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# A 110,000-year history of change in continental biogenic emissions and related atmospheric circulation inferred from the Greenland Ice Sheet Project Ice Core

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**Abstract.** The 110,000-year record of ammonium concentrations from the Greenland Ice Sheet Project 2 (GISP2) ice core provides the basis for an analysis of terrestrial biological production and atmospheric circulation patterns involved in the transport of biologically produced ammonium to the Greenland atmosphere. The directly measured concentration series was selected for analysis, rather than that of estimated ammonium flux, after a detailed analysis of the relationship among ice core glaciochemical concentrations and a high-resolution simultaneous record of snow accumulation from the GISP2 core. Analysis of the ammonium concentration series shows that maxima in background levels of ammonium in the Greenland atmosphere are strongly related to and synchronous with summer forcing associated with the precessional cycle of insolation. Minima in background levels, on the other hand, are delayed relative to minima in summer insolation at those times when ice volume is significant. The duration of these delays are similar in magnitude ( $\approx 6000$  years) to other paleoclimatic responses to changes in ice volume. Decadal and centennial scale variation about background levels of ammonium concentration exhibit two modes of behavior when compared to a record of polar atmospheric circulation intensity. During warmer periods ammonium transport to Greenland is similar to present patterns. Under coldest conditions the low levels of ammonium transported to Greenland are the result of extreme southerly excursions of the predominantly zonal polar circulation. The rapid transitions ( $\approx 200$  years) between these two climatic conditions appear to be associated with a critical volume or extent of the continental ice sheets.

## 1. Introduction

The reconstructed history of terrestrial biogenic production and atmospheric circulation developed here is based upon the ammonium component of the multivariate glaciochemical record of concentrations of eight major ions (calcium, potassium, magnesium, sodium, chloride, sulfate, nitrate, and ammonium) from the Greenland Ice Sheet Project 2 (GISP2) ice core recovered at Summit, Greenland (72.6°N, 38.5°W, 3200-m elevation). The GISP2 record from the present to 110,000

years ago (calendar years before 2000 A.D.) consists of ion concentrations from 10,979 samples taken continuously to a depth of 2796 m. The sampling protocol, analytical methods, and dating procedures of the GISP2 core have been described in detail elsewhere [Mayewski *et al.*, 1986, 1987; Buck *et al.*, 1992, Whitlow *et al.*, 1994; Sowers *et al.* 1993; Mayewski *et al.*, this issue; Meese *et al.*, this issue].

This work joins two other recent studies of ammonium concentrations in Greenland ice. Discontinuous studies of ammonium concentrations deposited during the most recent glacial/interglacial cycle have recently been reported from the Renland ice core [Hansson, 1994] and the Greenland Ice Core Project (GRIP) ice core [Fuhrer *et al.*, 1996]. The Holocene component of the Renland record consists of 55 samples dated 1812–1820 A.D. and the glacial/interglacial component, dated from 10–145,000 years ago, was taken from the lower 19 m of the core and is, necessarily, at low resolution. The

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ammonium record presented by *Fuhrer et al.* [1996] is the result of high-resolution continuous measurements over the depth intervals 100-600, 1300-2060, and 2280-3020 m corresponding to the time intervals 300-3000, 8000-25,000, and 40,000-100,000+ years ago, respectively.

The primary sources of ammonium in the atmosphere have recently been reviewed and the magnitudes of their contributions estimated by *Dentener and Crutzen* [1994]. The primary natural sources (nonanthropogenic) of ammonium arise from biological emissions of ammonia from plants, soils, and animals and the burning of biological material (forest and grass fires). Ammonia is the major gaseous base for the atmospheric neutralization of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  and, under conditions which generally prevail, once emitted to the atmosphere it is rapidly converted (in a matter of hours) to  $\text{NH}_4\text{HSO}_4$  and  $(\text{NH}_4)_2\text{HSO}_4$  [*Dentener and Crutzen*, 1994; *Legrand and Kirchner*, 1990]. Once converted, the resulting ammonium compounds have an atmospheric lifetime of the order of days and can be transported relatively long distances by atmospheric circulation processes. As a consequence, background levels of  $\text{NH}_4$  deposited in high-latitude glaciers, especially during the preanthropogenic era, derive primarily from continental biological production with other poorly quantified (and presumably smaller) sources from marine biological emissions and decaying organic matter on rotting pack ice [*Dentener and Crutzen*, 1994; *Talbot et al.*, 1992].

In addition to background levels due to these sources, high-resolution records of ammonium concentrations from ice cores generally include a number of unusually large "spikes" that originate through tropospheric transport of the products of biomass burning and have been used to reconstruct histories of such events [*Fuhrer et al.*, 1993, 1996; *Whitlow et al.*, 1994; *Legrand, et al.*, 1992; *Legrand and De Angelis*, 1996; *Dibb et al.*, 1996; *Taylor et al.*, 1996]. These events are short-lived [*Dibb et al.*, 1996] and their ice core signals are diminished as the time span represented by the ice sample increases with core depth [*Whitlow et al.*, 1994; *Fuhrer et al.*, 1996]. As a consequence, studies of biomass burning events are generally restricted to the Holocene period and biannual, or higher, sampling resolution.

Here our focus is not on biomass burning events nor subdecadal variation of the Holocene portion of the GISP2 core (which will be discussed in detail elsewhere); rather, we utilize two distinctive features of the GISP2 record, continuous sampling and simultaneous measurement of the eight major ions, to develop a continuous history of terrestrial biogenic production and related atmospheric circulation patterns over the past 110,000 years. Our discussion will be based primarily on two series derived from the original GISP2  $\text{NH}_4$  series by application of spline-based, robust, low-pass filters. Such filters are of advantage here as they are insensitive to outliers and applicable to nonuniformly

sampled time series [*Meeker et al.*, 1995]. The original  $\text{NH}_4$  series was subjected to a low-tension filter tuned to remove subdecadal variation and a high-tension filter tuned to remove suborbital scale variation. Figure 1 displays the original series and the low-tension output, DB, and high-tension output, OB, representing decadal-to-centennial and orbital scale variation in ammonium concentrations, respectively. In addition to the two series, DB and OB, we will utilize a resampled version of DB using uniform 50-year samples for those statistical procedures requiring uniformly sampled time series.

The record of biological activity we develop below complements those recently derived from time series of methane concentrations from the GISP2 ice core [*Chappellaz et al.*, 1993; *Brook et al.*, 1996]. Unlike methane, the lifetime of ammonium in the atmosphere is too short in comparison to atmospheric mixing times to generate a hemispheric or global ammonium signal. As a consequence of its short atmospheric lifetime, the amount of ammonium scavenged from the atmosphere by precipitation at a particular site (e.g., Summit, Greenland) is the result of contemporaneous production in source areas (biological, anthropogenic, or other) and atmospheric circulation patterns. Thus the decadal scale variability of  $\text{NH}_4$  concentrations described by the DB series represents a detailed view of paleobiological activity and atmospheric circulation not available from the history of methane concentrations.

