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High northern latitude forest fires and vegetation emissions over the last millennium inferred from the chemistry of a central Greenland ice core

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Abstract. We have analyzed the soluble portion of impurities trapped in solid precipitation that accumulated at Summit (central Greenland) from 1193 A.D. to the present. Seventy-three ice layers show elevated concentrations of ammonium and formate, caused by high-latitude biomass burning debris reaching Greenland. While a mixture of ammonium and formate close to the molar ratio is generally observed in these ice layers, a large depletion of formate relative to ammonium is found in a few cases. The chemical composition of such layers indicates the presence of a mixture of ammonium, formate, and nitrate with a $\text{NH}_4^+(\text{HCOO}+\text{NO}_3^-)$ molar ratio close to 1. These differences may be related to the fire type (flaming versus smoldering) or to meteorological conditions encountered by plumes during their transport toward Greenland. The high-resolution ammonium and formate profiles are used to reconstruct the frequency and the intensity of high-latitude biomass burning input having reached central Greenland since 1193 A.D. Three periods of enhanced biomass burning input over central Greenland are identified: 1200-1350 A.D., 1830-1930 A.D., and to a lesser extent 1500-1600 A.D. The 1200-1350 A.D. time period coincides with warm and dry conditions which characterized the Medieval Warm Period. After a period of infrequent biomass burning input during the coldest period of the Little Ice Age (1600-1850 A.D.), the frequency was enhanced at the turn of the last century and then decreased throughout this last century. Aside from high-latitude biomass burning, the background levels of formate show a slight and persistent decreasing trend over the last 800 years probably reflecting the deterioration of the boreal vegetation from North America.

1. Introduction

The study of chemical parameters that are stored in solid precipitation and accumulated on polar ice sheets in the past provides a unique tool for obtaining information on the composition of the preindustrial atmosphere and its natural variability over various timescales. Studies of ice cores have dealt with various chemical species including those related to sea salt and dust atmospheric aerosols as well as those derived from the sulfur cycle (see *Legrand* [1995] for a review). Recently, a few studies have been dedicated to ammonium and light carboxylic acids. These species were suggested as a means of reconstructing past continental biogenic emissions. For instance, Greenland deep ice cores spanning the climatic change that occurred 15,000 years ago have shown that the background levels of ammonium [*Fuhrer et al.*, 1996; *Mayewski et al.*, 1994] and of formate [*Legrand and De Angelis*, 1995, 1996] were significantly reduced during the ice age with respect to present-day climatic conditions. This is related to the extension of the ice sheet covering North America during the ice age when the biogenic sources (soils and vegetation) were ice covered. Furthermore, other studies revealed that the background levels of ammonium [*Legrand et al.*, 1992; *Whitlow et al.*, 1994] and of formate [*Legrand et al.*, 1995] have been sporadically

enhanced in the past as a result of high-latitude biomass burning plumes that reached Greenland. These studies point out the possibility of investigating the biomass burning history of the boreal zone as a function of past climatic conditions. In addition, detailed studies of the chemical composition of Greenland snow layers containing biomass burning input may also provide information on the chemistry of burning plumes after they have travelled a few days in the free troposphere at high latitudes.

This work is a comprehensive study of the impurities present in a central Greenland ice core spanning the 1193-1767 A.D. time period. Together with a previous study of the 1767-1980 A.D. time period by *Legrand and De Angelis* [1996], this work provides continuous high-resolution chemical profiles that may serve to trace several aspects of the biomass history of North America back over the last millennium, in particular, the intensity and the frequency of forest fires and the intensity of carboxylic acid emissions from vegetation. Such an extended study of numerous forest fire input in Greenland precipitation reveals some departures from the overall chemical signature previously identified. These differences are discussed in terms of fire types and/or chemical processes that occur during the aging of plumes.

2. Dating, Sampling, and Methods

As a part of the European EUROCORE project, a 305-m-long core was extracted in July 1989 at Summit, central Greenland (72°34'N, 37°38' W, 3240 m above sea level). Along the upper 203 m of this main core, numerous measurements have been carried out, including continuous solid conductivity

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measurements [Clausen *et al.*, 1995], and measurements of hydrogen peroxide [Sigg and Neftel, 1991], formaldehyde [Staffelbach *et al.*, 1991], methane [Blunier *et al.*, 1993], and CO₂ [Barnola *et al.*, 1995]. Therefore only small ice lamellae (2 to 5 cm wide, 1 to 3 cm thick, 55 cm long) were available to perform the study of soluble species between 72- and 203-m depth. All lamellae were packed in the field into sealed polyethylene bags, kept frozen, and sent to Grenoble. During the transport to Grenoble, many lamellae were broken, sometimes into small pieces of a few centimeters in length. Owing to the variable quality (number of breaks, thickness) of lamellae reaching the Grenoble laboratory, we have employed two procedures for removing the contamination from the outer part of ice pieces. For lamellae of good quality (70 of a total of 241), the outer parts were shaved off with scalpels, a method previously used by Legrand *et al.* [1993]. Poor quality lamellae were processed by washing ice pieces with ultrapure water under a clean air bench. In Table 1, we report concentrations observed in the inner and outer parts of four ice lamellae, cut in a 50 cm-long ice core. Two lamellae were cleaned with scalpels, two other ones with ultrapure water. As expected, low to moderate contamination has taken place on the outer part of lamellae for sodium, ammonium, magnesium, calcium, formate, chloride, nitrate, sulfate, and oxalate, as suggested by the increase by a factor of 2 to 5 observed in the outer parts with respect to the inner parts of ice sections (Table 1). For these species, concentrations observed in the inner parts of washed lamellae are very similar to those observed by shaving the ice. For these species, the validity of the two cleaning procedures of lamellae is confirmed by the excellent agreement observed (Table 2) between mean concentrations of cleaned lamellae and those observed on other Summit cores sampled by using "contamination free" techniques. In contrast, for acetate, concentrations observed in the inner parts of lamellae are significantly higher in washed lamellae ($18.2 \pm 0.8 \text{ ng g}^{-1}$) compared to the concentrations in shaved lamellae ($8.2 \pm 1.0 \text{ ng}$

g^{-1}) (Table 1). Furthermore, a large standard deviation is exhibited by acetate data set obtained along lamellae (7.7 ng g^{-1}) with respect to the one obtained by Legrand and De Angelis [1996] by cleaning entire ice core sections (2 ng g^{-1} , Table 2). This conclusion is in agreement with the study by Legrand and De Angelis [1996], which pointed out difficulties in cleaning small pieces of ice for acetate. Slightly higher concentrations of potassium are also detectable in the inner parts of washed lamellae compared to the ones of shaved lamellae (Table 1). For this species, we also noted severe contaminations in the outer parts of lamellae (Table 1). The observed large standard deviation of mean potassium concentrations in the samples reported in this study (3.8 ng g^{-1} , Table 2) with respect to the one observed by Legrand and De Angelis [1996] (0.8 ng g^{-1}) also suggests difficulties in cleaning the ice for this species, as was already noted by Legrand *et al.* [1984]. We therefore conclude that for acetate, and to a lesser extent for potassium, the two decontamination procedures achieved on such a small amount of ice material are not necessarily sufficient to guarantee the validity of measurements at the level of a few nanograms per gram. Thus potassium and acetate concentrations observed between 72- and 203-m depth have to be considered with caution.

