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Impact of Preindustrial Biomass-Burning Emissions on the Oxidation Pathways of Tropospheric Sulfur and Nitrogen

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[1] Ice core measurements (H_2O_2 and CH_4/HCHO) and modeling studies indicate a change in the oxidation capacity of the atmosphere since the onset of the Industrial Revolution due to increases in fossil fuel burning emissions [e.g., *Lelieveld et al.*, 2002; *Hauglustaine and Brasseur*, 2001; *Wang and Jacob*, 1998; *Staffelbach et al.*, 1991]. The mass-independent fractionation (MIF) in the oxygen isotopes of sulfate and nitrate from a Greenland ice core reveal that biomass-burning events in North America just prior to the Industrial Revolution significantly impacted the oxidation pathways of sulfur and nitrogen species deposited in Greenland ice. This finding highlights the importance of biomass-burning emissions for atmospheric chemistry in preindustrial North America and warrants the inclusion of this impact in modeling studies estimating changes in atmospheric oxidant chemistry since the Industrial Revolution, particularly when using paleo-oxidant data as a reference for model evaluation. *INDEX TERMS:* 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1040 Geochemistry: Isotopic composition/chemistry; 1610 Global Change: Atmosphere (0315, 0325); *KEYWORDS:* atmospheric chemistry, biomass burning, ice cores

1. Introduction

[2] Our knowledge of the effect of anthropogenic emissions from industrial processes, fossil fuel, and biomass burning on the oxidation chemistry of the atmosphere is highly uncertain. Such activities emit trace species that will tend to both decrease the oxidative capacity of the atmosphere by acting as a sink for the hydroxyl radical (OH), and increase the oxidative capacity through a series of tropospheric ozone (O_3) forming reactions. The oxidative capacity of the atmosphere determines the lifetime of trace species such as CH_4 and CO that have implications for climate change and human health. The understanding of how human activities are impacting the atmospheric oxidation capacity in different regions is of utmost importance in designing future greenhouse gas and air pollution mitigation strategies.

[3] The oxidation capacity is often defined by global mean OH concentrations, computed either by weighting by atmospheric mass or volume, or by the reaction with long-lived CH_4 or CH_3CCl_3 [see *Lawrence et al.*, 2001] whose primary sink is through reaction with OH. Alterna-

tively, it can be defined as global gross OH formation [e.g., *Lelieveld et al.*, 2002]. OH is formed through the reaction of water vapor with $O(^1D)$ following the photolysis of ozone, making OH concentrations dependent upon ozone formation. The lifetime of ozone-precursors (such as CO, NO_x, CH_4 and hydrocarbons) is regulated by OH concentrations, and ozone formation and destruction is highly sensitive to the NO/O_3 ratio. This complex behavior and the uncertainty in the budgets of ozone precursors makes it difficult for photochemical models to estimate the effect that humans are having on the overall oxidative capacity of the atmosphere.

[4] Due to the large spatial and temporal variability of OH, H_2O_2, and O_3, measurements of oxidant concentrations in both the present atmosphere and in paleo-archives provide, at best, a regional picture of oxidant levels. We rely on photochemical transport models to present a more integrated measure of the atmospheric oxidation capacity and address the potential effects of anthropogenic emissions, with regional concentration measurements serving as a metric for model validation. Anthropogenic influence on the chemistry of the atmosphere is generally assumed to coincide with the start of the Industrial Revolution mainly due to increasing emissions from fossil fuel burning. On the basis of this, most models predict global increases in ozone from anthropogenic activities that vary in magnitude. In contrast, the affect of anthropogenic emissions on estimated OH number densities vary from model to model in both sign and magnitude (see Table 1 for examples and references).

[5] Such discrepancies between different models can be resolved by comparing the model results with estimates of past oxidant concentrations obtained through the use of proxies. Such proxies include concentration measurements

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Table 1. Some Examples of Estimated Change in Tropospheric OH and O_3 Concentrations Since Preindustrial Times From Model and Measurement Studies[a]

Authors	Tropospheric OH (% Change Since Preindustrial)	Tropospheric O_3 (% Increase Since Preindustrial)	Comments
Lelieveld and Dentener [2000]		+25% (column abundance)	3D model; with NMHC. Biomass burning doubles between 1860 and 1993, shifts from high to low latitudes.
Lelieveld et al. [2002]	0% (global concentration) +60% (global production)		3D model; with NMHC.
Grenfell et al. [2001]	−4% (global concentration)	+40% (global mass)	3D model; no NMHC. Preindustrial biomass burning 10% of present-day with same geographical distribution.
Hauglustaine and Brasseur [2001]		+57% (global mass) +85% (global production)	3D model; with NMHC. Preindustrial biomass burning 20% of present-day with similar geographical distribution.
Wang and Jacob [1998]	−9% (mass weighted below 150 mbar)	+63% (global concentration) +120% (global production)	3D model; with NMHC. Preindustrial biomass-burning amount and distribution similar to that of today.
Martinerie et al. [1995]	+6% (mass weighted)		2D model; no NMHC.
Volz and Kley [1988]		~+100% (concentration in Paris, France)	Reconstruction of preindustrial measurements.
Staffelbach et al. [1991]	−30% (polar concentration)		Ice core measurements of CH_2O.