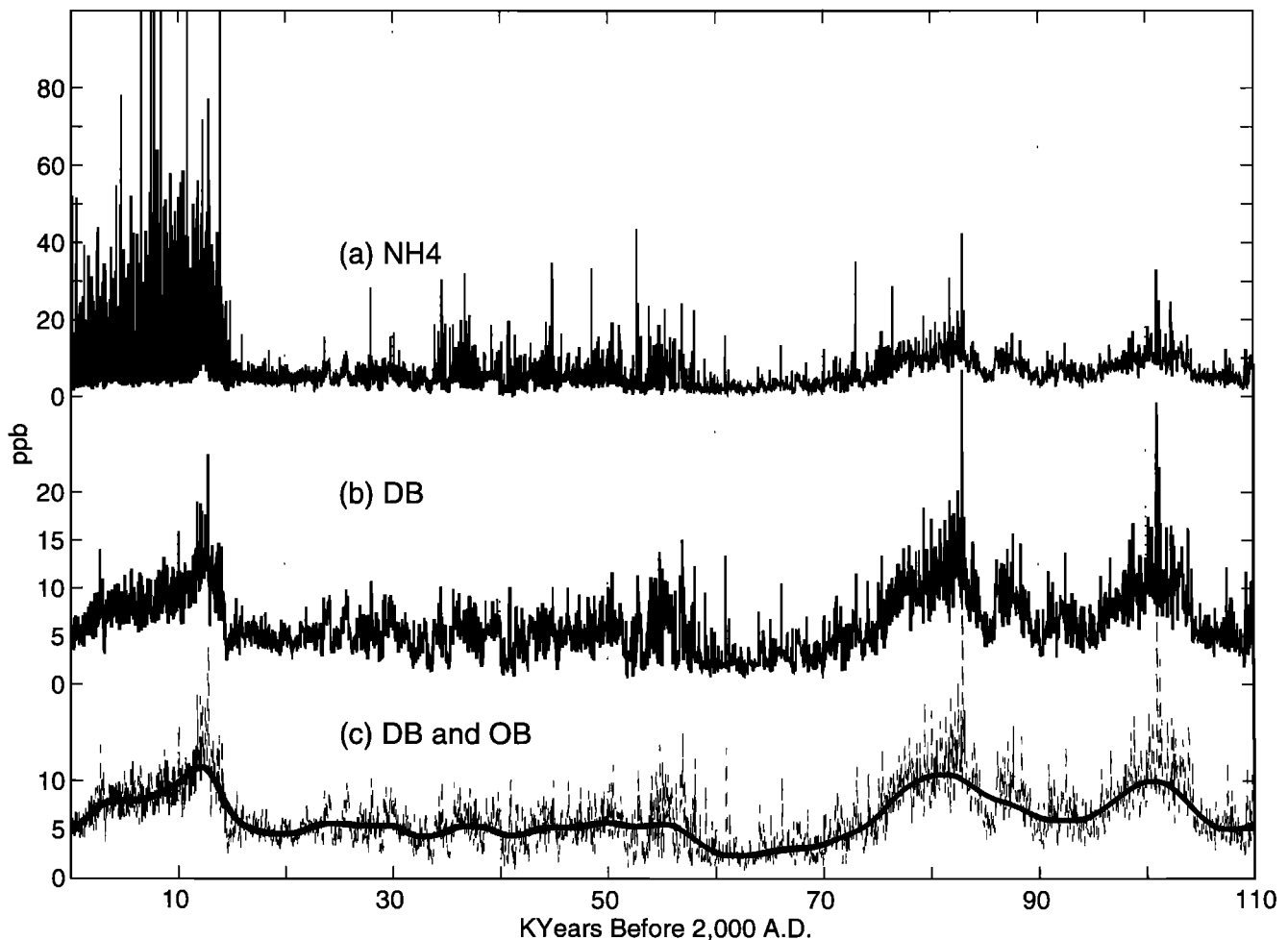
## 2. Ion Concentration and Flux

Two distinct procedures are common in the analysis of time series of ice core chemical concentrations. The first is based on the directly measured concentrations (e.g., in parts per billion), while the second is based on estimated chemical flux (e.g., in nanomoles per square meter per year). Chemical fluxes to the ice have been estimated by multiplying the sample concentrations by estimates of the  $\text{H}_2\text{O}$  flux (accumulation) obtained either (1) by directly measuring annual layers in the ice core and correcting for layer thinning by mathematical models of ice dynamics [*Meese et al.* 1994a, 1994b] or, (2) in the absence of measured annual layers, by using a previously derived empirical relationship between  $\text{H}_2\text{O}$  accumulation and the stable isotope,  $\delta^{18}\text{O}$  series [*Dansgaard et al.* 1993; *Hansson*, 1994].

While statistical analyses of concentrations or estimated fluxes do, in general, yield qualitatively similar results, they sometimes provide different quantitative comparisons. For example, during very cold periods accumulation can be greatly reduced in both magnitude and variation. As a consequence, changes in magnitude within estimated flux series can be severely muted in comparison to those in concentration series [*Mayewski et al.*, 1993; *Fuhrer et al.*, 1996].

The rationale for the flux estimates is a simple model [*Davidson et al.*, 1989; *Alley et al.*, 1995]

$$f_t = C_t(Wp_t + D). \quad (1)$$



**Figure 1.** The Greenland Ice Sheet Project 2 (GISP2) record of ammonium concentrations over the past 110,000 years: (top) Original samples (labeled “NH4”), (middle) a smoothed (low-tension spline filter) version of the original series describing decadal and centennial scale variation (referred to as DB in text), and (bottom) DB series (dashed) and a smoothed (high tension spline filter) version of the original series describing orbital scale variation in ammonium concentrations (referred to as OB in the text).

relating average flux  $f_t$  of a given chemical species over time interval  $t$  to the average atmospheric concentration  $C_t$  and average flux of  $H_2O$   $p_t$  in terms of  $D$  and  $W$ , the dry-deposition velocity and scavenging ratio, respectively.

Equation (1) implies a similar relationship for the concentration  $x_t$  of the species in surface snow or ice

$$x_t = \frac{f_t}{p_t} = C_t \left( W + \frac{D}{p_t} \right). \quad (2)$$

If  $D$  is not zero (that is, if dry deposition makes a significant contribution to the flux for the ion species), (2) predicts an inverse relationship between concentration values and  $H_2O$  accumulation and implies that changes in ice concentrations can be the result of changes in accumulation, even under conditions of constant atmospheric concentration  $C_t$ . The estimation of chemical flux, given measured concentration and estimated  $H_2O$  accumulation  $\hat{p}_t$  by

$$\hat{f}_t = x_t \hat{p}_t. \quad (3)$$

is intended to remove this dependency in order to obtain an improved estimate of atmospheric concentrations and thereby to provide a more accurate estimate of changes in atmospheric concentration over time.

Flux calculations based on (3) have proven useful in short term studies (i.e., single storm events) for which an assumption of constant  $C_t$  is reasonable and one is certain that chemical deposition occurred at the same time as the measured accumulation of  $H_2O$ . However, the chemical concentrations derived from typical ice core samples are, in general, the result of deposition over several precipitation events, several seasons, or even several years. It is (2) which motivates the “flux correction” of (3) and it is not clear a priori that it is a valid representation of physical reality when considered over extended time periods. For this reason we conducted an empirical study of the relationships among soluble ion concentrations from the GISP2 ice core and

**Table 1.** Joint Empirical Orthogonal Function (EOF) Analysis of Original Chemistry Samples, 0-17,000 Years Ago

Species	Eigenvector Components				Percent Variance Explained				
	EOF1	EOF2	EOF3	EOF4	EOF1	EOF2	EOF3	EOF4	Sum
Ca	0.96	-0.12	-0.08	0.06	91.4	1.4	0.6	0.4	93.8
K	0.89	-0.04	-0.15	0.09	79.8	0.1	2.2	0.4	83.1
Mg	0.97	-0.11	-0.07	0.05	94.6	1.3	0.4	0.2	96.6
Na	0.97	-0.10	-0.06	0.00	94.1	1.1	0.4	0.0	95.6
Cl	0.96	-0.07	-0.03	-0.02	92.4	0.6	0.1	0.0	93.1
SO <sub>4</sub>	0.83	-0.09	0.04	0.26	68.6	0.8	0.2	7.0	76.5
NO <sub>3</sub>	0.58	0.56	0.58	0.10	33.6	31.1	33.3	1.0	99.0
NH <sub>4</sub>	0.11	0.91	-0.39	0.04	1.3	83.0	15.2	0.2	99.6
H <sub>2</sub> O	-0.80	-0.09	-0.06	0.56	64.1	0.9	0.3	31.5	96.7
				Total *	68.9	13.4	5.9	4.6	92.7

\*Values are percent of total variance explained.

estimates of H<sub>2</sub>O accumulation from the same core samples in order to test the viability of (2) in the context of a multi-year sampling protocol.

To explore the relationships among eight chemical species and H<sub>2</sub>O accumulation we used the 17,415-year record of annual accumulation estimated from the GISP2 core by measured annual layers (using multiple annual indicators) corrected for layer thinning [Meese *et al.*, 1994a, b]. This time series is the longest continuous and directly measured history of annual accumulation available. The chemistry samples collected from the same 1867-m core section are based on 6293 time intervals with an average duration of 2.8 years and standard deviation of 1.9 years. The record of annual accumulation was resampled in order to estimate H<sub>2</sub>O accumulation over the time intervals of the chemical samples and to directly investigate the relationship between the accumulation and chemical concentration records.

Equation 2 implies a simple inverse relationship between concentration and rate of accumulation which could be estimated by a linear regression of species concentration versus  $1/p$ . This, however, can be misleading. As time  $t$  varies over an extended period, the atmospheric concentration  $C_t$  can be expected to vary with some of the same climate factors which influence a variable accumulation rate  $p_t$ . For this reason, a simple regression would involve a confounding of climate effects which could obscure the true relationship between the variables. In recognition of this possibility Alley *et al.* [1995] performed their analyses over different time intervals (Bolling-Allerod, Younger Dryas, and Preboreal) in order to compare atmospheric concentrations, which were assumed to be essentially constant during each period. Our goal, however, is to study these relationships in the presence of mutual variation induced by change in common climate forcing factors and so we utilize a standard tool of multivariate statistical analysis for our investigation.

## 2.1. EOF Analysis: Ion Concentrations and H<sub>2</sub>O Accumulation

Table 1 summarizes the results of the empirical orthogonal function (EOF) analysis (see appendix) of the nine-dimensional record of combined chemistry and accumulation.

The signs and magnitudes of the entries of the scaled eigenvector in the first column of Table 1 (which define the first EOF) show that each chemical species, except ammonium, is strongly anti-correlated with accumulation as predicted by (2). This is the dominant feature of the first EOF which, alone, explains 69% of the total variance of the multivariate record, 64% of the variance in accumulation, and a large component of variance in all the chemical species except ammonium. The second and third EOFs are dominated by the two nitrogen species, while the fourth explains most of the remaining variance in accumulation and 7% of sulfate variance. From this analysis it appears that the relationships between rate of H<sub>2</sub>O accumulation and chemical species concentrations that we seek to understand are contained in the first and fourth EOFs.