Above 72-m depth, because of the increasing porosity of the material, firm lamellae were strongly contaminated for carboxylic acid measurements during their storage in plastic bags. This sequence of Summit snow layers has been studied by Legrand and De Angelis [1996] by working on the entire firm cores, without any storage in plastic bags. This latter study guarantees the validity of all measurements including those of potassium and of acetate.

The dating of the upper part of the Summit record, from the surface down to 73-m depth (i.e., 1767-1993 A.D.) was achieved by Legrand and De Angelis [1996]. Between 72- and 203-m depth, the dating is based on the presence of a huge volcanic perturbation (1152 ng g^{-1} of sulfate) at 187.64-m depth, which

Table 1. Ion Concentrations (in Nanograms per Gram) in Outer and Inner Parts of Four Ice Lamellae From Summit.

Species	Exterior	Interior (Scalpel)	Interior (Washing)
Na ⁺	26.5 ± 2.0	4.2 ± 2.5	5.6 ± 3.0
NH ₄ ⁺	10.0 ± 0.3	5.1 ± 8.3	1.8 ± 7.0
K ⁺	36 ± 18	0.4 ± 0.2	2.0 ± 0.4
Mg ⁺⁺	3.7 ± 1.0	1.1 ± 1.1	2.1 ± 1.2
Ca ⁺⁺	57 ± 18	9.0 ± 5.8	10.7 ± 5.3
CH ₃ COO ⁻	32 ± 11	8.2 ± 1.0	18.2 ± 0.8
HCOO ⁻	19.4 ± 8.0	8.2 ± 2.4	11.6 ± 2.9
Cl ⁻	44 ± 11	9.2 ± 3.0	8.2 ± 3.2
NO ₃ ⁻	69 ± 2	64.9 ± 16.8	58.4 ± 17.9
SO ₄ ⁻	51 ± 12	27.5 ± 17.5	59.0 ± 17.1
C ₂ O ₄ ⁻	2.9 ± 0.3	0.2 ± 1.4	2.7 ± 1.1
C ₂ H ₃ O ₃ ⁻	1.8 ± 0.8	0.5 ± 0.3	1.3 ± 0.4

Two lamellae have been washed with ultrapure water; two others, with scalpels.

Table 2. Comparison of Ion Concentrations (in Nanograms per Gram) in Cleaned Summit Ice Lamellae (This Work) With Previous Measurements Achieved by Different Authors on Entire Summit Ice Cores by Using “Contamination Free Techniques”

Species	Summit 1200-1770 A.D. (This Work)	Summit 1250-1900 A.D. [Whitlow <i>et al.</i> , 1992]	Summit 1770-1890 A.D. [Legrand and <i>De Angelis</i> , 1996]
Na ⁺	5.9 ± 6.8	5.7 ± 2.6	6.2 ± 5.4
NH ₄ ⁺	5.1 ± 8.4	6.1 ± 4.8	5.1 ± 9.2
K ⁺	1.5 ± 3.8	2.0 ± 3.3	1.2 ± 0.8
Mg ⁺⁺	1.4 ± 1.1	1.3 ± 0.4	1.4 ± 1.1
Ca ⁺⁺	6.9 ± 6.7	7.6 ± 3.0	7.1 ± 6.7
CH ₃ COO ⁻	10.0 ± 7.7	ND	6.5 ± 2.0
HCOO ⁻	9.7 ± 7.7	ND	9.9 ± 15.4
Cl ⁻	12.2 ± 9.1	13.1 ± 4.6	12.3 ± 8.1
NO ₃ ⁻	62.1 ± 19.0	70.4 ± 10.3	62.7 ± 16.6
SO ₄ ⁻	34.9 ± 38.5	37.1 ± 22.0	38.6 ± 61.2
C ₂ O ₄ ⁻	0.55 ± 1.22	ND	0.39 ± 1.12
C ₂ H ₃ O ₃ ⁻	1.2 ± 1.2	ND	1.0 ± 0.6

ND, not determined.

was previously attributed by *Langway et al.* [1988] to a 1259 A.D. eruption. Using volcanic horizon as a reference, we have established the dating of the ice core between 72- and 203-m depth (i.e., 1767 to 1193 A.D.) by counting the yearly variations in calcium and ammonium concentrations, both of which exhibit a well-marked seasonal cycle in Summit snow layers [*Whitlow et al.*, 1992].

3. Identification of Forest Fire Input in Greenland Snow Layers

In order to investigate the past frequency, intensity, and chemical fingerprint of high-latitude forest fire smoke plumes having reached the Greenland ice sheet, we first need to establish an adequate statistical and chemical criterion able to identify snow layers containing traces of biomass burning material and to quantify the magnitude of the corresponding perturbation relative to the background level. Previous studies have shown that the overall chemical fingerprint of boreal biomass burning in Greenland snow layers is the presence of a mixture of ammonium and formate close to the molar ratio [*Legrand et al.*, 1992; *Legrand and De Angelis*, 1995, 1996]. The authors concluded that biomass burning input is present in Summit snow layers when ammonium concentrations are higher than 18 ng g⁻¹. The high-resolution formate, ammonium, and nitrate profiles allow us here to examine in more detail the way to distinguish sporadic biomass burning input from the variability of the background level of these two species. The formate profile exhibits a very stable background level (Figure 1) with a slight and persistent decreasing trend from 10.5 ng g⁻¹ at 1250 A.D. to 6 ng g⁻¹ at present time. As is discussed in section 7, such

changes reflect natural phenomena, as well as the impact of man-made activities. The ammonium profile exhibits noisier behavior (Figure 1). The examination of this high-resolution profile indicates that ammonium values can reach up to 40 ng g⁻¹ in snow layers revealing no change of the formate level. These ammonium peaks correspond to a well-marked summer maximum of ammonium content in Summit snow layers, as has already been mentioned by other authors [*Whitlow et al.*, 1992; *Silvente and Legrand*, 1993; *Fuhrer et al.*, 1996]. The linear regression of ammonium and nitrate concentrations (expressed in microequivalents per liter) in summer snow layers free of biomass burning input (individual samples as well as mean 10-year seasonal values, Figure 2) yields [NH₄⁺] = 0.94 [NO₃⁻] - 0.66, with a correlation coefficient *R* of 0.83. That suggests that these summer ammonium maxima are accompanied by an input of nitrate. The previous ammonium criterion ([NH₄⁺] > 18 ng g⁻¹) applied to identify snow layers containing biomass burning debris is therefore too selective for high-resolution time series in which the seasonally higher summer ammonium values are incorrectly detected as biomass burning events. A double condition on both formate and ammonium is therefore needed to accurately identify sporadic biomass burning input along such high-resolution profiles.

