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Major Features of Glaciochemistry Over the Last 110,000 Years in the Greenland Ice Sheet Project 2 Ice Core

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Major features of glaciochemistry over the last 110,000 years in the Greenland Ice Sheet Project 2 ice core

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Abstract. Major chemical species (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and $\delta^{18}O$ covering the last 110,000 years from the Greenland Ice Sheet Project 2 (GISP2) ice core were utilized in this study in order to reconstruct the soluble chemistry of the atmosphere over Greenland and interpret major climate events that have affected the region. During the Holocene the major chemical species and $\delta^{18}O$ do not display any significant relationship. However, a strong inverse correlation was found between concentrations of the major chemical species and $\delta^{18}O$ (a proxy for temperature) during the last glacial period, suggesting that in general during periods of decreased temperature, there is an increase in atmospheric chemical loading. Examination of changes in major chemical composition over the last 110,000 years of the GISP2 ice core reveals that during the Holocene, the atmosphere was acidic; during interstadials the atmosphere was neutral or alkalescent; and during stadials the atmosphere was alkaline. In addition, the relative abundance of major chemical species varied during the Holocene, stadials, and interstadials. During the Holocene, NH_4^+ and NO_3^- are the dominant cations and anions; while Ca^{2+} and SO_4^{2-} are the dominant cations and anions during the stadials and interstadials. This suggests that source regions or types differed between the Holocene and the last glacial period. In addition, changes in chemical composition and changes in chemical ratios also indicate that source regions differed during the Holocene, stadials, and interstadials. Twenty-four previously identified Dansgaard-Oeschger (stadial/interstadial) events [*Dansgaard et al.*, 1993] were in the GISP2 chemical series. The duration of the stadials is inversely correlated with variations in sea level over the last glacial period (i.e., the more extensive the northern hemisphere ice sheet, the longer the duration of the stadial). There is also a close correspondence between the duration of interstadials and the timing of Heinrich events (massive icebergs discharged into the ocean) in the GISP2 ice core. Long (up to 2000 years) warm periods follow each Heinrich event, suggesting perhaps that enhanced deep-water circulation is re-initiated following Heinrich events.

1. Introduction

Polar ice cores provide both direct and highly resolved views of paleoclimate spanning seasons to hundreds of thousands of years. They preserve a rich history of the Earth's volcanic activity, terrestrial and marine biological activity, terrestrial dust sources, and anthropogenic activity [e.g., *Mayewski et al.*, 1986, 1993, 1994; *Legrand et al.*, 1988; *Dansgaard et al.*, 1993; *Zielinski et al.*, 1994].

Recent results from two Greenland ice cores demonstrate dramatic climatic fluctuations during the last glacial period [*Dansgaard et al.*, 1993; *Grootes et al.*, 1993; *Mayewski et al.*, 1993, 1994; *Taylor et al.*, 1993a]. Particularly notable in these cores are the extremely rapid reorganizations in atmospheric circulation that occur between stadials and interstadials [*Alley et al.*, 1993; *Taylor et al.*, 1993b; *Mayewski et al.*, 1994, 1997]. Changes in the chemical concentration of ice cores during these events can be related to changes in source regions, volcanic activity, atmospheric circulation, ocean ice cover extent, and temperature [*De Angelis et al.*, 1987; *Legrand et al.*, 1988; *Delmas and Legrand*, 1989; *Mayewski et al.*, 1993, 1994, 1997; *Zielinski et al.*, 1994].

Alternations between stadials and interstadials during the last glacial period are believed to reflect changes in atmospheric circulation and ocean-atmosphere inter-

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actions [*Broecker and Denton*, 1990; *Greenland Ice-Core Project (GRIP) Members*, 1993; *Mayewski et al.*, 1994, 1997]. Several climate forcing agents have been used to explain the occurrence of these stadial and interstadial events. These include changes in insolation, ice sheet volume, heat exchange between the subpolar North Atlantic Ocean and the atmosphere, rapid discharge of large volumes of ice into the ocean, solar variability, sea ice extent, and the greenhouse effect [*Broecker and Denton*, 1990; *Bond et al.*, 1992, 1993; *Lehman and Keigwin*, 1992; *Bender et al.*, 1994; *Mayewski et al.*, 1994, 1997].

Investigation of the relationship between the chemical concentration of soluble species (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and oxygen isotopes ($\delta^{18}O$) recorded in the GISP2 ice core provides information concerning changes in atmospheric circulation, wind speed, and the source regions that influence variations in the chemical concentration of this ice core. Details of changes in chemical composition and chemical ratios of chemical species during the Holocene, stadials, and interstadials can provide useful information to assess whether the source regions differed during these periods.

2. Data Description

The Greenland Ice Sheet Project Two (GISP2) ice core (3053.44 m deep) was retrieved from Summit, Greenland (76.6°N; 38.5°W; 3200 above sea level). This ice core was cut at uniform lengths of 20 cm and sampled in a field laboratory where temperatures were maintained at <-15°C at all times. Sample resolution for soluble ions and stable isotopes is 0.6-2.5 years per sample through the Holocene, a mean of 3.48 years through the deglaciation, and ~3-116 years throughout the remainder of the 110,000-year-long portion of the core for a total of 16,395 samples.

To avoid possible contamination of samples used for chemical analyses, strict protocol was used at all times during processing. For example, three pairs of blanks were analyzed at the beginning, middle, and end of each processing day. Duplicate samples were analyzed every 10 samples.

All samples were analyzed for the major chemical species (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) using a Dionex^{TM} Ion Chromatography system described previously [*Mayewski et al.*, 1990; *Buck et al.*, 1992; *Whitlow et al.*, 1992]. $\delta^{18}O$ was sampled, analyzed and provided by the University of Washington [*Grootes et al.*, 1993; *Stuiver et al.*, 1995].