There are two obvious and competing interpretations of Table 1. The first considers EOF1 as directly exhibiting the effect of accumulation on the chemical concentrations. Ion concentrations in the ice are reduced by dilution with increased H<sub>2</sub>O accumulation and enhanced by concentration when H<sub>2</sub>O accumulation decreases. From this perspective, accumulation rate would be the dominant explanatory factor in the multivariate data set and the corresponding time series  $w_1$  (see A3), which describes the temporal evolution of EOF1, would essentially be a rescaling of the accumulation series. With this interpretation, EOF4 represents an additional positive connection between accumulation and sulfate concentration.

The second interpretation considers EOF1 as representing a strong climate factor influencing both chemi-

cal concentrations and rate of accumulation. This view implies that the joint influence factor creates environments in which chemical concentrations increase under conditions in which accumulation is reduced and conversely. It also suggests (given (A4)) that, if the strong negative correlation of some species and H<sub>2</sub>O accumulation indicated by EOF1 is due to exogenous factors, the influence of accumulation rate upon chemical concentrations in these series is primarily restricted to the small positive influence on sulfate concentrations shown in EOF4.

Fortunately, these two opposing interpretations can be tested. Under the first interpretation, i.e., if variation in chemical concentrations is the result of variation in accumulation, sample-to-sample variation in accumulation should be strongly anticorrelated with sample-to-sample variation in all the chemical species. That is, a decrease in accumulation should induce a related increase in concentration and vice versa. Under the second interpretation, the dominant climate factor would be expected to influence the time varying mean level of ice accumulation but not, necessarily, the short term variation represented by sample to sample differences. Since these two alternatives depend upon the multivariate relationships among the sample-to-sample first differences of the concentrations and those of accumulation, we can repeat our EOF analysis on the differenced multivariate series.

### 2.2. EOF Analysis: First Differences of Ion Concentrations and H<sub>2</sub>O Accumulation

Table 2 summarizes the results of EOF analysis of the first differences of the combined multivariate chemistry and accumulation record.

As shown in Table 2, the data strongly support the second interpretation discussed above. These data fail to show any significant relationship between short-term variation in H<sub>2</sub>O accumulation and that of the concentration of any chemical species. Evidently, any enhancement or dilution of measured concentrations in the ice by patterns of wet or dry deposition over the sample in-

tervals, as is sometimes observed over short observation periods, is minimized by the multiyear averaging of the GISP2 samples.

From this analysis it is clear that the time series w<sub>4</sub> associated with the fourth EOF shown in Table 1, which is uncorrelated with the other EOFs of that analysis, contributes new climate information not available from the combined chemistry series. Figure 2 shows the accumulation rate series and its first and fourth EOF components. The results found from the EOF analysis of first differences can be seen in Figure 2. The first EOF clearly describes the overall level of accumulation, while the fourth describes its short-term variation about the time-varying mean. The climate process represented by this new component is not clear. However, because it is uncorrelated with all the chemical species which together represent local to regional terrestrial, marine, and biological sources, it is most likely recording local influences on accumulation such as temperature or humidity anomalies.

### 2.3. Regression Analysis of First Differenced Series

In addition to the EOF analyses above, other tests of (2) were performed. Equation (2) implies that

$$\Delta x_t \equiv x_{t+1} - x_t = (C_{t+1} - C_t) \left( W + \frac{D}{p_t} \right) - C_{t+1} D \left( \frac{p_{t+1} - p_t}{p_{t+1} p_t} \right) \quad (4)$$

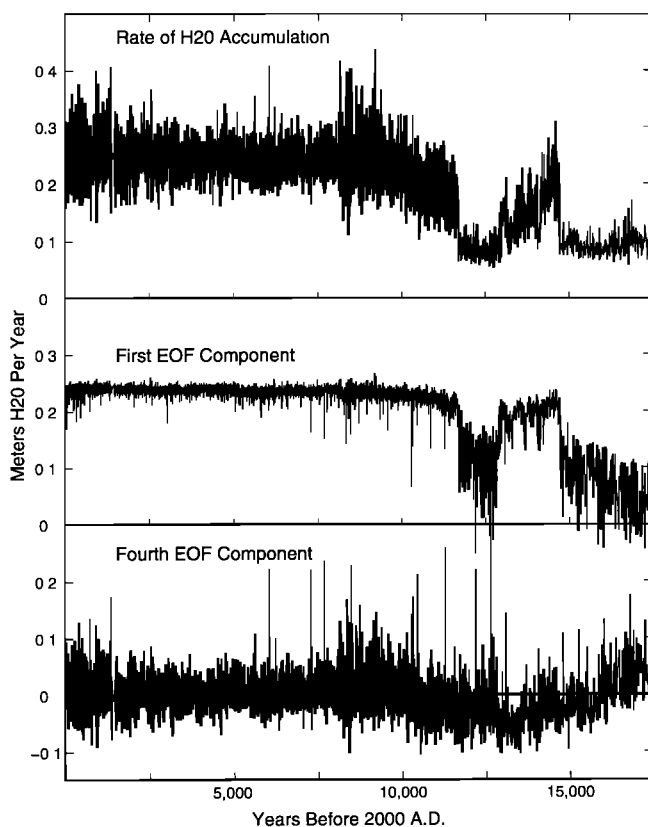
implying that if the dry deposition velocity *D* is not zero,  $\Delta x_t$  is a function of  $1/p_t$  and/or  $\Delta p_t/p_{t+1} p_t$ . Such relationships were tested by estimating the coefficients of the multiple regression model

$$\Delta x_t = A_0 + A_1 \frac{1}{p_t} + A_2 \left( \frac{\Delta p_t}{p_{t+1} p_t} \right) + \epsilon_t$$

for each ion species. The results (not shown) were consistent with the earlier analyses. None of the regression

**Table 2.** Joint EOF Analysis of First Differences

Species	Eigenvectors			Percent Variance		
	EOF1	EOF2	EOF3	EOF1	EOF2	EOF3
ΔCa	0.83	-0.08	-0.03	69.3	0.7	0.1
ΔK	0.59	0.21	0.06	34.7	4.6	0.3
ΔMg	0.89	-0.15	-0.02	79.9	2.3	0.0
ΔNa	0.87	-0.15	0.02	75.1	2.2	0.0
ΔCl	0.78	-0.07	0.04	61.5	0.5	0.1
ΔSO <sub>4</sub>	0.51	-0.17	-0.01	26.3	2.8	0.0
ΔNO <sub>3</sub>	0.48	0.57	-0.03	22.9	32.9	0.1
ΔNH <sub>4</sub>	0.09	0.86	0.03	0.8	74.4	0.1
ΔH <sub>2</sub> O	-0.02	-0.02	1.00	0.1	0.0	99.3
			Total	41.2	13.4	11.1



**Figure 2.** Time series describing the annual rate of H<sub>2</sub>O accumulation at Summit, Greenland, over the past 17,415 years estimated from the GISP2 ice core and its first and fourth EOF components (see text).

models explained more than 1% of the variance in the differenced ion series, and none of the estimates of  $A_1$  or  $A_2$  was significantly different from zero.

#### 2.4. Implications of Joint Chemistry and Accumulation Investigations

The regression analysis and two preceding multivariate EOF analyses of these series, the longest joint record of accumulation and chemical concentrations presently available, implies that if (2) is valid under the conditions at Summit, Greenland, over the past 17,000 years:

1. dry deposition must be negligible in comparison to wet deposition (a nonzero  $D$  for a given ion species would imply a strong inverse correlation between differenced accumulation and concentration series for the species) and, consequently,
2. the chemical concentrations estimated from multiannual ice core samples are essentially proportional to the average atmospheric concentrations over those time periods, furthermore,
3. the strong connection between the concentration of chemical species and H<sub>2</sub>O accumulation shown in Table 1 is a consequence of a shared climate forcing factor, rather than an intrinsic physical connection.

The EOF analysis also shows that flux estimates formed by multiplication of accumulation and concentration series will confound common climate forcing factors. This possibility is most important when harmonic analysis is contemplated. If chemical concentrations and accumulation are influenced by the same periodic forcing, their multiplication will introduce products of the common periodic components into the flux record. This has the effect of complicating spectral analysis of the flux estimate series by introducing low-order harmonics and compound frequencies into what may have been simple harmonic relationships in the original series.

### 3. Ammonium Concentrations: Relationship to Other Ions

The GISP2 glaciochemical series provide a high-resolution, continuous record of the chemical composition of the atmosphere that includes over 95% of its soluble ionic components. Climate factors influence the concentrations in polar ice of different ion groups (e.g., of terrestrial dust, sea salt, volcanic, or biological origin) through amplification or suppression of their generating mechanisms, by shifting primary source areas, and/or by altering their atmospheric transport from source to site of deposition. As a consequence, interrelationships among the concentrations of the glaciochemical species provide a multifaceted and complex history of climate change. The analytical process of EOF analysis (see above and appendix) has proven a useful tool for investigating this history [Mayewski *et al.*, 1993, 1994, this issue]. Table 3 continues this process by summarizing the EOF analysis of the complete GISP2 glaciochemical record of ion concentrations (10,979 original samples) from the present to 110,000 years ago.