A numerical treatment was applied to the formate and ammonium profiles. Each concentration greater than the average value plus one standard deviation (~16 ng g⁻¹ and ~13 ng g⁻¹ for HCOO⁻ and NH₄⁺, respectively, Table 2) was removed from the profiles in order to estimate the background concentration of both species. A moving window of 10 years was applied to the resulting profiles to calculate mean (*m_t*) and standard deviation (*σ_t*) as a function of time. Then we subtracted from all

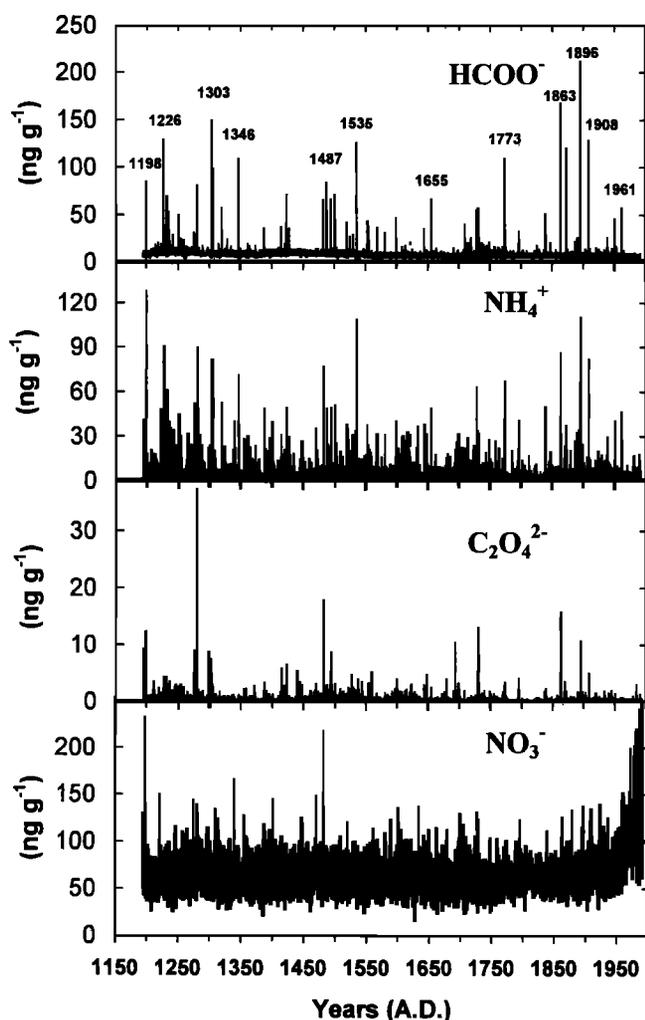


Figure 1. Continuous high-resolution formate, ammonium, oxalate, and nitrate depth profiles of Summit snow layers deposited over the 1200-1770 A.D. time period together with similar data from *Legrand and De Angelis* [1996] over the 1770-1980 A.D. time period.

concentrations the corresponding background value and divided the result by σ , to standardize the concentrations. For formate concentrations (C_i) of samples included in the 10-year interval, the standardized formate values (C_{sd}) were obtained as follows:

$$C_{sd} = (C_i - m_i) / \sigma_i$$

These calculated C_{sd} values are independent of the temporal variability of the background value over the studied time period. In order to isolate snow layers contaminated by biomass burning input, we first selected standardized formate values (C_{sd}) equal to or higher than 3 (i.e., $[\text{HCOO}^-] \geq \sim 18 \text{ ng g}^{-1}$). This first condition corresponds to a statistical criterion for which a C_{sd} formate value higher than 3 has a 99.8% confidence level to correspond to a sporadic perturbation with respect to the background concentration. Such a procedure discards moderate seasonal increases of ammonium for which no formate change is detected. Conversely, to eliminate from the selection snow layers having a C_{sd} formate value higher than 3 and revealing no simultaneous increase of the ammonium content, we applied a second condition: ammonium C_{sd} equal to or higher than 2 ($[\text{NH}_4^+] \geq \sim 11 \text{ ng g}^{-1}$).

4. Chemical Fingerprint of Forest Fires in Greenland Snow Layers

Using the above discussed procedure, 73 Summit snow layers have been identified as contaminated by biomass burning input over the 1193-1980 A.D. time period. In their previous study of Greenland snow layers deposited over the last two centuries, *Legrand and De Angelis* [1996] observed a formate to ammonium molar ratio of 1.05 along ammonium rich layers. As is shown in Figure 3a, when all biomass burning input having taken place over the 1193-1980 A.D. time period is considered, a quite different picture emerges, with a decreased correlation coefficient R of the relationship between ammonium and formate contents (0.85 instead of 0.99). Figure 3a suggests that this weaker correlation between ammonium and formate contents is due to the presence of an excess of ammonium relative to the formate content along a few events having occurred during the 1193-1770 A.D. time period. Nitrate concentrations are sometimes enhanced in layers also enriched in ammonium and formate (Figure 1). *Whitlow et al.* [1994] also noted the presence of elevated nitrate level in biomass burning signals in ice cores, but this phenomenon is not always prevalent, as previously discussed by *Legrand and De Angelis* [1996]. Figure 3b shows a better fit when considering the excess of ammonium versus the sum of excess formate and of excess nitrate ($\Delta[\text{NH}_4^+] = 1.08 (\Delta[\text{HCOO}^-] + \Delta[\text{NO}_3^-]) + 0.43$, with a correlation coefficient R of 0.96) instead of the excess of ammonium versus the one of formate ($\Delta[\text{NH}_4^+] = 1.3 \Delta[\text{HCOO}^-] + 0.71$, with a correlation coefficient R of 0.85). This suggests that when present in snow layers, the excess of ammonium relative to formate corresponds to the presence of a mixture of ammonium and nitrate close to the molar ratio.

Increases of the background level of some other species, including acetate, glycolate, oxalate [*Legrand and De Angelis*, 1996], and potassium [*Whitlow et al.*, 1994; *Legrand and De Angelis*, 1996], have also been detected previously in a few of these events. However, these observations have been obtained by studying the limited number of events recorded over the last 200 years. We here extend the chemical study of Summit snow layers containing biomass burning input that have occurred since 1193 A.D. As is seen in Figure 4, which depicts the chemical composition of an ammonium rich snow layer, in addition to the level of potassium the levels of other cations like those of calcium, and to a lesser extent magnesium, are also enhanced.

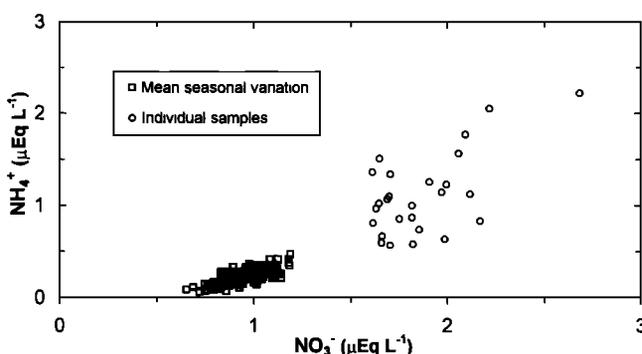


Figure 2. Ammonium as a function of nitrate concentrations (expressed in microequivalents per liter) observed in Summit snow layers free of formate input ($[\text{HCOO}^-] < 10 \text{ ng g}^{-1}$). Squares correspond to values obtained from 10-year averaged seasonal variations observed over the 1200-1300 and 1700-1800 A.D. time periods. Circles correspond to individual summer samples containing more than 100 ng g^{-1} of nitrate.