The GISP2 depth-age timescale was established based on multiparameter counting of annual layers to a depth corresponding to about 40.5 kyr ago [*Meese et al.*, 1994]. Beyond this age, it was developed based on a correlation of the $\delta^{18}O$ of atmospheric O_2 between GISP2 and Vostok ice cores [*Sowers et al.*, 1993; *Bender et al.*, 1994]. Current estimated age errors for the GISP2 time series are 2% for 0-11.64 kyr BP, 5% for 11.64-17.38 kyr BP, <10% for 17.38-40.5 kyr BP [*Alley et al.*, 1993], and up to 10% for the remainder of the record [*Bender et al.*, 1994].

3. Results and Discussion

3.1. Correlation Between Chemical Species and With $\delta^{18}O$

Concentrations of major chemical species (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) are plotted along with $\delta^{18}O$ in Figure 1 in order to investigate variations from the present to 110,000 years ago. During the Holocene both chemical concentrations and $\delta^{18}O$ values are relatively constant in contrast to the last glacial period. It is apparent from Figure 1 that chemical species demonstrate stadial and interstadial oscillations similar to those found in the $\delta^{18}O$ record presented by *Dansgaard et al.* [1993] and *Grootes et al.* [1993]. Concentrations of chemical species of Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+} display synchronous oscillations for the last glacial period. Over the period 11,600 to 110,000 years, increases in chemical concentrations are in general accompanied by decreases in oxygen isotope value (more negative) and vice versa.

To investigate quantitatively the relationship between $\delta^{18}O$ values and concentrations of major chemical species, a series of correlation analyses was performed for the Holocene and pre-Holocene (11,600-110,000 years) (Table 1). No significant correlation exists between oxygen isotopes and major chemical species during the Holocene. In addition, correlation coefficients among major species are also very low for this period. In contrast, between 11,600 and 110,000 years ago, six of eight major ions show a strong negative correlation to $\delta^{18}O$. Most correlation coefficients (r) during the period of 11,600-110,000 years in Table 1 are statistically significant at the 95% level. R values of 0.7 or lower suggest that less than 50% of total variance can be explained by such a linear relationship. It is also found that the correlation coefficient between chemical species and oxygen isotopes is slightly higher during stadials than during interstadials. Thus the correlation between the major chemical species in the GISP2 ice core decreases with increasing temperature.

Correlation coefficients in Table 1 reveal that concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, and Cl^- are highly correlated to each other during the last glaciation. Figure 1 shows that six of the major ions (Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+}) display synchronous increases or decreases in concentrations during the pre-Holocene period. To maintain such synchronous variations and concentration they must be transported in a well-mixed atmosphere [*Mayewski et al.*, 1994]. The highly inverse correlation between the major ions and $\delta^{18}O$ during pre-Holocene suggests that atmospheric circulation patterns during this period were not as complex as during the Holocene [*O'Brien et al.*, 1995]. During the last ice age the maximum ice cover extent reached about 40N in North America, with an average

