	1341	39±0	5±3	6±0	8±0
881 (B)	1385	52±0	BD	10±1	11±0
883A (B)	1388	47±1	9±2	10±3	13±2
883B		57±2	8±1	10±2	16±1
895 (B)	1406	37±0	8±1	9±3	8±0
900	1413	35±0	5±1	BD	7±0
920	1443	62±0	8±2	10±2	10±0
928	1455	29±1	7±2	BD	7±1
954	1493	48±2	7±4	11±5	10±0
987	1542	30±0	4±1	5±0	5±1
990	1546	42±2	8±2	8±2	8±2
1000	1561	49±2	4±1	8±3	9±1
1006	1570	32±2	4±1	BD	6±1
1015	1583	34±2	6±1	7±3	10±1
1023	1595	25±0	5±1	3±2	4±0
1036	1614	63±0	7±1	5±3	11±1
1037 (B)	1616	39±1	4±2	BD	7±0

APPENDIX: (Cont'd).

Core tube no.	Depth* (m)	Na ⁺ ($\mu\text{g/l}$)	K ⁺ ($\mu\text{g/l}$)	Ca ²⁺ ($\mu\text{g/l}$)	Mg ²⁺ ($\mu\text{g/l}$)
1047	1630	31±1	3±2	3±2	6±1
1049	1634	33±1	4±1	BD	5±0
1066	1659	44±1	5±1	6±4	8±0
1083	1684	18±1	2±1	BD	3±1
1100	1709	25±1	3±2	3±2	4±0
1102	1712	45±1	3±2	3±2	7±0
1119	1737	39±0	5±3	7±4	10±0
1134	1760	36±0	2±0	3±1	7±0
1135	1761	34±1	3±1	6±2	7±0
1147	1778	29±1	2±0	BD	5±0
1150	1783	41±0	4±1	6±2	6±0
1165	1805	66±1	8±2	4±1	10±0
1184	1833	36±0	10±4	BD	7±1
1191	1843	31±1	3±2	3±2	6±1
1203	1860	44±1	5±1	3±2	9±1
1215	1878	40±1	4±1	8±2	7±0
1231	1902	38±0	3±2	7±4	6±0
1240	1915	38±0	3±2	3±2	7±0
1251	1931	25±1	2±1	1±0	4±0
1255	1937	26±0	BD	8±1	4±0
1268	1956	35±0	5±2	6±3	6±0
1301	2005	29±1	3±1	4±0	4±0
1305	2011	27±1	4±1	3±2	4±0
1330	2048	33±2	3±2	5±1	5±0
1342	2065	37±0	4±1	3±2	6±0
1359	2090	26±1	3±1	BD	4±1
1366	2100	19±1	4±2	BD	2±1
1388	2132	23±0	3±2	BD	3±0
1400	2150	19±0	3±2	3±2	2±1
1402	2153	13±1	6±3	BD	2±0
Avg		31	4	4	5

* July 1966 snow surface as zero reference; values represent true vertical depth.

† Below detection observations (taken as 1 $\mu\text{g/l}$) for calculation of mean values.

** Banding in the samples.

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13. ABSTRACT
Eighty-five ice samples taken from the Byrd Station, Antarctica, ice core were analyzed for Na⁺, K⁺, Ca²⁺ and Mg²⁺ concentrations by atomic absorption spectroscopy. From 168 to 1243 m of the portion of the ice core analyzed the mean Na⁺, K⁺, Ca²⁺ and Mg²⁺ concentrations were 21, 3, 2 and 3 ug/l respectively, increasing to 37, 5, 5, and 7 ug/l respectively from 1264 to 2090 m, then decreasing to 19, 4, 2, and 2 ug/l respectively from 2100 to 2153 m. The 1264 to 2090-m region represents snow accumulations deposited over the last 13,000 to 60,000 years, based on independent stable isotope analysis; this correlates roughly with the Wisconsin stage cold interval, 11,000 - 74,000 years before the present.

14. Key Words

Atomic absorption spectrophotometry
Cations
Contaminants
Glaciology
Ice core
Ultrasonic cleaning