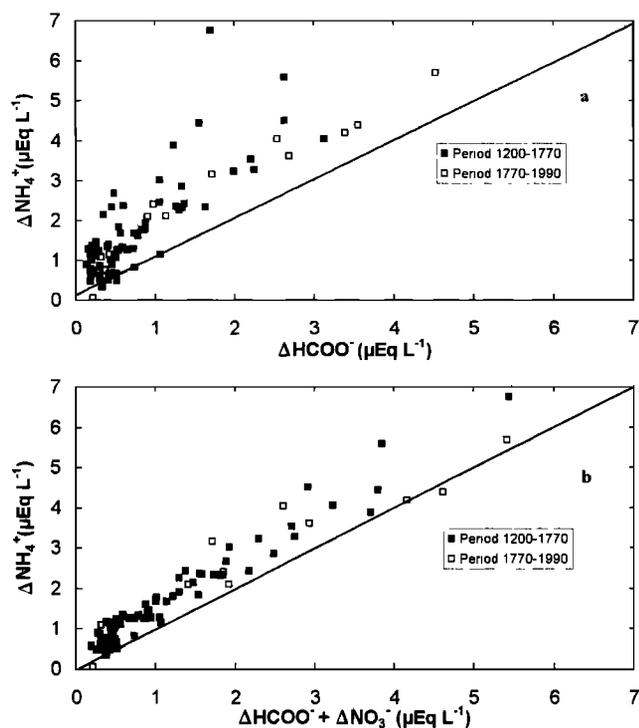


Figure 3. Enhancement of ammonium (ΔNH_4^+) above the background level (see text) as a function of (a) excess of formate and (b) excess of formate plus excess of nitrate expressed in microequivalents per liter. Solid squares correspond to the 1200-1770 A.D. time period; open squares correspond to data obtained by Legrand and De Angelis [1996] over the 1770-1990 A.D. time period. Solid lines refer to the molar ratio.

The presence of calcium in ammonium rich Summit snow layers is not surprising, since biomass burning is known to represent a source of inorganic aerosols containing calcium and potassium as major cations [Echalar *et al.*, 1995; Gorzelska *et al.*, 1994]. Figure 5 summarizes the concentrations of all ions, for which elevated levels with respect to the background level are observed in snow layers containing biomass burning input, as a function of ammonium concentrations. They include the non-sea-salt contribution of potassium, calcium, and magnesium (denoted nssK^+ , nssCa^{++} , and nssMg^{++} , respectively). These non-sea-salt contributions have been calculated by using data on sodium, a good tracer of sea salt, and the K/Na, Ca/Na, and Mg/Na bulk seawater ratios (0.037, 0.037, and 0.12, respectively). Figure 5 shows that ammonium and formate rich layers contain sometimes elevated concentrations of oxalate, glycolate, nitrate, nssK^+ , and nssCa^{++} . However, some snow layers containing more than 100 ng g^{-1} of ammonium do not reveal elevated concentrations of oxalate, glycolate, nitrate, nssK^+ , and nssCa^{++} (Figure 5). That makes it difficult to use these species as unambiguous tracers of high-latitude biomass burning input in Greenland snow layers. Finally, the ammonium rich layer depicted in Figure 4 shows an enhanced sulfate concentration (66 ng g^{-1}) with respect to the background level (35 to 40 ng g^{-1} , Table 2). However, our data do not reveal a general increase of sulfate in ammonium rich snow layers. Although elevated concentrations of sulfate have been observed in air masses impacted by biomass burning plumes [Andreae *et al.*, 1988; Gorzelska *et al.*, 1994], on a global scale, the sulfur emissions from biomass burning weakly contribute to the natural sulfur cycle, which is dominated by other natural sources including

marine biogenic emissions and noneruptive volcanic emissions [Bates *et al.*, 1992].

In Figure 6, we observe a good relationship between nssK^+ and nitrate concentrations (correlation coefficient R of 0.71 instead of 0.50 for the relationship between nssK^+ and ammonium). Furthermore, a better fit is also observed for calcium and magnesium (Figure 6). Conversely, formate levels are not dependent on the nitrate level, and the formate to ammonium molar ratio tends to be lower when large amounts of nitrate are present. Table 3 summarizes the mean chemistry of the 73 snow layers contaminated by biomass burning as a function of the nitrate level. Biomass burning events characterized by nitrate contents higher than 100 ng g^{-1} are accompanied by higher mean nssCa^{++} contents than the ones containing less than 100 ng g^{-1} of nitrate (8.9 instead of 3.3 ng g^{-1} , Table 3). In spite of difficulties encountered in obtaining valid potassium data over the 1193-1770 A.D. time period (see section 2), Table 3 indicates that high nitrate contents of snow layers containing biomass burning input are also accompanied by enhanced nssK^+ content. No significant changes of nssMg^{++} content as a function of the nitrate content is revealed ($1.0 \pm 1.2 \text{ ng g}^{-1}$ for samples containing more than 100 ng g^{-1} of nitrate instead of $0.4 \pm 0.5 \text{ ng g}^{-1}$ in those containing less than 100 ng g^{-1} of nitrate). In summary, this extended study of the chemical composition of Summit snow layers containing biomass burning input indicates an overall presence of a mixture of ammonium and formate close to the molar ratio, in addition to a variable amount of ammonium and nitrate in stoichiometric proportions. The concentrations of cations like potassium and calcium tend to be higher in nitrate rich snow layers.

These differences in the chemical composition of biomass burning material reaching the Greenland ice cap may be related to phenomena occurring during the transport of the plume toward Greenland and/or the fire type. In agreement with a dominance of smoldering processes in boreal forest fires [Lebel *et al.*, 1991], the partitioning between nitrogen-derived species is in favor of ammonium relative to nitrate in biomass burning material reaching Greenland. However, the good relationship observed between nssK^+ and nitrate concentrations tends to suggest that the fire type influences the chemistry of material reaching Greenland. Flaming fires may emit more nitrogen oxides than smoldering fires [Lebel *et al.*, 1991]. In addition, Echalar *et al.* [1995] observed larger emission factors for potassium under flaming conditions with respect to smoldering conditions. It is therefore possible that the chemistry of material reaching Greenland is partly related to fire conditions. The presence or the absence of nitrate and nssK^+ in Summit snow layers contaminated by biomass burning may also be related to the history of plumes, in particular, the efficiency of scavenging processes during the travel of the plume toward the Greenland ice cap. At present, it remains difficult to evaluate this effect because of the complexity of the chemistry of a biomass burning plume. Biomass burning plumes reaching Greenland contain aerosols and water soluble gases such as nitric acid, ammonia, and carboxylic acids, as observed by Dibb *et al.* [1996]. Owing to removal during the transport, these species may be depleted. However, during transport, oxidation mechanisms of hydrocarbons may occur in the gas phase: oxidation of alkenes by ozone, for instance, as well as by aqueous phase chemistry through the oxidation of formaldehyde. The occurrence of this aqueous chemistry is supported by the observation of enhanced formaldehyde content in ammonium rich Summit snow layers [Fuhrer *et al.*, 1993] and by other arguments developed by Legrand and De Angelis [1996]. Our observation of a lower formate to ammonium ratio in snow layers containing high levels