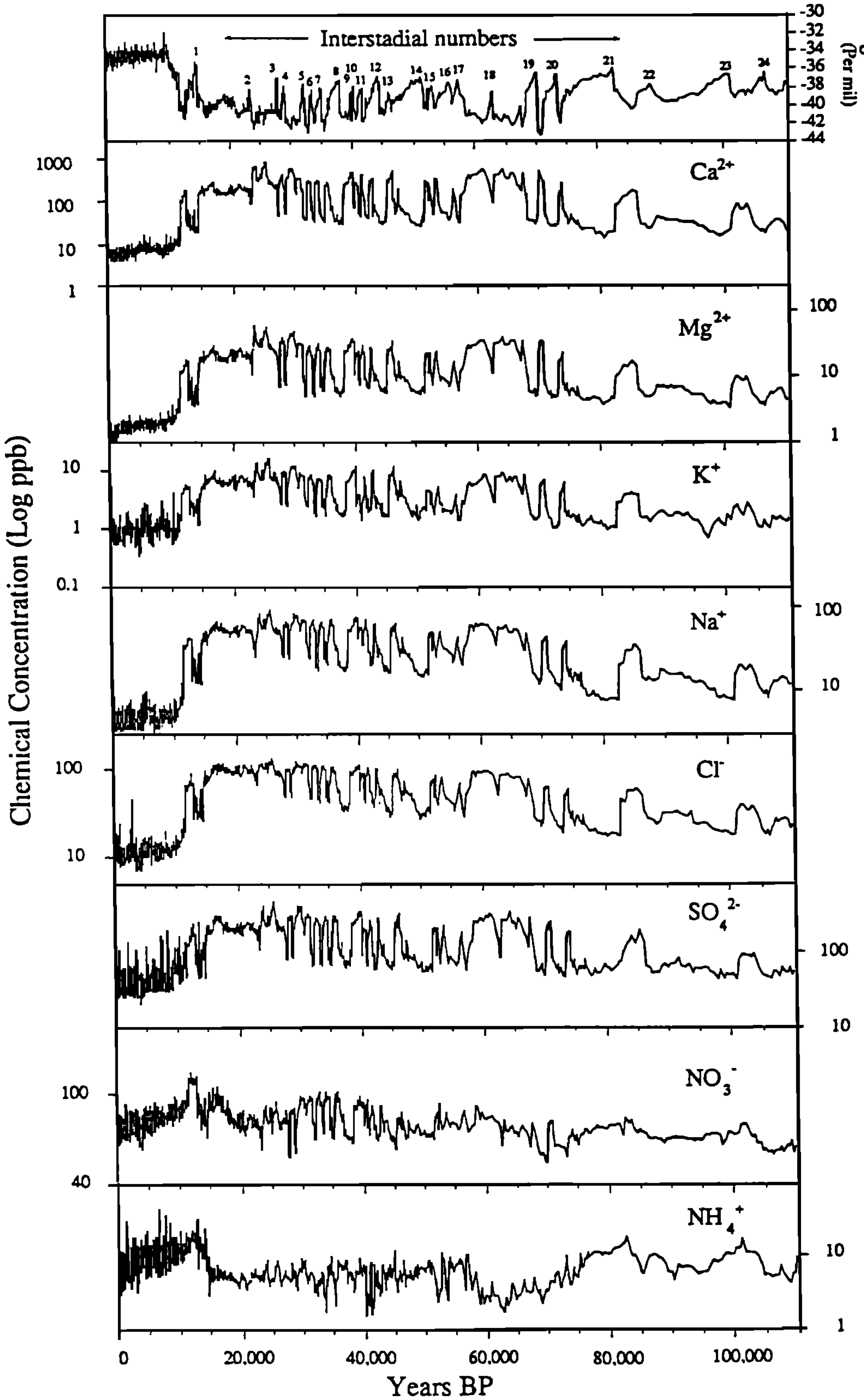

Figure 1. Concentrations (log ppb) of major chemical species versus δ^{18}O record for the last 110,000 years in the GISP2 ice core.

Table 1. Correlation Coefficients Between $\delta^{18}O$ and Major Chemical Species for the Periods 0-11,600 and 11,600-110,000 Years in the GISP2 Ice Core

	$\delta^{18}O$	Ca	Cl	K	Mg	Na	NH_4	NO_3
				0-11,600 Years BP (Holocene)				
Ca	-0.01							
Cl	-0.20	0.35						
K	-0.09	0.28	0.34					
Mg	0.02	0.68	0.37	0.04				
Na	-0.19	0.55	0.61	0.55	0.50			
NH_4	0.11	0.28	0.07	0.07	0.39	0.10		
NO_3	0.03	0.25	0.33	-0.01	0.34	0.07	0.32	
SO_4	-0.01	0.28	0.31	0.03	0.39	0.17	0.05	0.47
				11,600-110,000 Years BP				
Ca	-0.75							
Cl	-0.81	0.81						
K	-0.79	0.91	0.92					
Mg	-0.80	0.97	0.89	0.96				
Na	-0.82	0.87	0.98	0.94	0.93			
NH_4	0.22	-0.25	-0.30	-0.21	-0.28	-0.32		
NO_3	-0.45	0.38	0.53	0.49	0.43	0.51	0.43	
SO_4	-0.78	0.91	0.93	0.95	0.95	0.95	-0.21	0.56

latitude of the ice edge maximum over the land area of the hemisphere of 52°N [*Budd and Rayner*, 1990]. Thus a large ice-sheet coupled polar atmospheric cell dominated variations of the atmospheric circulation system during the pre-Holocene period through positive feedback [*Manabe and Broccoli*, 1985]. Therefore we suggest that the atmosphere is well-mixed and atmospheric circulation patterns were relatively simple during the pre-Holocene period.

Neither NH_4^+ nor NO_3^- concentrations are accounted for in the dust and sea salt. However, it is apparent in Table 1 that NH_4^+ is the only chemical species whose behavior differs significantly from the other species. NH_4^+ concentrations are generally not associated with other species during the last glaciation. The discrepancy between NH_4^+ and Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, and Cl^- may be due to their difference in source and transport pathways. The dominant sources of NH_4^+ include biogenic activity and biomass burning, and NH_4^+ has a relatively short residence time in the atmosphere [*Warneck*, 1988; *Langford et al.*, 1992]. It is apparent in Figure 1 that the concentration of NH_4^+ is higher during long interstadials and the Holocene and lower during long stadials. During a long stadial period, ice sheets expand southward in the northern hemisphere [*Budd and Rayner*, 1990], productivity of NH_4^+ may be damped due to a decrease in continental area, and colder and drier climates. However, NH_4^+ shows a weak positive correlation coefficient to NO_3^- over the last 110,000 years. This may be because some of the NO_3^- measured in the ice core is derived from similar sources to that of NH_4^+, namely, soil exhalation and biomass burning [*Legrand and Kirchner*, 1990]. Significant increases in NH_4^+ over the last 110,000 years have been attributed to variations in insolation (L.D. Meeker et al., A 110 ka history of change in continental biogenic source strength and related atmospheric circulation, submitted to *Journal of Geophysical Research*, 1997; hereinafter referred to as submitted paper).

3.2. Changes in Wind Strength

Marine aerosols (Na^+, Cl^-) and terrestrial dusts (Ca^{2+}, Mg^{2+}) make up the two major types of chemical components in Greenland snow. The large variation of major chemical concentrations between stadials and interstadials is believed to reflect changes in ocean ice cover extent, and strength and size of the atmospheric circulation system over Greenland [*Mayewski et al.*, 1993, 1994]. In general, stadials are characterized by dramatic increases in chemical concentration, suggesting that both marine and terrestrial inputs increased rapidly as a result of higher wind speed at the sea surface and greater meridional transport capacity [*Petit et al.*, 1981; *De Angelis et al.*, 1987; *Mayewski et al.*, 1997]. In contrast, interstadials are characterized by a decrease in chemical concentrations, suggesting that both marine aerosols and terrestrial dusts decreased dramatically as a result of calmer wind speed at the sea surface and a dampened size and strength of the atmospheric circulation system [*Herron and Langway*, 1985; *Mayewski et al.*, 1994, in press; L.D. Meeker et al., submitted paper, 1997].