The first, second, and third EOF components (see (A2)) represent 93.6% of the total variance in the eight chemical concentration series. The first component explains almost all the variance in the nonnitrogen species time series and 11% of that in the nitrate series. The negative entry in the first column of Table 3 for ammonium indicates that, in general, the concentration of this species decreases as the concentrations of the others increase and vice versa (see appendix). Considered as proxies for atmospheric concentrations, the rescaled time series of the first EOF (A3) describe a well-mixed, obviously large scale, atmospheric circulation system in which all components, except that of ammonium, increase and decrease together in fixed proportions. The time series ( $w_1$  of (A2)) describing the dynamics of this circulation system has been termed the polar circulation index (PCI) [Mayewski *et al.*, 1993, 1994, this issue]. It represents 70% of the total joint variance in the 110,000-year-long record of the eight chemical species. In general, the PCI increases during colder periods (stadials) and decreases during warmer periods (Holocene and interstadials) as the extent and magnitude of the

**Table 3.** EOF Analysis, Original Chemistry Samples, 0-110,000 Years Ago

Species	Eigenvectors			Percent Variance			
	EOF1	EOF2	EOF3	EOF1	EOF2	EOF3	Sum
Ca	0.94	-0.05	-0.11	88.1	0.2	1.3	90.4
K	0.95	0.02	-0.10	90.4	0.1	0.9	91.4
Mg	0.98	-0.05	-0.09	95.4	0.3	0.8	96.7
Na	0.97	-0.04	-0.01	94.4	0.2	0.0	94.7
Cl	0.95	-0.02	0.02	90.3	0.1	0.0	90.4
SO <sub>4</sub>	0.93	0.04	0.01	86.7	0.2	0.0	99.0
NO <sub>3</sub>	0.33	0.78	0.53	11.2	60.8	27.7	99.7
NH <sub>4</sub>	-0.18	0.85	-0.49	3.4	72.1	24.3	99.8
			Total	70.0	16.7	6.9	93.6

polar atmospheric circulation responds to the growth and decrease of the great continental ice sheets.

The first EOF contribution to the variance of the sulfate series is the smallest of the nonnitrogen species. The remainder of the sulfate variance (the largest of any component not of EOF1-3) is associated with EOF5 (not shown) and the corresponding time series,  $w_5$  (see appendix), has been shown to provide a 110,000-year-long record of explosive volcanism [Zielinsky *et al.*, 1996].

Table 3 shows that the nitrate concentration series is alone in having significant components associated with each of the first three EOFs. Nitrate concentrations increase with the PCI and increase (decrease) with ammonium increases associated with the second EOF (third EOF). This three-part pattern is consistent with the known multiple-source character of atmospheric nitrogen and the general complexity of its atmospheric chemistry. For these reasons we postpone a full discussion of the complex interactions between the two nitrogen species and restrict our discussion below to an analysis of the ammonium series.

Ammonium, unlike the nonnitrogen species, has most of its variance (96%) associated with the second and third EOFs. The small negative loading of NH<sub>4</sub> on EOF1 implies a weak negative correlation with the PCI (The correlation is  $-0.18$ , which is significant at the 0.05 level.). This negative relationship is to be expected. Ammonium concentrations have been shown to be positively correlated with temperature [Langford and Fehsenfeld, 1992] and to decrease during colder periods [Hansson, 1994; Fuhrer *et al.*, 1996] when polar circulation intensity and the PCI increase. Since ammonium is derived primarily from continental biogenic sources [Logan, 1983; Dentener and Crutzen, 1994], the ammonium reaching central Greenland during most of the pre-Holocene portion of the record would have had its source region south of the northern hemisphere ice sheet margins. Furthermore, since ammonium has a relatively short residence time in the atmosphere, concentrations reaching Greenland during the pre-Holocene were most probably derived from mid- to possibly low-latitude continental source regions, which were characterized by colder and drier climates [Chappellaz *et al.*,

1993] and decreased biogenic activity during times of PCI expansion.

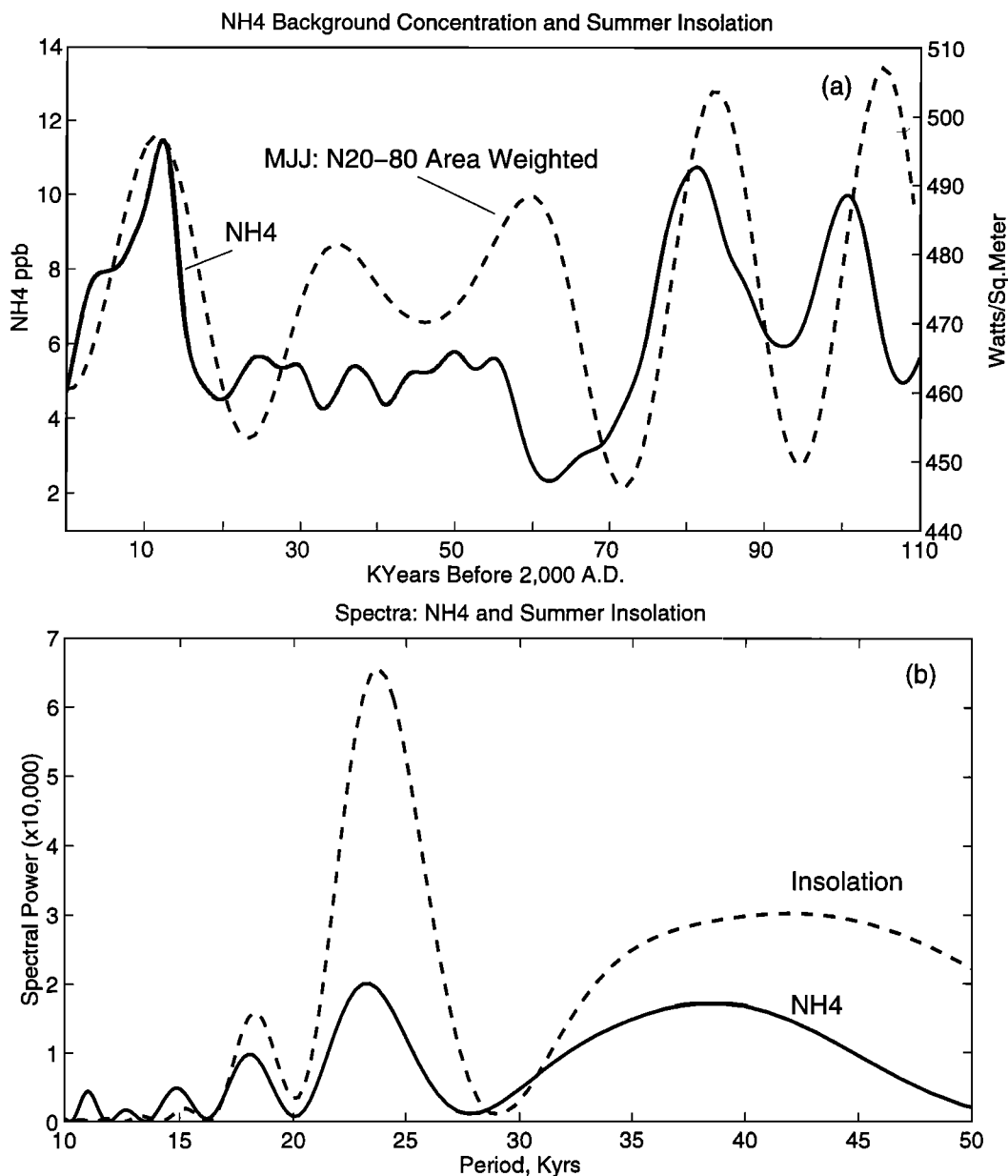
This is fully consistent with the negative loading of ammonium on the PCI. We expect intrusions into Greenland by southerly air masses to be less frequent and to contain lower concentrations of ammonium during times of advancing ice sheets and increasing extent and intensity of polar circulation (increased PCI). During the Holocene and presumably the warmest interstadials (periods of reduced ice sheet extent) we should expect the dominance of the polar circulation to diminish, high-latitude continental biogenic source regions to increase in importance, intrusion into the Greenland atmosphere by air masses rich in ammonium to be more frequent, and enhanced mixing of air masses having different chemical signatures as a result of different transport histories. EOF analyses performed on portions of the GISP2 Holocene record (e.g., Table 1) or the longer interstadials are, in general, supportive of this expectation. During such periods, ammonium and nitrate concentrations show significant variation on several EOFs and strong associations with several other ion species.