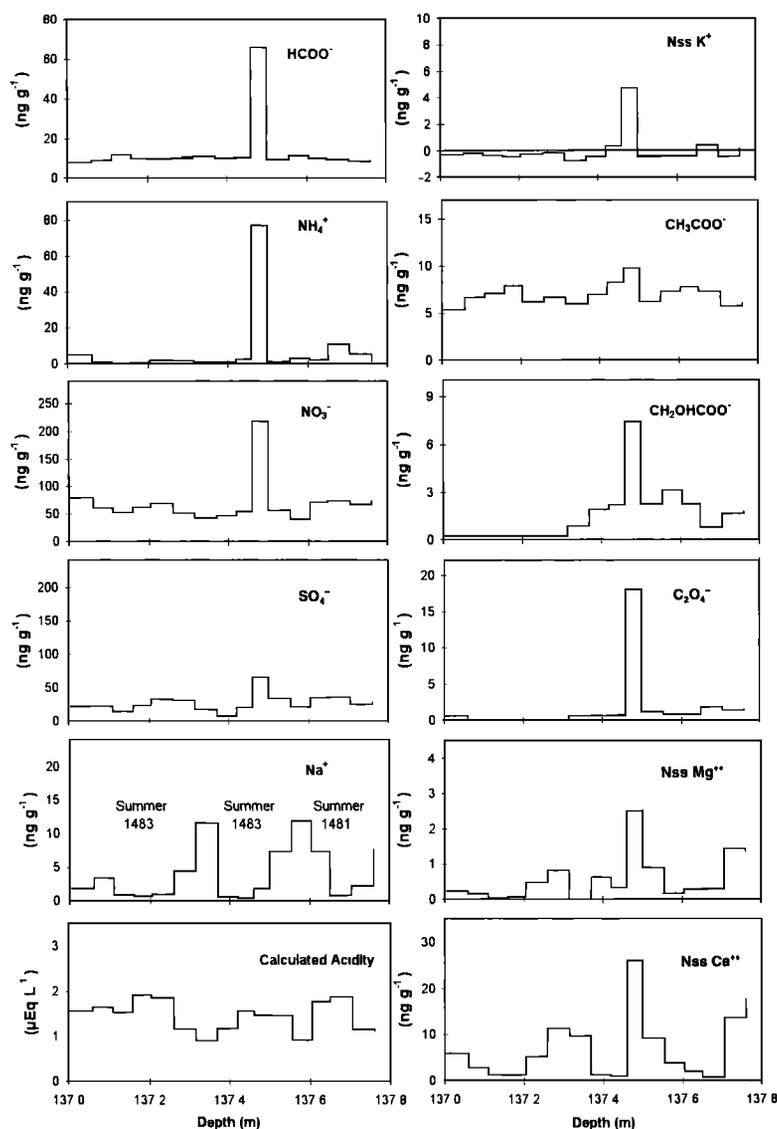


Figure 4. Formate, ammonium, nitrate, sulfate, sodium, acidity, non-sea-salt potassium (nssK⁺), acetate, glycolate, oxalate, non-sea-salt magnesium (nssMg²⁺) and non-sea-salt calcium (nssCa²⁺) contents along Summit snow layers showing biomass burning input (ammonium and formate peaks) accompanied by a large enhancement of nitrate content at 137.45-m depth (dated at 1482 A.D.). The acidity values have been calculated from the positive imbalance between cations and anions [see Legrand and De Angelis, 1995].

of nssK⁺ and nitrate may be related to plumes having experienced weak wet removal and subsequently less aqueous phase formic acid production. Further work is needed to explore in more detail the chemical changes that occur during the aging of biomass burning plumes.

5. The 1193-1980 A.D. Fire History

In contrast to tropical biomass burnings, which are primarily related to human activities, natural fires (lightning) account for 80% of the total area burned in the boreal zone [Stocks, 1991]. A large interannual variability in the occurrence and the extent of forest fires is therefore expected in response to past climatic conditions (length and intensity of dry season, lightning

occurrence). Two possibilities have previously been explored in reconstructing past fire activity.

First, the study of charcoal fossils preserved in lake sediments can provide information on regional fire history. Although a large amount of data is available on charcoal deposition in lakes [Swain, 1973, 1978; Terasmae and Weeks, 1979; Clark, 1988a, 1990a; Gajewski et al., 1993], Clark [1988b] pointed out difficulties in translating charcoal records in terms of frequency and intensity of fires. Furthermore, a recent study from Whitlock and Millspaugh [1996], who examined modern charcoal accumulation versus the fire history in Yellowstone National Park, concluded that charcoal accumulation in deepwater sediments may lag several years after the actual fire event and that the abundance may vary with lakes and watershed characteristics.

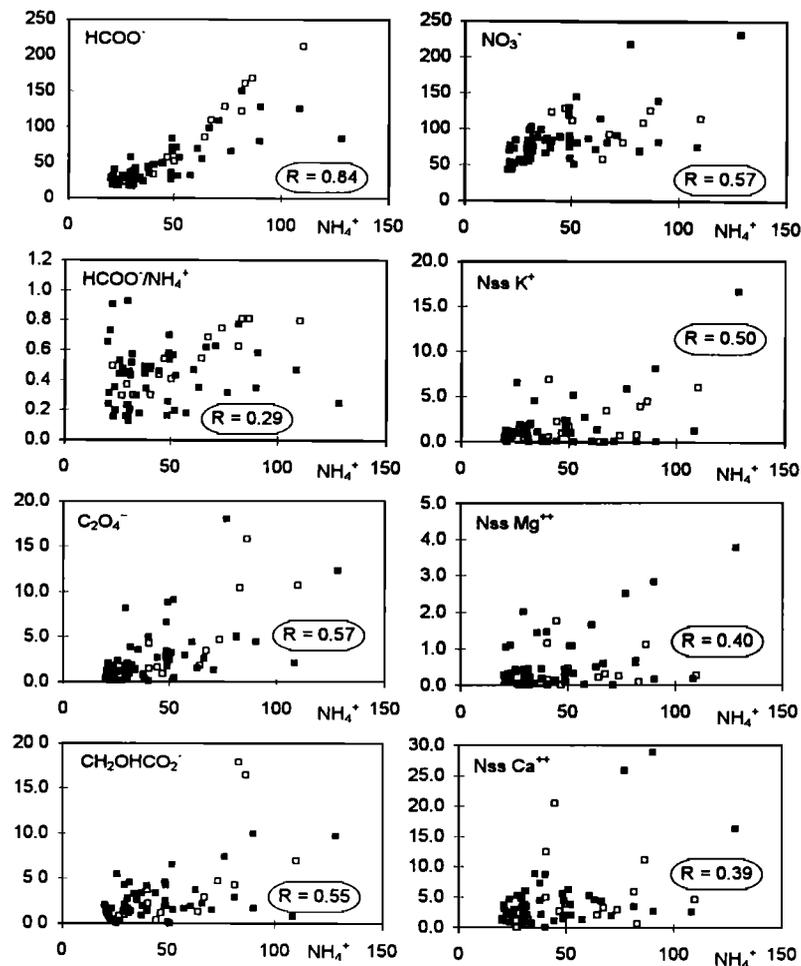


Figure 5. Formate, oxalate, glycolate, nitrate, nssK⁺, nssMg⁺⁺ and nssCa⁺⁺ contents (in nanograms per gram) and the molar ratio R of excess of formate to excess of ammonium as a function of ammonium content in Summit snow layers revealing biomass burning input. Open squares refer to data obtained by Legrand and De Angelis [1996] over the 1770–1980 A.D. time period, and solid squares refer to data obtained in this work over the 1200–1770 A.D. time period.

A second approach is based on the counting of tree rings between fire scars to establish a fire history at an individual site [e.g., Cogbill, 1985; Swetnam, 1993; Mann et al., 1994]. As with charcoal sediments, dendrochronological records have some strong limitations in studying the “climate–fire” relationship. Despite the important number of available data, it still remains difficult to reconstruct a global fire history of a region. For instance, the comparison between fire scars and climate is rendered difficult owing to the influence of local parameters like physiographic factors (slope exposure, wetland distribution, soil texture) [Heinselman, 1973]. At this local/regional scale, a purely statistical approach carried out by Flannigan and Harrington [1988] showed that weather and climate parameters may account for only 11 to 30% of the variance in fire occurrence.