To quantitatively estimate past sea surface wind strength, *Petit et al.* [1981] used the formula $\log C = AV+B$, where C is the sea-salt aerosol atmospheric concentration, V is the sea surface wind speed, and A varies between 0.16 and 0.25. During stadials and interstadials, mean sea-salt concentration in the GISP2 ice core is about 10 and 5 times higher, respectively, than during the Holocene. Based on *Petit et al.* [1981], therefore, stadial sea surface wind speed would have been about 4 ($a = 0.25$) to 6.3 ($a = 0.16$) m s^{-1} higher, and during interstadials, sea surface wind speed would have been about 2.8 ($a = 0.25$) to 4.4 ($a = 0.16$) m s^{-1} higher than that during the Holocene. Although such estimates are rather simplistic and do not consider sea-salt concentration changes that occur during long distance transport, they provide an approximate reconstruction of past sea surface wind speed that could be of value for climate modeling.

3.3. Changes in Chemical Concentrations and Ratios

In order to calculate mean chemical concentration for each stadial and interstadial, we first identified the inflection points on the roughly sinusoidal variations of Ca^{2+} series from Figure 1. Stadial concentration was taken as the average of all sample concentrations higher than the inflection points, and interstadial concentration the average of all concentrations lower than the inflection points.

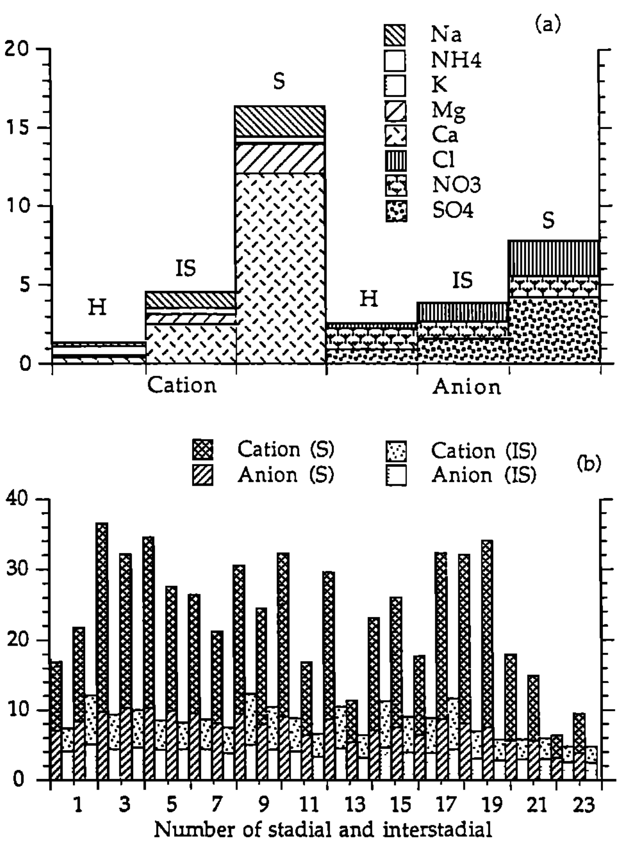

Figure 2. (a) Chemical concentrations (μeq/L) for the period of Holocene, stadial, and interstadial. (b) Mean cations and anions for each stadial and interstadial (S, stadial; IS, interstadial).

In Figure 2a, each chemical species (presented in μeq/L) is averaged over the periods: Holocene, total of all interstadials and total of all stadials. During the Holocene, mean anion (Cl^-, NO_3^-, SO_4^{2-}) concentration (2.60 μeq/L) is about twice mean cation (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) concentration (1.34 μeq/L). The unbalanced concentrations of anions and cations suggest a missing amount of the cation H^+. To balance the mean of the anions and cations, 1.26 μeq/L H^+ must be added. Based on this unbalanced chemical composition, it appears that during the Holocene the atmosphere has been acidic. During stadials, the mean cation concentration is 16.37 μeq/L, and the mean anion concentration is 7.84 μeq/L. Mean cation concentration is more than twice that of the anions. The missing amount of anion is believed to be primarily HCO_3^- [*Mayewski et al.*, 1994]. Thus, during stadials, the atmosphere was characterized by an alkaline atmosphere. During interstadials, mean cation concentration is 4.53 μeq/L, and mean anion concentration is 3.87 μeq/L. Since the mean concentration of cations is about 18% more than mean anion concentration, the interstadial atmosphere was alkalescent or close to neutral.

In Figure 2b, mean anions and cations for each stadial and interstadial reveal that, in general, chemical concentrations do not vary significantly during interstadials. However, during stadials, chemical concentrations fluctuate by a factor of 6. The cause of these large variations is believed due to changes in the size and intensity of polar atmospheric circulation system between stadials [*Mayewski et al.*, 1994, 1997].

The respective chemical concentrations during the Holocene, interstadials, and stadials are mutually distinct. For example, cation concentrations averaged over all stadials (16.37 μeq/L) exceed those during the Holocene (1.34 μeq/L) by an order of magnitude. Concentrations follow the order stadials > interstadials > Holocene. In addition to the changes in chemical concentrations, chemical constituents in the atmosphere varied among the three periods. Figure 3 reveals that during the Holocene, NO_3^- is the dominant anion and NH_4^+ is the dominant cation, while SO_4^{2-} and Ca^{2+} are the dominant anion and cation, respectively, for stadials and interstadials. It is, however, worth noting that if the assumed concentrations of H^+ and HCO_3^- determined from ion balance equations were used, the dominant anions would be NO_3^-, SO_4^{2-}, and HCO_3^- for the Holocene, interstadials, and stadials, respectively. The respective dominant cations would be H^+, Ca^{2+} and Ca^{2+}. Changes in dominant chemical species suggest that the source regions differed from one period to another.