It is important to note that the major components of the ammonium series are described by EOFs 2 and 3, which are statistically uncorrelated with the PCI. As a consequence, the ammonium concentrations in the GISP2 core do not simply record a passive response to the dynamics underlying the PCI. On the contrary, the biological sources of ammonium create an active component that responds to different forcing factors than the PCI or, at least, responds to the same factors through independent mechanisms. Therefore, unlike the glaciochemical series originating from terrestrial dust or marine sea salt, 96% of the variation in the complex pattern of increase and decrease in ammonium concentrations during the past 110,000 years is not explained by the PCI.

#### 4. Orbital Scale Variation in Biological Production

Background levels of ammonium described by the high-tension spline series OB of Figure 1 vary from a maximum of 11.5 ppb at  $\approx 12,000$  years ago midway





**Figure 3.** Comparisons between the orbital scale background levels of ammonium (OB) from the GISP2 ice core (solid curve) and area-weighted northern hemisphere summer insolation ( $20^{\circ}\text{N}$  to  $80^{\circ}\text{N}$ ) (dashed curve). (a) OB series in parts per billion and summer insolation in watts per square meter. (b) Estimated spectra of the ammonium concentration series (solid curve) and the area-weighted summer insolation (dashed curve).

through the Younger Dryas cold event (YD) to a minimum of 2.3 ppb at  $\approx 62,000$  years ago in marine isotope stage 4 (MIS 4), a time period noted for extensive ice sheet expanse [Ruddiman and McIntyre, 1979; Ruddiman et al., 1980]. The OB shows relative maxima at  $\approx 100,000$  and 80,000 years ago, preceding its minimum for the 100,000-year record in MIS 4, and varies  $\approx 5$  ppb for the period 55,000 to 20,000 years ago, during which the final expansion of the Laurentide Ice Sheet took place. Following its maximum during the YD, the OB shows a diminishing rate of decrease during the Holocene, followed by a more rapid drop to its 1985 value of 4.7 ppb.

The decrease during the most recent 9000 years has been attributed to a decrease in temperature in high latitude source areas [Fuhrer et al., 1996]. Given the known influence of temperature on ammonia emissions this is reasonable. However, since background OB levels were above current values during a 30,000 year interval when ice-covered much of the high latitudes, factors other than temperature may be more important.

#### 4.1. Summer Insolation and OB Maxima

Figure 3 compares the OB series with monthly average, area-weighted, northern hemisphere (NH) summer

insolation (May, June, July from 20N to 80N, [Berger, 1978]). There is one-to-one correspondence between the three major peaks in the two series. The final and two earliest insolation maxima, which occur at times of NH summer perihelion, are clearly paired with maxima in OB. The final and best dated peak of the ammonium background series is coincident with the most recent NH summer perihelion. Because the differences in time between the first two insolation and OB peaks (2600 and 4500 years) are each less than the estimated GISP2 dating errors at that depth, they may be considered synchronous.

The effects of the lesser maxima in summer insolation are not as strongly evident in the OB series. The reduced levels of insolation represented by these peaks occurred during a time when the Laurentide Ice Sheet was expanding to its final southerly extent and driving the polar atmospheric circulation to its maximum intensity and expansion [Mayewski *et al.*, this issue]. During this same period the Atlantic polar front was pivoting from its interglacial orientation north-northeasterly from Newfoundland to an easterly direction at  $\approx 43^\circ\text{N}$  latitude, inducing a shift from meridional to zonal oceanic and atmospheric circulation [Ruddiman and McIntyre, 1977]. The combined effect of these events would have limited ammonium concentrations in the Greenland atmosphere by forcing its terrestrial biological sources to the south, far beyond the ice margins, and restricting transport of ammonium-rich air masses from those more distant sources to Greenland. The more southerly position and predominantly zonal nature of polar circulation would have reduced the interglacial pattern of meridional circulation in the high latitudes and shifted the zone in which the mixing of polar and mid- to low-latitude air masses could take place as far south as the  $\approx 43^\circ\text{N}$  position of the Atlantic polar front. Thus, during this time period, ammonium concentrations in the Greenland atmosphere were diminished not only by reduced biological forcing of the lesser (obliquity modulated) precessional peaks in summer insolation, but also by the southerly shift in source areas and changes in atmospheric circulation associated with the growth of the continental ice sheets.

#### 4.2. OB Minima

Three prominent minima in OB levels appear to be linked to minima in summer insolation (Figure 3). The first, at  $\approx 95,000$  years ago, is coincident (within GISP2 dating accuracy) to a minimum in insolation, but the following OB minima ( $\approx 62,000$  and  $\approx 19,000$  years ago) lag the corresponding insolation minima by 9700 and 3500 years, respectively, which, at those depth levels, cannot be assigned to dating inaccuracy.

The insolation minimum at  $\approx 70,000$  years ago occurs near the transition between MIS 4 and 5 (shown in Figure 4) and is considered an important factor in the rapid expansion of the Laurentide Ice Sheet during the

following 10,000 years [Ruddiman and McIntyre, 1979]. This rapid expansion appears to have been the result of the juxtaposition of a cold continent and a warm ocean whose temperature decrease lagged ice sheet growth by 4000 to 5000 years [Ruddiman and McIntyre, 1979]. This situation created strong thermal gradients that directed cyclonic storm tracks from lower latitudes toward regions of ice sheet growth [Ruddiman, *et al.*, 1980]. This same circulation pattern would continue the transport of ammonium from source areas gradually moving to the south in advance of the growing ice sheets.

This analysis suggests that the MIS 4 minimum in OB is a lagged response to the preceding insolation minimum induced by a  $\approx 6000$ -year lag in ice sheet response [Mayewski *et al.*, this issue] influencing the biogenic source area and a similar 4000-5000 year lag in ocean cooling acting to maintain a meridional pattern of atmospheric circulation. The continued expansion of the Laurentide Ice Sheet over the following  $\approx 5000$  years and the concomitant rotation of the Atlantic polar front toward the equator following ocean cooling amplified the effects of the absolute minimum (over the past 110,000 years) in summer insolation to create the absolute minimum in OB at  $\approx 62,000$  years ago.

The shortened delay in OB response to the insolation minimum at  $\approx 20,000$  years ago is to be expected, given that the level of insolation is higher and the continental ice sheets are receding rather than growing. The combined effects of the precession cycle, i.e., increasing summer insolation and shorter colder winters, created an environment in which biogenic production appears to have been rapidly reestablished in the newly ice free areas.

#### 4.3. The Holocene

Background ammonium concentrations show a continuing decrease during the Holocene; however, unlike the pattern following earlier maxima in insolation, the rate of decrease varied markedly during the period (Figures 1 and 3). The background ammonium concentrations described by OB decreased at an approximate rate of 0.6 ppb per 1000 years following the two maxima at 80,000 and 100,000 years ago, yielding a decline which paralleled that of the summer insolation (Figure 3a). However, following the maximum at 12,000 years ago, ammonium concentrations described an initial rapid decline of  $\approx 0.7$  ppb per 1000 years, which slowly moderated to form a "plateau" of  $\approx 8$  ppb at 6000 years ago. Concentrations were maintained near that level until 4000 years ago, when the rate of decrease gradually increased until reaching its present rate of 0.9 ppb per 1000 years. Several factors, undoubtedly, were responsible for this behavior.

As evidenced by sea level records (see discussion in Mayewski *et al.* [this issue], extensive ice sheets existed during the peaks in OB at 80,000- and 100,000-years ago. The continuing presence of substantial ice sheets

in high latitudes may have provided a degree of forcing that acted to amplify the cooling and antibiogenic influence of the decline in NH summer insolation and the corresponding increase in winter insolation and temperature. Expansion of the high-latitude ice sheets in response to decreased summer melting and increased winter precipitation could have combined with decreased summer biogenic forcing to create a steady decline in biological production of ammonium. In addition, these factors would increasingly restrict atmospheric transport of ammonium-rich air masses to Greenland (see above). The general retreat of the ice sheets preceding and following the insolation maximum at 12,000 years ago would create a much different biogenic response to decreasing insolation during the early and mid-Holocene.

The early Holocene is a time in which biogenic production and ammonium transport to Greenland were subject to two competing influences. Decreasing summer insolation acted to shorten the growing season and decrease biological production, especially in the high latitudes. However, on the other hand, the continuing northerly retreat of the ice margins opened additional biological source areas, provided the summer moisture required by the plant communities, and altered atmospheric circulation patterns by reducing the intensity of the predominately polar circulation and inducing more meridional transport of air masses from warmer, more productive areas to the south. Each of these factors would tend to increase ammonium concentrations in the Greenland atmosphere.

The pattern of ammonium concentrations described by the OB during the Holocene is typical of a non-linear response to two such competing influences. Initially, in this instance the negative forcing (decreasing summer insolation) dominates and concentrations decrease while the positive forcing (melting ice sheet) continues to increase to a point where approximate equilibrium is established. The equilibrium is maintained until the positive forcing can no longer increase to the extent required to balance the continued influence of the negative forcing and a new period of enhanced decline is initiated. In this instance, sharp decline occurs because the positive factor does not simply fail to increase at the rate needed to balance declining summer insolation but actually stops increasing with the final melting of the Laurentide Ice Sheet. It is during the period of approximate balance between the two forcing factors that they combine to create temperatures in the mid-to high-latitudes reaching their Holocene maximum.