The study of formate and ammonium in Greenland ice cores from Legrand et al. [1992] offers the possibility of reconstructing past biomass burning events from northern North America. From this point of view, Greenland ice records would represent an excellent complementary tool to analyze the link between past large forest fires and climate. Canada and Siberia

represent the two major contributors of high northern latitude biomass burning sources. However, prior to 1920, no direct forest fire statistics are available for circumpolar regions [Stocks, 1991]. Biomass burning material entering the Greenland atmosphere in summer is likely related to fire activity in Canada [Legrand et al., 1995; Whitlow et al., 1994; Fuhrer et al., 1996]. To record a biomass burning event in the ice, it is decisive that the meteorological conditions favored the transport of biomass burning plumes to Greenland and deposited the debris there. There are fires every summer in the boreal forest. Since biomass burning events are not detected every year in Greenland snow layers, we can speculate that the Greenland record only refers to large fires. Thus the probability of detecting a forest fire event in Greenland ice is linked to the area burned and to the transport. The Summit ice record of $\delta^{18}\text{O}$, a proxy for the meteorological conditions influencing central Greenland, suggests that the circulation pattern has not significantly changed over the last 10,000 years. Fuhrer et al. [1996] observed a decreasing frequency of ammonium spikes in ice deposited at Summit over the Holocene, in agreement with enhanced fire activity in the early to middle Holocene with respect to the present suggested

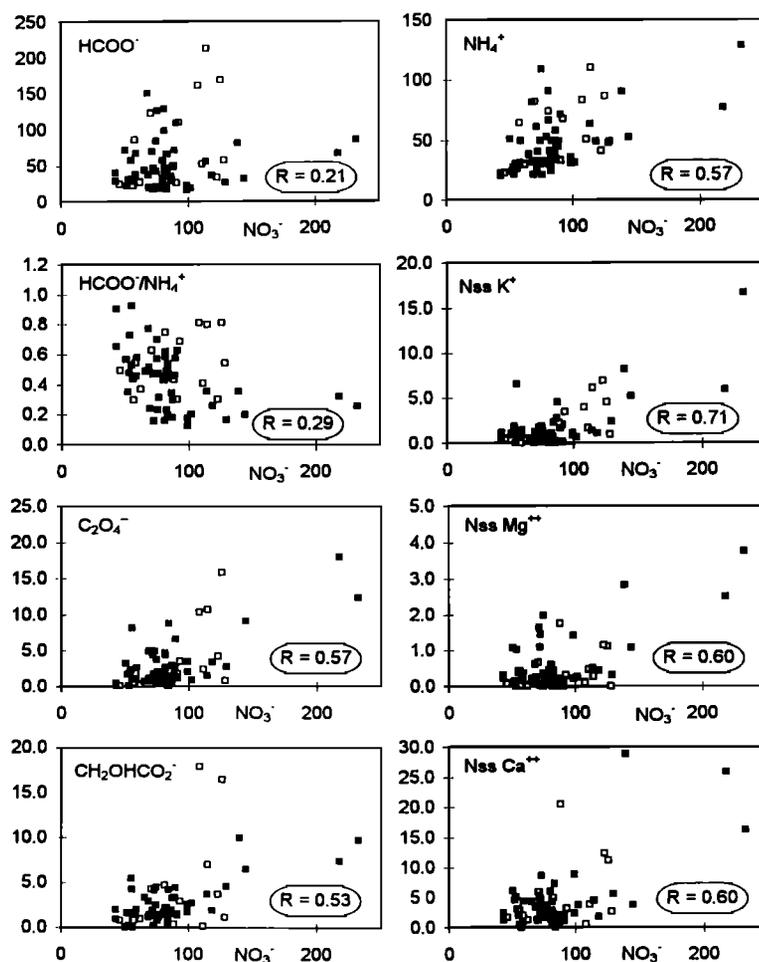


Figure 6. Formate, oxalate, glycolate, ammonium, nssK⁺, nssMg⁺⁺, and nssCa⁺⁺ contents (in nanograms per gram) and the molar ratio R of excess of formate to excess of ammonium as a function of nitrate content in Summit snow layers revealing biomass burning input. Open squares refer to data obtained by *Legrand and De Angelis* [1996] over the 1770-1980 A.D. time period, and solid squares refer to data obtained in this work over the 1200-1770 A.D. time period.

Table 3. Comparison of the Chemical Fingerprint of Summit Snow Layers Containing Biomass Burning Input With Nitrate Concentrations Higher and Lower Than 100 ng g⁻¹

Species	[NO ₃ ⁻] <100 ng g ⁻¹ (58 Events), ng g ⁻¹	[NO ₃ ⁻] >100 ng g ⁻¹ (15 Events), ng g ⁻¹
NO ₃ ⁻	73.3 ± 14.7	136.6 ± 39.0
NH ₄ ⁺	41.9 ± 20.0	68.5 ± 28.3
HCOO ⁻	51.0 ± 35.2	77.2 ± 60.0
C ₂ O ₄ ⁻	2.1 ± 2.0	9.6 ± 9.9
C ₂ H ₃ O ₃ ⁻	2.0 ± 1.3	6.6 ± 5.4
CH ₃ COO ⁻	10.6 ± 7.0	13.8 ± 4.9
Nss K ⁺	1.0 ± 1.2	4.6 ± 4.2
Nss Mg ⁺⁺	0.4 ± 0.5	1.0 ± 1.2
Nss Ca ⁺⁺	3.3 ± 3.2	8.9 ± 8.9
ΔHCOO ⁻ /ΔNH ₄ ⁺	0.46 ± 0.20	0.41 ± 0.21

by charcoal records in lakes from most regions in Canada. Thus on a long-term basis, the ammonium spike record in Greenland ice is dominated by the surface area burned. However, over the timescale of the last millenium discussed in this paper, we are still aware that short-term variability of the circulation pattern may have biased the record.

Using the method described in section 3, biomass burning input reaching Greenland can be accurately identified from the ammonium and formate profiles. Each sample suspected of containing biomass burning debris is rated 1; all other samples are rated zero. A running window of 50 years, corresponding to the longest time period over which no event is recorded, is then applied to the sum of all peaks appearing in the length of the window. The result is then divided by 50 to calculate the mean number of fire input over Greenland per year as a function of time (Table 4). A similar procedure is employed for estimating the mean amount of material per fire deposited in ice as a function of time (Table 4). Finally, a fire index is constructed in order to depict both frequency and intensity of forest fires reaching Greenland over the past by multiplying the fire frequency signal by the fire flux signal. As is shown in Figure 7d, this index points to three active periods of fire input: 1200-1350, 1830-1930, and, to a lesser extent, 1500-1600 A.D. Table 4, which summarizes the main characteristics of these three active periods in terms of frequency and intensity, indicates that the three time periods had a different dynamic feature. The two oldest time periods (1200-1350 and 1500-1600 A.D.) correspond to a high frequency of fire events with a low flux of deposition compared with the 1830-1930 A.D. time period, which was characterized by less frequent events of high intensity. As a result of a rather slow degradation of organic matter at the ground, the boreal forest is characterized by a large accumulation of dead organic matter (18 to 19 x 10⁶ grams per hectare [Braque, 1988]). The fire frequency is partly controlled by the fuel accumulation [McBride, 1983; Clark, 1988a, 1990a; Mann *et al.*, 1994], and this may explain our observation of a reverse relationship between the frequency and the flux of deposition debris of fires. Such a reverse relationship between the frequency and the amount of material of fire events recorded in Greenland ice was also observed on a more local scale from a study of tree trunk fire scars in a western North America forest [Swetnam, 1993]. This study indicates that the extent of fires varies inversely with burning frequency, and the author suggested that low fuel accumulation occurring over time periods of high fire frequency restricted burned area, whereas time periods of low fire frequency lead to an accumulation of a large amount of fuel permitting new fires to be more widespread and intense.