During the last glacial period, sea level lowered due to an increase in land ice cover [*Chappell and Shackleton*, 1986; *Budd and Rayner*, 1990], exposing $CaCO_3$- and $CaMg(CO_3)_2$-enriched sediments from the continental shelf. Further, during the last glacial period, tropical latitude arid zones were 5 times larger than at

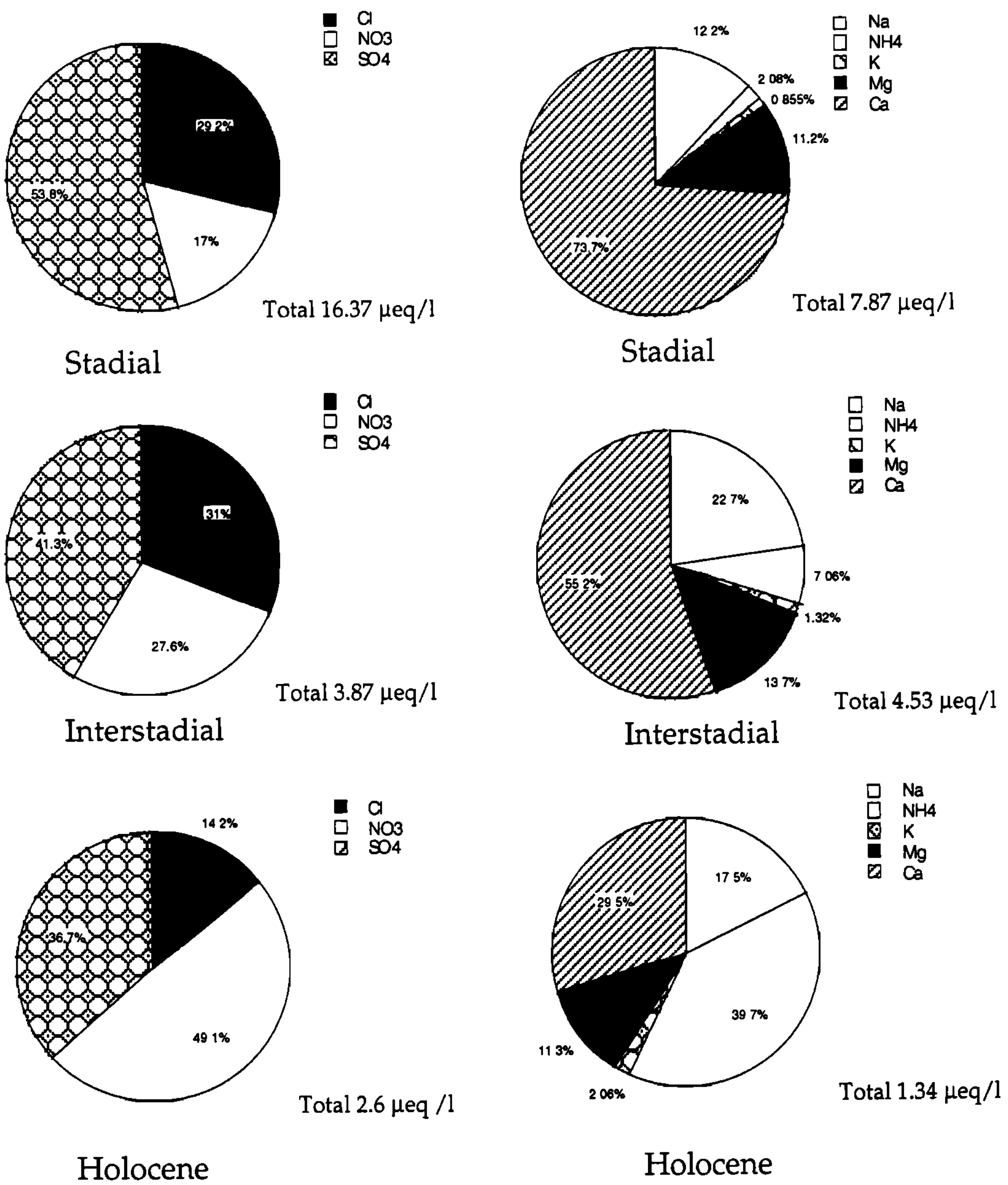

Figure 3. Chemical composition (μeq/L) for the period of Holocene, stadial, and interstadial.

present [*Petit et al.*, 1981], providing additional sources of Ca^{2+} and Mg^{2+}. During the last glacial period, expansion of polar atmospheric circulation [*Mayewski et al.*, 1993, 1994], and thus higher terrestrial dust incorporation, potentially resulted in large increases in dust transported to Greenland. Dust from arid areas in Asia [*Fang and Wallace*, 1994] (P. Biscaye et al., Asian provenance of last-glacial maximum dust in the GISP2 ice core, Summit, Greenland, submitted to *Journal of Geophysical Research*, 1997) and southern North America, where mineral compositions show high amounts of calcite ($CaCO_3$) and gypsum ($CaSO_4 \cdot 2H_2O$), have been suggested as potential sources for central Greenland snow [*Prospero*, 1990; *Gomes and Gillette*, 1992; *O'Brien et al.*, 1995].