This analysis shows that the background ammonium concentration during the Holocene records the biogenic response to the complex environmental conditions (temperature, hydrology, etc.) created by orbitally induced decline in summer insolation and the melting of the remnant(s) of the Laurentide Ice Sheet. The influence of declining summer insolation and the orbitally related increase in winter insolation and duration during this

period is, perhaps, the explanation for the observed increase in the "length fraction of winter concentrations" noted by *Fuhrer et al.* [1996, p.4154] during recent times.

#### 4.4. Spectral Analysis

As is to be expected from the preceding discussion, spectral analysis [*Bloomfield*, 1976] of the uniformly re-sampled ammonium series shows strong spectral peaks in the Milankovitch frequency bands whose relative strength matches those of the summer insolation series (Figure 3b). The dominant peak at a periodicity of 23,100 years is obviously of precessional origin. Unlike the spectrum of reconstructed ocean temperatures [*Ruddiman and McIntyre*, 1981] the ammonium concentration series shows a strong obliquity band periodicity of 38,100 years, which is somewhat shifted from the 41,600-year period of the obliquity peak in the theoretical insolation series. The presence of the obliquity influence in the ammonium series reflects the negative influence of the advancing Laurentide ice sheet and expanded PCI on biogenic production, factors which apparently were not a major influence on ocean temperatures during this period. It is likely that the indirect, lagged, and nonlinear response of biogenic production to obliquity scale forcing acting through ice sheet growth and decay underlies the difference in estimated periodicity.

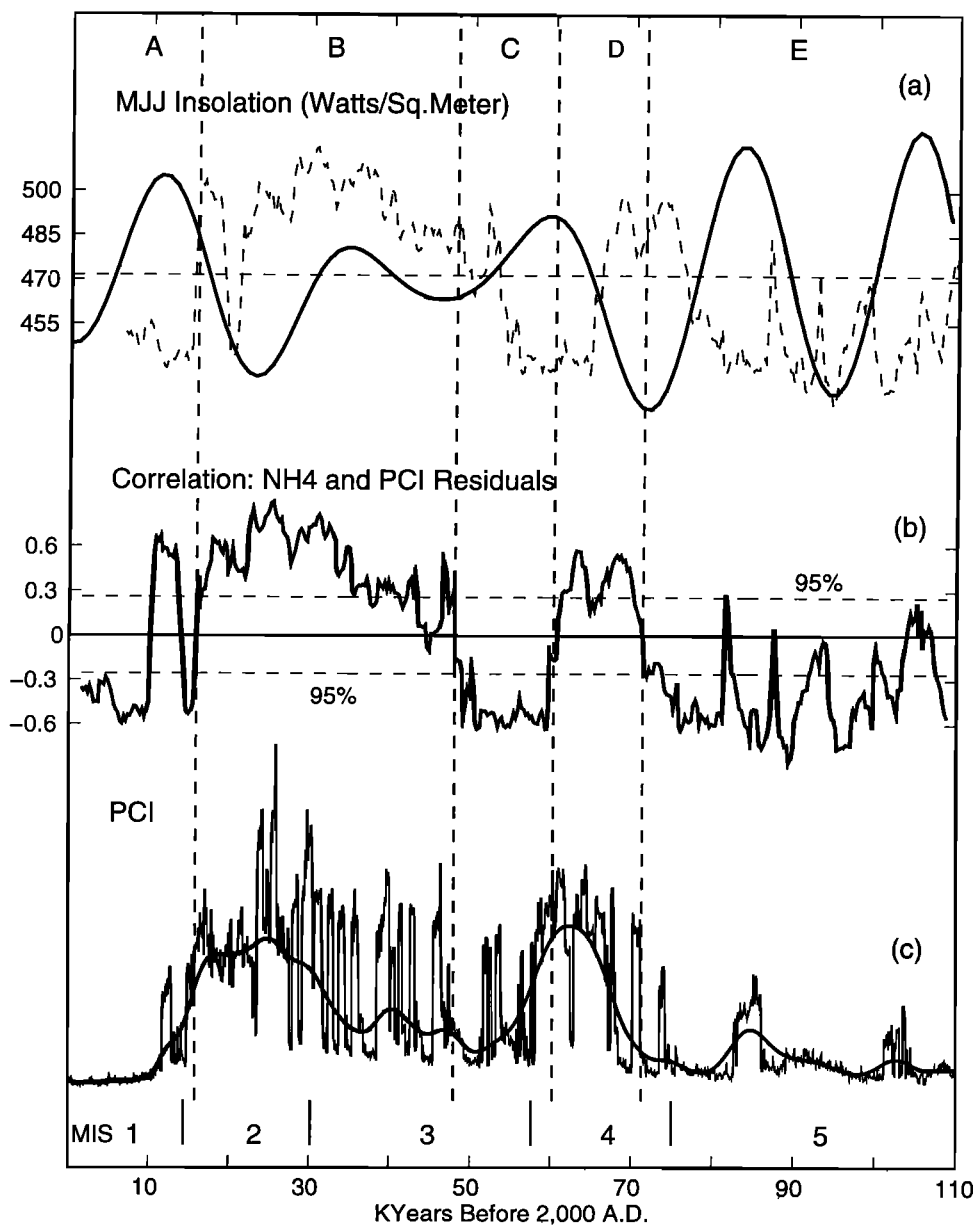
#### 4.5. Summary: Orbital Scale Variation in Biological Production

Maxima in long-term levels of the biogenically produced ammonium concentrations from the GISP2 ice core occur at times of major maxima in summer insolation. This basic relationship is modified by the effects of growing or retreating ice sheets on source areas and atmospheric circulation patterns. In particular, these relationships cause minima in biogenic production and alterations in atmospheric transport processes to lag behind minima in summer insolation.

### 5. Decadal and Centennial Scale Variation in Biological Production

The OB series discussed above does not reflect changes in ammonium concentrations on scales less than a millennium. The low-tension spline series, DB, on the other hand, records changes in ammonium source areas, source strength, and atmospheric circulation patterns and intensity that persist for only a few decades or centuries. The identification of the most probable of these mechanisms associated with any particular feature in the DB record can be, of course, a difficult problem. Nevertheless, the multivariate GISP2 record and its summary by the PCI, in particular, provide considerable guidance in the task.

The DB series represents variation about the orbital scale record of biogenic production described by the



**Figure 4.** Comparison of decadal and centennial scale variation in ammonium concentrations (DB) with similar scale variation in the polar circulation index (PCI) series (see text). (a) Plot of area-weighted summer insolation (solid curve) and correlation curve of Figure 4b lagged 5250 years (dashed curve). (b) Plot of windowed correlation between ammonium and PCI residuals based on overlapping windows of 4500 year duration stepped 250 years. Prominent zero crossings of the correlation series were used to define intervals A through E. (c) PCI series and the high-tension spline smoothing used to define the residuals used in windowed correlation of Figure 4b.

OB (Figure 1). From Figure 1 (lower) it is clear that factors operating on decadal to centennial scales create sustained deviations from the background level of production predicted by orbital scale forcing. There is a prominent decrease occurring at  $\approx 85,000$  years ago that interrupted a general increase in ammonium levels induced by the precession cycle. The decrease is associated with a rapid increase in the PCI (Figure 4c and Mayewski *et al.* [this issue]) indicative of a shift to colder climate and stronger atmospheric circulation in the higher latitudes. Such an inverse relationship be-

tween these two series is consistent with the EOF analysis summarized in Table 3. That is, when the most recent 110,000 years of the GISP2 record are considered, increases in the PCI are associated with decreases in ammonium concentrations. This relationship, however, is not strictly observed when shorter time intervals are involved. For example, as previously noted by Fuhrer *et al.* [1996], ammonium concentrations show the opposite behavior, i.e., increasing during colder periods and declining during warmer periods, in the interval 28,000 to 20,000 years ago around the glacial maximum. Several

possible mechanisms that could explain this observation were suggested, including a possible change in deposition efficiency during the coldest periods, but little conclusive evidence was available. Clearly, it is important to study the duration and frequency of events in which ammonium concentrations are “in phase” or “out of phase” with the polar circulation.

### 5.1. Windowed Correlation Analysis

Using the 50-year resampled GISP2 record, we conducted a correlation analysis of the PCI and DB series in order to compare and investigate the extent of the two climatic modes associated with the different patterns of ammonium deposition discussed above. Correlations between the deviations of the DB series from its orbital scale background (OB) and the deviations of the PCI series from the high-tension spline shown in Figure 4c were calculated using overlapping windows of 4500 years, stepped at 250 year intervals. The window length was chosen in order to get good resolution of behavior on the scale of the Dansgaard/Oeschger (D/O) events ( $\approx 1500$  year periodicity, [Mayewski *et al.*, this issue]).