In Figure 7c, we report charcoal sediment data obtained from three sites in Maine (Conroy Lake and Basin Pond) and New York (Clear Pond) by Gajewski [1985]. The vegetation at these

three sites, located at the transition of boreal forest with the deciduous forest, is similar [Gajewski, 1987]. As is depicted in Figure 7c, charcoal records at the three sites are in fairly good agreement and reveal a period of high level of fire from 1830 to 1930 A.D. This picture is consistent with our index of fire input reaching Greenland, which also suggests that the 1830-1930 A.D. time period was the most active period of fire events of the last 800 years (Figure 7d).

6. Index of Fire and Paleoclimate

There is a general consensus among climatologists that two time periods characterized by quite well-marked temperature changes had occurred during the late Holocene. The first time period is the so-called "Little Ice Age" (LIA). During this time period, temperatures dropped to their lowest values since the end of the last glaciation in many areas of both northern and southern hemispheres [Lamb, 1977; Bradley and Jones, 1992]. It appears that the LIA is of global extent with slight difference in timing of its paroxysm, depending on the geographical location [Lamb, 1977; Bradley and Jones, 1992]. The second climatic time period is characterized by warmer conditions than those having prevailed over this last century and has been called the "medieval warm period" (MWP). This warm time period is estimated to have lasted in Europe between 1000 and 1300 A.D. [Lamb, 1977]. Several authors have recently suggested that the MWP is not a global phenomenon [Thompson *et al.*, 1995] and is more difficult to identify in the southern hemisphere records [Hugues and Diaz, 1994]. Even over the northern hemisphere, some geographical differences are seen, for instance, between Scandinavia and western Europe [Briffa *et al.*, 1992]. This lack of common features of climatic fluctuations over the last millennium for the northern hemisphere may partly be due to the low range of temperature variations (~1°C). Therefore the proxy records of LIA and MWP can sometimes be obscured in insensitive natural sites [Williams and Wigley, 1983; Briffa *et al.*, 1990]. Finally, only a limited number of sites provide records of climatic and environmental fluctuations covering the entire last millennium [Jacoby *et al.*, 1996].

Biomass burning plumes reach the Greenland ice cap in summer when the general atmospheric circulation brings air masses originating from the North American continent toward Greenland [Whitlow *et al.*, 1994]. The index of fire built up from the Greenland ice record is therefore compared with available data from northern North America (Figure 7). These data include the ring width index obtained by Archambault and Bergeron [1992], who obtained a 802-year (1186-1987 A.D.) northern white cedar ring width chronology based on 38 trees growing on rocky substrate at Lac Duparquet, western Québec. While this site is not very sensitive to temperature changes, precipitation

Table 4. Past Frequency of Forest Fire Events and Mean Deposition Fluxes of Formate and Ammonium Over the Three Active Periods of Fires Recorded in Snow Layers Deposited at Summit Between 1193 and 1980 A.D.

Periods, A.D.	Frequency (Number of Events per Year)	Mean Flux per Event, g km ⁻²	
		HCOO ⁻	NH ₄ ⁺
1200-1350	0.15	11.1	11.1
1500-1600	0.19	15.0	15.0
1830-1930	0.09	84.6	38.4

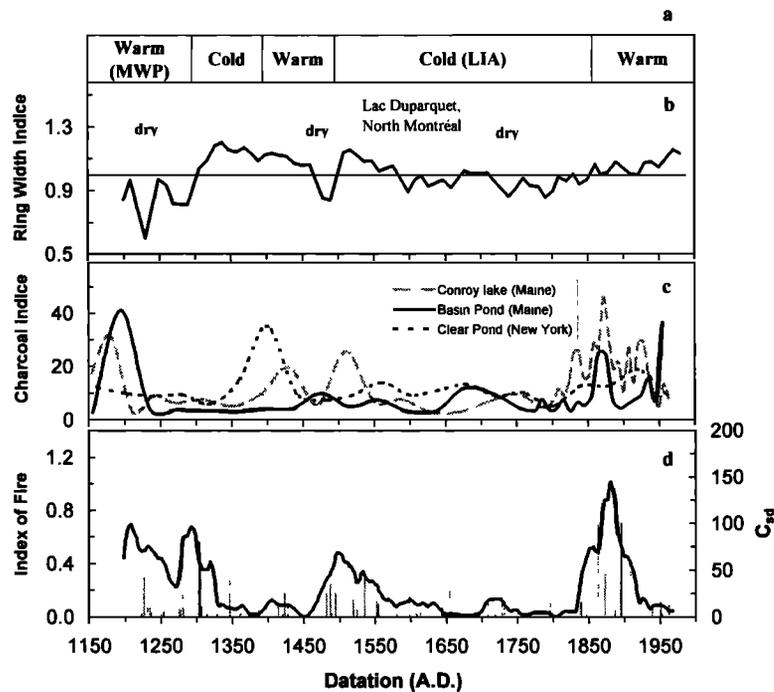


Figure 7. (a) Characteristics of climate in eastern Canadian Arctic regions defined by *Williams and Wigley* [1983]. (b) Ring width index from *Archambault and Bergeron* [1992] giving insights of long-term precipitation changes. (c) Charcoal index in three lakes located in Maine [*Gajewski*, 1985]. (d) Occurrence of fires detected in the Summit ice core (C_{fire} , vertical bars) and index of fires (solid line) (see text).

largely controls the growing processes of trees at this site. The Lac Duparquet trees show significant correlation with the drought code data as established by the Canadian Forest Service [*Archambault and Bergeron*, 1992]. We have therefore used this index as a signal of drought in this region of Québec during the last millennium. *Gajewski* [1988] has reconstructed past summer temperatures over the last 2000 years by analyzing well-dated pollen profiles obtained from six sites located from Maine to Minnesota. Summer temperatures estimated from these pollen diagrams show a long-term cooling with superimposed fluctuations. However, since this study is based on discontinuous sampling with a typical 40-year interval between samples, a direct comparison between our fire index and this study is not easy because of the different temporal resolution of the two data sets. *Williams and Wigley* [1983] have compiled data from glaciers, tree lines, tree rings, pollens, and ice cores from North America, Greenland, and Europe covering the last 2000 years. Despite the overall uncertainties in dating, interpretation, response times, and "noise level" of these proxy climatic data, these authors identified the several-centuries-long cold period of the LIA and the warm MWP during the twelfth century in all records from these regions (Figure 7a). However, the timing of the paroxysms of these climatic episodes seems to have regionally varied [*Williams and Wigley*, 1983].