The ratio of chemical species in ice cores can provide valuable information about the source of these chemicals. If a source region for an air mass traveling to Greenland is constant over time, the ratio of a given species to a reference species should remain relatively constant. Na^+ is the most conservative sea-salt species in Greenland snow. More than 98% of Na^+ measured in the Holocene portion of GISP2 ice core is derived from marine sources [*O'Brien et al.*, 1995]. Based on the sea-salt estimation [*O'Brien et al.*, 1995], more than 75% of Na^+ measured during pre-Holocene is marine source. Therefore we present ratios of Cl^-/Na^+, K^+/Na^+, Mg^{2+}/Na^+, Ca^{2+}/Na^+, and SO_4^{2-}/Na^+. Since NO_3^- and NH_4^+ are associated with neither marine aerosols nor terrestrial dusts, we have excluded them from Figure 4. The horizontal line in Figure 4 represents the modern sea-salt ratio. It is apparent in Figure 4 that chemical ratios are not always constant during stadials, interstadials, and the Holocene. In general, chemical ratios of Ca^{2+}/Na^{+}, Mg^{2+}/Na^{+}, K^{+}/Na^{+}, and SO_4^{2-}/Na^{+} are well above the sea-salt ratio over the last glacial period, suggesting that terrestrially derived dusts played an important role in the chemical composition of the atmosphere.

During stadials, Ca^{2+}/Na^{+}, Mg^{2+}/Na^{+}, and K^{+}/Na^{+} are higher than during interstadials. The ratio of Ca^{2+}/Na^{+} differs significantly among stadials; however, it is relatively constant during interstadials, suggesting that the size and intensity of polar atmospheric circulation remains similar during interstadials. Since concentration of K^{+} in Greenland snow is low (less than 1.5% of total ion burden during interstadials and ~2% during stadials), ratios of K^{+}/Na^{+} may provide a sensitive measure reflecting changes in source regions. The high concentration (up to 100 ppb) of K^{+} from the surface of the Guliya Ice Cap, China [*Yao et al.*, 1995], in contrast to 1-2 ppb in snow pits from Greenland [*Yang et al.*, 1996], indicates that the Chinese Gobi Desert and desert lands are the most likely source region of K^{+}. The high ratio of K^{+}/Na^{+} during the Holocene is believed to be due more to biomass burning activities, which increase the atmospheric concentration of K^{+} [*Whitlow et al.*, 1994; *Dibb et al.*, 1996].

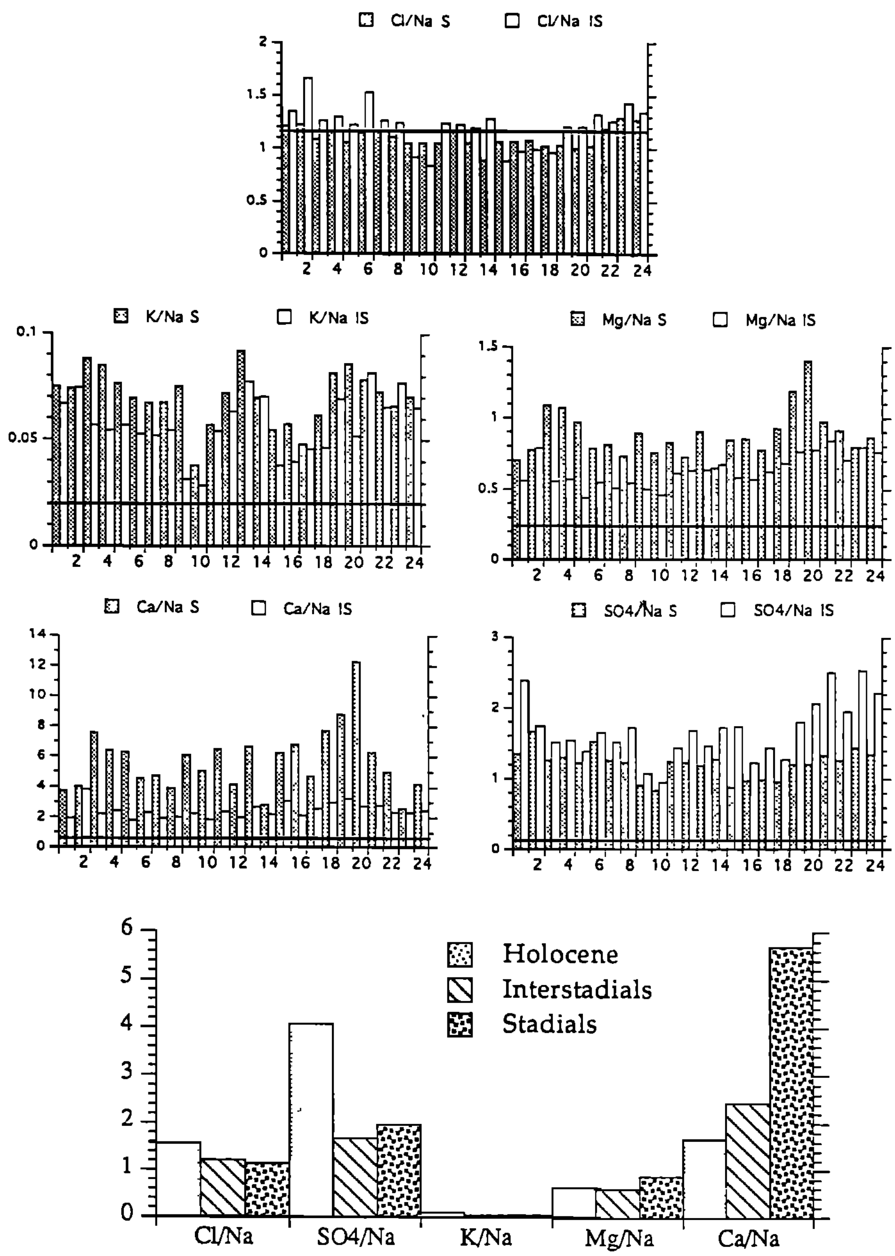

Figure 4. (above) Ratios between major chemical species to Na^{+} for each stadial and interstadial. (below) Mean chemical ratios for the period of Holocene, stadial, and interstadial (S, stadial; IS, interstadial).