The result of this analysis is shown in Figure 4b. Two basic patterns of behavior between the two residual series are apparent. Correlation values (positive or negative) well in excess of the 95% level of significance occur over well-defined time intervals. Through MIS 5, the early part of MIS 3, and the Holocene the series are negatively correlated. During most of MIS 4, MIS 2, and the latter part of MIS 3 the correlations are positive. Transitions between the two types of behavior are definite and abrupt and were used to define five intervals shown in Figure 4 (denoted A through E). Detailed comparisons between the two residual series in intervals B through E are shown in Figure 5.

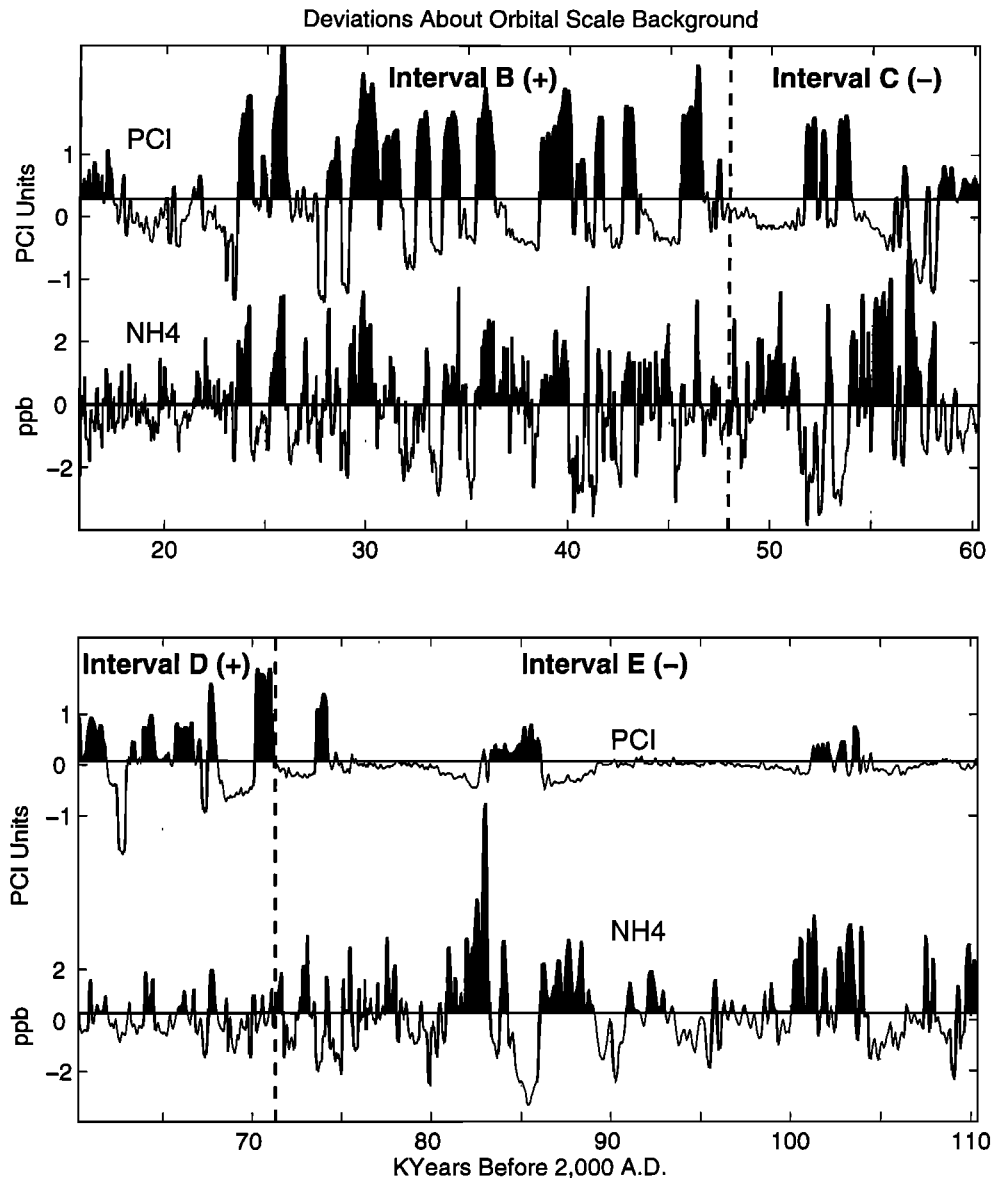
**5.1.1. Negative correlations: “Warm” intervals C and E.** Investigation of intervals C and E suggests climate conditions were much like Holocene conditions in which colder events are associated with decreases in ammonium concentrations and vice versa. The scale of the deviations (especially toward cool conditions) were much larger than those occurring in the Holocene, but the biological response was fairly consistent. This suggests a general pattern of Holocene-like atmospheric circulation during warm modes involving active biogenic production in the ice-free areas, frequent occurrence of meridional circulation patterns, and mixing of air masses of polar and mid- to low-latitude origin during the biologically productive summer seasons. During the cooler portions of intervals C and E, biological production, especially in the high latitudes, would be reduced and circulation about the polar cell would increase in intensity, creating a more zonal flow, thereby altering average storm tracks and decreasing the frequency of sustained meridional flow. As a consequence, there would be decreased transport of air masses from southern regions to Greenland and, consequently, de-

creased transport of ammonium from southerly source regions.

The out of phase behavior of the two series is obvious in interval C (Figure 5). Interval E (representing nearly 40,000 years) does not show such a consistent pattern. However, the cold event at  $\approx 85,000$  years ago (see Figures 4c and 5) provides an interesting example. Biological production was increasing from its minimum associated with the low in summer insolation at  $\approx 95,000$  years ago when the abrupt transition into cooler conditions recorded by the PCI record (Figure 4c) essentially returned ammonium transport to Greenland to its previous minimum level. For some 1600 years, ammonium levels were reduced by atmospheric circulation patterns and cooler temperatures in northern source areas. Presumably, however, increasing summer insolation stimulated ammonium production in southerly regions, which, however, rarely reached Summit, Greenland, because of the reduction in meridional flow. Finally, the PCI records a weakening in polar circulation and, after an initial “false start,” warm-mode circulation patterns prevail and high levels of ammonium are again transported to central Greenland. This situation generally continued until the prominent cold period shown in the PCI record near the MIS 4-MIS 5 boundary.

**5.1.2. Positive correlation: “Cold” intervals B and D.** Intervals B and D include the coldest portions of the 110,000-year record. As suggested by the analysis of the GRIP  $\text{NH}_4$  record, the period 28,000 to 20,000 years ago is one of strong positive correlation [Fuhrer, *et al.*, 1996]. The positive correlation increases, following its abrupt switch from negative values in MIS 3, and reaches a consistent 95% level of significance  $\approx 40,000$  years ago. This period includes the D/O rapid change events and the Heinrich events [Bond *et al.*, 1992], periods of massive discharge of icebergs into the North Atlantic. Interval D follows the MIS 5-MIS 4 transition and contains a period in which ice volume has been estimated to have reached 75 to 90% of its MIS 2 maximum, and snow and ice fields extended to at least  $50^\circ\text{N}$  latitude over eastern Canada [Ruddiman and McIntyre, 1979].

The reason for the generally low background levels of ammonium in the Greenland atmosphere during these intervals is easily understood from the previous discussion of factors influencing the OB series. These same forcing agents make it extremely unlikely that increases in ammonium concentrations during the coldest portions of these cold periods is the result of an increase in source strength. Rather, the probable origin of synchronous increases in ammonium concentrations and the PCI during intervals B and D is an increase in the frequency of expansion of polar circulation into southern regions that were sufficiently far from the ice sheet margins to support significant biogenic activity. Such expansions of ammonium-poor air masses from polar regions into biologically producing areas would have pro-



**Figure 5.** Comparison of deviations about orbital scale background levels of ammonium concentrations and the PCI over intervals (top) B-C and (bottom) D-E. Intervals B and D record approximately synchronous behavior and yield positive windowed correlations, while intervals C and E record, primarily, asynchronous behavior and negative windowed correlations.

vided efficient incorporation and transport of ammonium [Langford and Fehsenfeld, 1992].

In addition to an expansion of the polar cell and intensification of polar circulation, decreasing temperature also enhances cyclonic activity in the margins of the cell. Each of these responses increases the possibility of entrainment of southerly air masses in a predominantly northern circulation system, creating a small but measurable increase in Greenland's atmospheric concentration of ammonium during colder periods of the record. This explanation is consistent with the observed variation of  $\pm 2$  ppb of ammonium during the D/O events. Evidently, the "warm" parts of the D/O cycles are too short to allow significant biological production within the reduced "capture zone" of the polar circulation.

As a consequence, ammonium concentrations drop to a level determined by the reduced rate of capture of air masses from biologically productive regions and only increase again following the abrupt shifts into the "cold" parts of the cycles.