The 1200-1350 A.D. time period corresponds to the MWP, which was characterized by a warm climate, as is seen in the qualitative estimate of climate from *Williams and Wigley* [1983] (Figure 7a) in the eastern Canadian Arctic. At this time, the Québec region seems to be dry, as is suggested by the ring width index from *Archambault and Bergeron* [1992]. The high fire event index revealed for this period by the Greenland ice is therefore in very good agreement with the warm and dry climatic

conditions having taken place at this time. High temperatures and low precipitation are climatic conditions favoring natural fire occurrence. As was previously mentioned (section 5), this high fire event index is characterized by a high frequency of fires and a rather low intensity (Table 4). Such behavior is expected in a warm and dry climate, which, because of a high probability of fire occurrence, has limited the fuel accumulation and thus the extent of fires.

During the following 1350-1500 A.D. time period, low fire activity is suggested by the Greenland ice index (Figure 7d) and may be the consequence of a wetter climate having prevailed in Québec at this time (Figure 7b). The colder climate during this period with respect to the preceding time period may also have decreased the fire activity. At around 1500 A.D., the fire activity increased, as interpreted from the Greenland index (Figure 7d). The 1500-1600 A.D. time period was also characterized by high frequency and low intensity of fires (Table 4). Over this period, while the climate seems to have been dry at least at the beginning of the period (Figure 7b), the climatic conditions suggested by *Williams and Wigley* [1983] remain unclear. During the fifteenth century, summers were warm in the eastern Canadian Arctic and southern Greenland, while a cold episode in Europe and western North America is suggested by *Williams and Wigley* [1983].

During the 1600-1830 A.D. period, all charcoal indices reported in Figure 7c agree with the very low fire activity suggested by the Greenland index (Figure 7d). The qualitative climate estimation from *Williams and Wigley* [1983] indicates the cold conditions of the LIA. The cold temperatures observed during the LIA have been accompanied by dry conditions (Figure 7c). Over this time period, it seems that the cold temperature was the major climatic factor that influenced fire

activity. Such conditions possibly limited the occurrence of lightning, a major natural cause of fire, in connection with very stable air mass conditions.

The transition time from the nineteenth to the twentieth century is marked by a high fire index (Figure 7d), with low frequency and high fluxes (Table 4). This behavior may result from the high amount of organic matter accumulated during the LIA. All charcoal indices support the idea of enhanced fire activity at this time in the northeastern United States (Figure 7c). Here we cannot exclude anthropogenic ignition of fires during this period. *McAndrews and Boyko-Diakonow* [1989], in studying pollen assemblage at Lac Crawford (Ontario), have shown that gradual forest clearance and farming had started in 1820.

Very little fire activity is recorded for the 1930-1990 A.D. time period, as is suggested in Figure 7. *Heinselmann* [1973] and *Clark* [1990a] have also reported decreased fire frequency over this time period in northern Minnesota sites. It is likely that the policy of fire suppression adopted by governments in 1910 contributed to this low fire activity despite the fact that warmer weather has occurred since the LIA. For instance, the effect of Canadian fire management activities on the total area burned is evident in Canada, with an increase in the percentage of fires with a small area burned and a decrease in fires with a large area burned over the past seven decades [*Stock*, 1991].

7. The Formate Background Level Over the Last 800 Years

As was mentioned in section 2, the background formate level (i.e., free of biomass burning input) of Summit snow layers exhibits a quite regular decreasing trend from 10.5 ng g⁻¹ to 8 ng g⁻¹ between 1200 and 1950 A.D. followed by a further decrease, with values dropping below 7 ng g⁻¹ after 1950 A.D. Since the level of formate was still high (14.8 ± 2.3 ng g⁻¹) in snow deposited at Summit some 120,000 years ago [*Legrand and De Angelis*, 1996], we can discard the possibility of a formate degradation over time in ice. As was discussed by *Legrand and De Angelis* [1996], such a decrease over recent decades may be related to human activities, which have increased the acidity of precipitation, therefore reducing the scavenging of this weak acid from the gas phase into precipitation in spite of growing hydrocarbon emissions. Previous studies of the preindustrial background level of formate from the Summit core have shown that formate values reached their maxima (13.5 ng g⁻¹) at 4000 years B.P. Thereafter, concentrations decreased, reaching 10 ng g⁻¹ at 1000 years B.P. (i.e., at the beginning of the last millennium) [*Legrand and De Angelis*, 1995]. This decrease in the formate level after 4000 B.P. coincides with the climatic deterioration of conditions experienced by eastern regions of Canada from 4500 to 6500 years B.P. to the present [*Matthews et al.*, 1989]. On the basis of this observation, the authors suggested that biogenic emissions from boreal vegetation are the main contributor to the budget of formate in central Greenland. Figure 8 indicates that the decreasing trend of formate observed over the last millennium had already started around 4000 B.P., suggesting that deterioration of the high-latitude vegetation has been going on over the last millennium. The shift from mixed to boreal forest at the transition of the forest regime suggested by increasing spruce and fir pollen abundance and the decline of beech and maple pollen has been pointed out by many authors [*Swain*, 1978; *Gajewski*, 1987] and has been called the "boreal trend" [*Davis*, 1984]. The southward advance of the boreal forest is thought to be related to cooler climate and a more open canopy. As an example, using the pollen abundance profiles

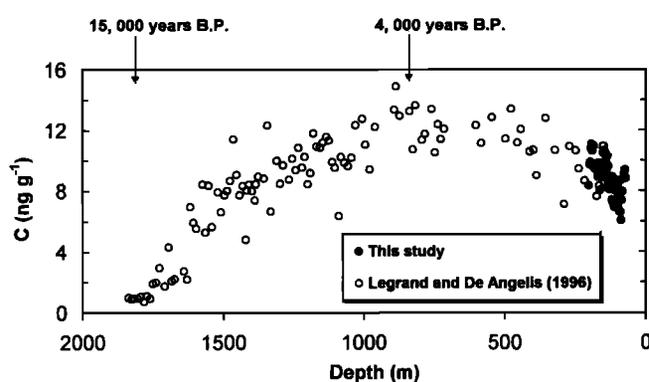


Figure 8. Temporal trend of the background (free of biomass burning input, see text) level of formate in Summit ice since the end of the last glaciation (15,000 years B.P.). Open circles are data obtained by *Legrand and De Angelis* [1996], and solid circles correspond to the study of the last millennium (this work).

obtained by *McAndrews and Boyko-Diakonow* [1989] over the two last millennia and a forest simulator, *Campbell and McAndrews* [1993] suggested that the total biomass of a southern Ontario forest was reduced by 30% over the last millennium. Our study of the background level of formate therefore supports the idea that formic acid emissions are very sensitive to the state of the vegetation from high latitudes.

8. Conclusions

This first high-resolution and comprehensive study of impurities present in central Greenland snow layers in a period covering the last millennium permits a detailed investigation of the evidence of forest fires from Canada that has reached Greenland in the past. The intensity and frequency of forest fire input have changed in the past in response to changes in climatic conditions occurring over North America. Except between 1500 and 1600 A.D., fire activity remained low during the Little Ice Age (1400 to 1850 A.D.). Conversely, greater fire activity is recorded during the Medieval Warm Period (1200 to 1350 A.D.). Finally, fire activity increased at the turn of the nineteenth century. Detailed chemical study of 73 forest fire events recorded in Greenland snow layers since 1193 A.D. confirms an overall presence of ammonium and formate whose ratio is that of stoichiometric proportions of ammonium formate that is sometimes accompanied by an input of ammonium and nitrate close to the molar ratio. Differences in the chemical fingerprint of forest fire events recorded in Greenland snow layers may be related either to the effect of plume aging during transport and/or fire types.

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