Based on sea-salt concentration and the sea-salt ratios, wind speeds were higher during stadials than during interstadials. However, increased wind speed alone cannot account for the large variations of chemical ratios between stadials and interstadials and different chemical constituents during the Holocene, stadials, and interstadials. Higher ratios of Mg^{2+}/Na^+ and Ca^{2+}/Na^+ during stadials versus interstadials and the Holocene, as well as different chemical compositions during these periods, indicate that new source regions enriched with Ca^{2+} and Mg^{2+} are involved during stadials and interstadials versus the Holocene.

The ratio of Cl^-/Na^+ varies insignificantly between stadials and interstadials and is close to the sea-salt ratio. The ratio of Cl^-/Na^+ is higher during the Holocene than during stadials and interstadials. This may be because the Holocene atmosphere is more acidic. In an acidic atmospheric environment, sea salt (mainly NaCl) reacts with H^+ to form gaseous HCl [*Legrand and Delmas*, 1988; *Keene et al.*, 1990]. Gaseous HCl can travel through the upper troposphere to the high-latitude atmosphere of Greenland, providing an important potential source for the budget of Cl^- in Greenland snow and ice.

SO_4^{2-}/Na^+ is higher during interstadials than during stadials. However, the ratio of SO_4^{2-}/Na^+ during the Holocene is 2 times higher than ratios during stadials and interstadials. Thus we propose that during the Holocene, marine biogenic activity and soil productivity increased due to increases in temperature [*Adams et al.*, 1981a, 1981b; *Herron*, 1982]. During the Holocene, a sharp decrease in Na^+ resulted from decreases in wind speed, and more localized atmospheric circulation patterns prevented both marine and terrestrial sources from being transported to Greenland [*Petit et al.*, 1981; *Herron and Langway*, 1985; *Delmas and Legrand*, 1989; *Mayewski et al.*, 1994, 1997; *O'Brien et al.*, 1995]. Hence the relative ratio of SO_4^{2-}/Na^+ during the Holocene is higher than during the pre-Holocene.

3.4. Duration of Stadial and Interstadial

The duration of stadials and interstadials (Table 2) was calculated and plotted in Figure 5 based on the Ca^{2+} series. Duration of interstadial events varies from 226 years (event 2) to 8373 years (event 21). Ten interstadial events over the last 110,000 years are longer than 2000 years (events 8, 12, 14, 16, 19, 20, 21, 22, 23 and 24). Table 2 also indicates that at the beginning of the last glacial period, interstadial duration was longer. Nine out of ten interstadial events longer than 2000 years occurred between 110,000 and 44,000 years ago. During the period 42,000 to 25,000 years BP there are nine stadial and interstadial events, indicating that shorter and more frequent events occurred prior to the last glacial maximum (LGM).

As noted in Figure 5, the rapid climate change events form a series of asymmetrical saw-tooth shapes (events 21-17, 16-15, 14-13, 12-9, 8-6, 5-2). The observed pattern coincides with a series of ice sheet oscillations, called Heinrich events, that discharge icebergs into the

Table 2. Length of Stadial and Interstadial for the Last Glaciation

IS Number	Period Covered, Years BP	Length, Years	S Number	Period Covered, Years BP	Length, Years
24 IS	107,170-104,453	2717	24 S	104,453-100,830	3623
23 IS	100,830-96,754	4076	23 S	96,754-89,052	7702
22 IS	89,052-86,792	2260	22 S	86,792-82,641	4151
21 IS	82,641-74,268	8373	21 S	74,268-73,681	587
20 IS	73,581-71,177	2404	20 S	71,177-70,071	1106
19 IS	70,071-67,989	2082	19 S	67,989-63,019	4970
18 IS	63,019-62,075	944	18 S	62,075-57,528	4547
17 IS	57,528-56,774	754	17 S	56,774-56,132	642
16 IS	56,132-53,872	2260	16 S	53,872-53,192	680
15 IS	53,192-52,717	475	15 S	52,717-51,675	1042
14 IS	51,675-49,152	2523	14 S	49,152-47,283	1869
13 IS	47,283-46,604	679	13 S	46,604-45,472	1132
12 IS	45,472-43,207	2265	12 S	43,207-42,604	603
11 IS	42,604-41,698	906	11 S	41,698-41,254	444
10 IS	41,254-40,754	500	10 S	40,754-40,309	445
9 IS	40,309-40,071	238	9 S	40,071-38,478	1593
8 IS	38,478-36,189	2289	8 S	36,189-35,370	819
7 IS	35,370-34,506	864	7 S	34,506-33,781	725
6 IS	33,781-33,079	702	6 S	33,079-32,400	679
5 IS	32,400-30,650	1750	5 S	30,650-29,223	1427
4 IS	29,223-28,650	573	4 S	28,650-27,962	688
3 IS	27,962-27,320	642	3 S	27,320-23,528	3792
2 IS	23,528-23,302	226	2 S	23,302-14,717	8585
1 IS	14,717-12,890	1827	1 S (YD)	12,890-11,700	1190

S, stadial; IS, interstadial; YD, younger Dryas.