**5.1.3. Interval A: Younger Dryas and Holocene.** The transition to negative correlations between ammonium and PCI residuals during the Bolling-Allerod warming at the MIS 2-MIS 1 boundary is consistent with the discussion above. However, the sharp return to positive values during the Younger Dryas cold period is not. Despite the cooling that accompanied the YD event, it was a time of strong biological production as the biota in the newly ice free regions responded to increasing summer insolation. Therefore, while the YD

appears to be the most recent in a long sequence of abrupt cooling events in the PCI record [Mayewski *et al.*, this issue], its inhibiting effect on biogenic production was minimized by its occurrence during the time of NH summer perihelion. This is in contrast to the decrease in biological production during the cold event at 85,000 years ago, discussed above, which occurred at an earlier stage of the precession cycle. As a consequence of these factors, the return to positive correlation between ammonium and PCI residuals during the YD does not imply the atmospheric circulation pattern common during intervals B and D. Following the YD the warm negatively correlated circulation mode returned and has continued to the present.

**5.1.4. Timing of transition between circulation modes.** As remarked above, transitions between positive and negative correlation intervals are definite and abrupt (within 250-500 years) indicating a brief period of transition between the two modes of atmospheric circulation contained in the interval pairs B and D and C and E. In order to investigate the timing of these transitional events, we conducted a lagged correlation analysis between the windowed correlation series and the summer insolation series. This analysis yielded a highly significant negative correlation with a minimum of  $-0.43$  at a lag of  $-5,250$  years. Fig. 4a displays a plot of summer insolation and the correlation series of Fig. 4b plotted with this time delay.

The E-D and D-C transitions, in particular, appear to be lagged responses to changes in summer insolation. This delay in atmospheric response is, most likely, associated with the growth of the Laurentide Ice Sheet during this time period. This is consistent with the finding that ocean cooling lagged some 3000 to 5000 years behind ice growth during MIS 4 and MIS 5 [Rudiman and McIntyre, 1979] and the estimated 5000 to 7000 year lag in the PCI response to latitudinal summer and winter variation in insolation [Mayewski *et al.*, this issue].

The fact that the transitions at the E-D, the D-C, and the C-B boundaries occur 5000 years after the passage of summer insolation levels below, above, and below, respectively, their 110,000-year average suggests that there is a minimum ice sheet extent required to sustain the cold circulation mode. After 5000 years of below average summer and above average winter insolation the critical ice volume (or extent) is attained and the circulation pattern changes from warm to cold mode in a matter of a few centuries or less. The return to the warm mode occurs when, after some 5000 years of "ice melting" conditions, the ice sheet again returns to subcritical size. The record of estimated sea level [Mayewski, *et al.*, this issue] indicates that the critical ice volume is associated with a lowering of sea level of  $\approx 50$  m.

If this explanation is valid, then the anomalous nature of the YD circulation mentioned previously becomes clear. The melting of the Laurentide Ice Sheet

beyond the critical 50 m equivalent volume induced the atmospheric B-A transition into the warm circulation pattern. The subsequent cooling associated with the YD expanded the polar cell, strengthened the polar circulation, and created an atypical positive correlation between the PCI and the insolation-induced strengthening of biogenic production.

## 5.2. Summary: Decadal and Centennial Scale Variations

This analysis has identified two climatic modes of short-term variation in atmospheric circulation and biological production which prevailed for periods comparable to, but not always contemporaneous with, the marine isotope stages.

Intervals E, C, and A (Fig. 4) represent a Holocene-like warm mode in which biogenic activity in the ice-free latitudes and meridional circulation patterns are modulated by short term (centennial scale) coolings and warmings so as to create asynchronous behavior in the ammonium concentration and PCI series. Intervals D and B represent a cold mode, similar to conditions prevailing during the glacial maximum, in which biogenic activity is restricted to regions far to the south of the average range of the predominantly zonal polar circulation, creating normally low concentrations of ammonium in the northern atmosphere. Ammonium concentrations increase in concert with PCI expansion into and increased cyclonic activity within the biologically productive areas to the south. Centennial scale transitions between these two climatic modes appear to be strongly linked to ice sheet growth and retreat past some critical threshold of ice volume or extent.

## 6. Summary

Our discussion of the 110,000-year history of atmospheric circulation and biological production has been based on the ammonium concentration record from the GISP2 ice core. The directly measured concentration series was selected for analysis, rather than that of estimated ammonium flux, after a detailed analysis of the relationship among glaciochemical concentrations and a high-resolution simultaneous record of snow accumulation from the GISP2 core. Our analysis of the ammonium concentration record shows that maxima in background levels of ammonium in the Greenland atmosphere are strongly related to and synchronous with summer forcing associated with the precessional cycle of insolation. Minima in background levels, on the other hand, are delayed relative to minima in summer insolation at those times when ice volume is significant. The durations of these delays are similar in magnitude to those of other paleoclimatic variates associated with changes in ice volume.

Decadal and centennial scale variation about background levels of ammonium concentration exhibit two modes of behavior when compared to the record of po-

lar circulation intensity. Transitions between these two climatic conditions appear to be related also to patterns in ice sheet growth and retreat responding to changes in insolation levels.

## Appendix: Empirical Orthogonal Functions

Empirical orthogonal function (EOF) analysis, a time series modification of principle-component analysis of multivariate statistics [Krzanowski, 1988] is used to analyze the covariance structure of multivariate time series [Peizoto and Oort, 1992]. Such a multivariate series of dimension  $m$  with  $N$  observations forms a matrix  $\mathbf{X}$  of dimension  $m \times N$ . The  $m \times m$  sample correlation matrix  $\mathbf{R}$  is calculated by first standardizing each row  $\mathbf{x}_j$  of  $\mathbf{X}$  by subtracting its sample mean  $m_j$  and dividing by its sample standard deviation  $s_j$  to construct the  $m \times N$  matrix of standardized variates  $\mathbf{Y}$  then forming  $\mathbf{R} = \mathbf{Y}\mathbf{Y}^T/(N-1)$ .  $\mathbf{R}$ , being symmetric and positive definite, has positive eigenvalues and orthogonal eigenvectors, which, when arranged in the order of decreasing eigenvalue magnitudes, form a new basis of coordinates that is most efficient in explaining the covariance structure of the multivariate series. If  $\mathbf{V}$  is the  $m \times m$  matrix having these orthonormal eigenvectors as its columns,  $\mathbf{Y}$  can be factored into a product

$$\mathbf{Y} = \mathbf{V}\mathbf{W} \quad (\text{A1})$$

with  $\mathbf{W}$  an  $m \times N$  matrix having orthogonal rows. This factorization can be written as a sum of  $m \times N$  matrices of rank 1

$$\mathbf{Y} = \mathbf{v}^1\mathbf{w}_1 + \dots + \mathbf{v}^m\mathbf{w}_m \quad (\text{A2})$$

formed by the product of  $m \times 1$  and  $1 \times N$  matrices  $\mathbf{v}^i$  and  $\mathbf{w}_i$ . Here  $\mathbf{v}^i$  is the  $i$ th column of  $\mathbf{V}$  and  $\mathbf{w}_i$  is the  $i$ th row of  $\mathbf{W}$ . Each matrix of this sum represents  $m$  time series (its rows) which are "parallel," in that each is a multiple of the common  $\mathbf{w}_i$ .

If  $v_{i,j}$  denotes the  $j$ th component of  $\mathbf{v}^i$ , rescaling the  $j$ th row of  $\mathbf{Y}$  leads to a representation of the  $j$ th series  $\mathbf{x}_j$ ,

$$\mathbf{x}_j = m_j + s_j(v_{1,j}\mathbf{w}_1 + \dots + v_{m,j}\mathbf{w}_m). \quad (\text{A3})$$

It is common for most  $\mathbf{x}_j$  to be well-represented (in the sense of explained variance) by only the first few terms of (A3), and if this is true for all rows  $j$ , the  $m$  series can be approximated by, for example,  $k$  series  $\mathbf{w}_1, \dots, \mathbf{w}_k$  using (A3). This can be an effective reduction in dimension, and if the factors  $\mathbf{v}^i\mathbf{w}_i$  can be associated with known processes, they provide increased understanding of the information content of the multivariate series. Clearly, from (A3), if  $v_{i,j}$  and  $v_{i,n}$  have the same sign, the  $i$ th components in the representation of the two series  $\mathbf{x}_j$  and  $\mathbf{x}_n$  increase together, while if they have opposite signs, one increases while the other decreases. In fact, if the scaling of (A2) is changed so

that the rows of  $\mathbf{W}$  are mutually orthonormal, the sample correlation of  $\mathbf{x}_j$  and  $\mathbf{x}_n$  is given by

$$\text{corr}(\mathbf{x}_j, \mathbf{x}_n) = \frac{(v_{1,j}v_{1,n} + \dots + v_{m,j}v_{m,n})}{N-1}. \quad (\text{A4})$$

The tabulated summaries of EOF analyses included in the text uses this scaling and shows eigenvectors as  $\mathbf{v}^i/\sqrt{N-1}$  in order that the products of two entries from the same column can be directly interpreted as the contribution to the corresponding two chemical species' correlation associated with that EOF.

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