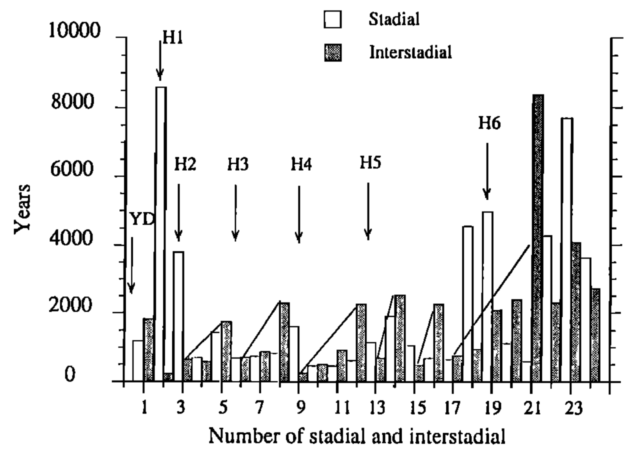

Figure 5. Length of stadial and interstadial versus their numbers (H represents Heinrich event, after *Bond et al.* [1993]).

ocean [*Heinrich*, 1988; *Bond et al.*, 1993]. The ocean is believed to play an important role in the rapid shifts between stadials and interstadials [*Broecker and Denton*, 1990; *Lehman and Keigwin*, 1992]. To explain the saw-tooth shapes, it is proposed that during each Heinrich event, meltwater from icebergs may have enhanced sea ice extent because fresh water has a higher freezing temperature than salty water. Thus, extended sea ice cover may have prevented heat exchange between the ocean and the atmosphere at high latitudes and, consequently, cooled the North Atlantic region.

Following each Heinrich event, interstadial duration is, in general, longer than that of adjacent interstadials. The prolonged warm interstadials following each Heinrich event have also been reported by *Maslin and Shackleton* [1995], using planktonic foraminiferal species abundance and $\delta^{18}O$. These abrupt prolonged interstadial events following each Heinrich event were suggested to be caused by decreases in meltwater flux, resulting in collapse and retreat of ice sheets following each Heinrich event [*Bond et al.*, 1993]. The high elevation of the Laurentide ice sheet is also believed to be responsible for increased northerly winds over the western part of the North Atlantic, and consequent cooling of the surface water [*Manabe and Stouffer*, 1995]. The reduced volume of icebergs to the ocean [*Bond et al.*, 1993] and reduced elevation of ice sheets following each ice sheet collapse could have enhanced salt buildup by evaporation and, consequently, triggered deep-water formation.

Stadial duration was plotted (Figure 6) along with reconstructed sea level based on coral-reef records [e.g., *Chappell and Shackleton*, 1986; *Edwards et al.*, 1993; *Gallup et al.*, 1994] to see if ice sheet volume has any relationship with length of stadials over the last glacial period. There is a general inverse relationship between duration of stadials and sea level during the last glacial period, suggesting that stadial duration tends to be longer when ice volume is greater. However, during the period 30,000-55,000 years ago, the correlation between sea level and stadial duration is not significant. This may be because during this period the ice sheet was relatively stable, so that the length of stadials did not respond significantly to change in ice volume.

4. Summary

Twenty-four well-defined cycles of stadials and interstadials defined by changes in the concentration of major chemical species were found to match similar variations in $\delta^{18}O$ record [*Dansgaard et al.*, 1993; *Grootes et al.*, 1993] over the last 110,000 years. Analysis of correlation between concentrations of major chemical species (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and values of $\delta^{18}O$ were performed. The results reveal that for the first 11,600 years (Holocene) there is no clear correlation. However, between 11,600 and 110,000 years BP, concentrations of Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, and Ca^{2+} are well-correlated to $\delta^{18}O$, and chemical species correlate to one another very well. This suggests that there were synchronous increases and decreases in sea-salt and dust levels during stadials and interstadials.

Analysis of the major ions in the GISP2 record reveals that atmospheric chemical concentrations and source regions were significantly different during the Holocene than during interstadials or stadials, which in turn were significantly different from each other. The atmosphere was characterized by acidic, alkalescent, and alkaline environments, respectively, during these periods. Atmospheric loading follows the order stadials > interstadials > Holocene. The respective dominant ions of the Holocene, interstadials, and stadials differed due to changes in source regions, wind strength, and size and strength of atmospheric circulation over the last 110,000 years. For example, NH_4^+ is the dominant cation during the Holocene, while Ca^{2+} is dominant during the last glacial period.

As reported by *Mayewski et al.* [1994, 1997], Heinrich events are clearly recorded in the GISP2 chemical series. Duration of interstadials indicates that a prolonged warm interstadial followed each Heinrich event, suggesting an enhanced deep-water formation, and then

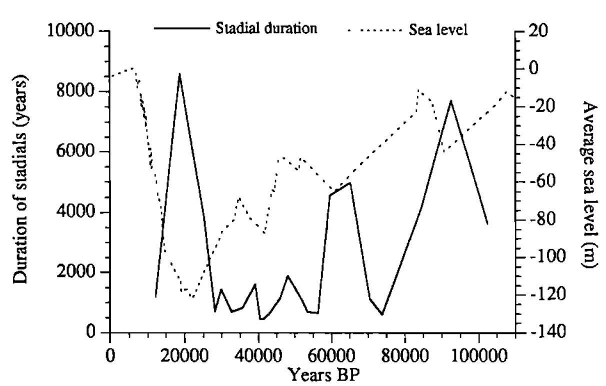

Figure 6. Length of stadial versus sea level based on coral-reef records [*Chappell and Shackleton*, 1986; *Edwards et al.*, 1993; *Gallup et al.*, 1994] for the past 110,000 years.

a period during which the durations of successive interstadials gradually decreased until another Heinrich event began the next cycle.

Examination of the GISP2 chemical series over the last 110,000 years demonstrates that the atmosphere responds more quickly than any other climate proxy of the Earth system on all timescales. For example, interannual scale changes in anthropogenic activity, rapid climate changes, and Heinrich events all are recorded in changes in the major chemical concentrations. Changes in concentrations of the soluble chemical species in the atmosphere reflect changes in wind strength, source regions, and size and strength of atmospheric circulation over the last 110,000 years. By comparing other measurements with the chemical measurements presented here (e.g., insoluble particle size distributions and mineral composition), the GISP2 core can be used to further refine the source regions for air masses and changes in atmospheric circulation patterns over the last glacial and interglacial cycle.

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