[a]NMHC, non-methane hydrocarbon.

of H_2O_2 [*Sigg and Neftel*, 1991] and the HCHO/CH$_4$ ratio [*Staffelbach et al.*, 1991] in ice cores. More recently, the mass-independent composition of the oxygen isotopes of sulfate preserved in ice cores has been proposed as a proxy for past oxidant variations [*Alexander et al.*, 2002]. Although such proxies have provided insight into variations in past oxidant levels on the regional scale, each has its limitations. Post-depositional effects on the gaseous species H_2O_2 and HCHO can alter snow/firn/ice concentrations independent of their atmospheric concentration [*Hutterli et al.*, 2003]. Although the oxygen isotopic composition of sulfate provides information on the relative amount of heterogeneous (H_2O_2, O_3) versus homogeneous (OH) oxidation of S(IV) species, the branching ratios can also vary with factors such as cloud processing efficiency or pH that are independent of the oxidant concentrations themselves. We note that the global oxidizing capacity of the atmosphere is dominated by oxidant concentrations in the tropics and that polar ice cores do not provide direct information about tropical oxidant concentrations. Regardless, they are currently the only paleo-archive that can provide information on past oxidant variations and thus serves as a metric for paleoclimate model validation.

2. Mass-Independent Composition of Sulfate and Nitrate

[6] Kinetic and equilibrium processes such as isotopic exchange or diffusion fractionate isotopes according to mass differences and form highly correlated arrays when plotted as $\delta^{17}O$ versus $\delta^{18}O$, following the relation

$$\delta^{17}\quad\quad 52 \times \delta^{18}O, \quad\quad (1)$$

where

$$\delta(\text{‰}) = \left[\frac{R_{sample}}{R_{standard}} - 1\right] \times 1000$$

and

$$\delta^{17}O : R = \frac{^{17}O}{^{16}O}; \delta^{18}O : R = \frac{^{18}O}{^{16}O}.$$

Any process that does not follow the above equation is referred to as having a mass-independent composition and is measured by

$$\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O. \quad\quad (2)$$

For mass-dependent fractionation, $\Delta^{17}O = 0$. Since the discovery of the mass-independent fractionation (MIF) occurring during ozone formation [*Thiemens and Heidenreich*, 1983], many other atmospheric species have been shown to possess $\Delta^{17}O \neq 0$ including H_2O_2, SO_4^{2-} and NO_3^- [*Thiemens et al.*, 2001].

[7] The positive $\Delta^{17}O$ in sulfate and nitrate originates from transfer mechanisms involving O_3 and H_2O_2 [*Savarino et al.*, 2000; *Michalski et al.*, 2002]. The origin of the positive $\Delta^{17}O$ in ozone has been explained with both kinetic [*Mauersberger et al.*, 1999; *Janssen et al.*, 1999] and symmetry [*Gao and Marcus*, 2001] effects in the 3-body ozone formation reaction:

$$O_2 + O \rightarrow O_3^* + M \rightarrow O_3 + M \quad\quad (3)$$
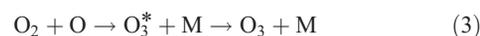
Using measured rate constants and branching ratios for O_3 formation [*Mauersberger et al.*, 1999; *Janssen et al.*, 1999]

in a photochemical equilibrium model, *Lyons* [2001] calculated $\Delta^{17}O = 35$‰ for tropospheric O_3, at the upper end of measurements from *Krankowsky et al.* [1995] and *Johnston and Thiemens* [1997]. The magnitude of the $\Delta^{17}O$ of O_3 is determined by the lifetime of the ozone intermediate (O_3^*), which is pressure and temperature dependent [*Morton et al.*, 1990; *Thiemens and Jackson*, 1990]. Over pressures and temperatures typical of the troposphere, we can estimate a tropospheric O_3 $\Delta^{17}O$ range of ±3‰. Since the $\Delta^{17}O$ of O_3 is only dependent on pressure and temperature, sink reactions from increased anthropogenic emissions will not affect the $\Delta^{17}O$ value of O_3.

[8] $\Delta^{17}O$ values of H_2O_2 in rainwater from La Jolla, California, show a range of $1.3-2.2$‰ [*Savarino and Thiemens*, 1999a]. The $\Delta^{17}O$ has its origin in the 3-body formation of HO_x (OH and HO_2) radicals [*Savarino and Thiemens*, 1999b],

$$H + O_2 + M \rightarrow HO_2 + M, \quad (4)$$
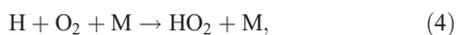
and through the interaction of O_3 in the HO_x cycle [*Lyons*, 2001],

$$OH + O_3 \rightarrow HO_2 + O_2, \quad (5)$$
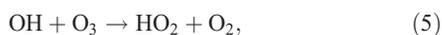
where the major source of H_2O_2 is

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2. \quad (6)$$

Any possible $\Delta^{17}O$ in OH is diluted through isotopic exchange between OH and water vapor ($\Delta^{17}O = 0$), so that $\Delta^{17}O$ of OH equals 0‰ [*Dubey et al.*, 1997; *Lyons*, 2001]. Since there is no significant variability in the $\Delta^{17}O$ of H_2O/OH, the variability in the $\Delta^{17}O$ value of H_2O_2 is dependent only upon the variations in the $\Delta^{17}O$ of O_3 and is expected to be small, irrespective of oxidant levels (discussed above).
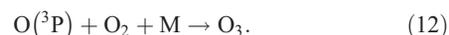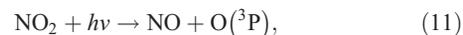
[9] The positive $\Delta^{17}O$ in sulfate originates from aqueous-phase oxidation of SO_2 by H_2O_2 and O_3 from a simple transfer of the isotopic anomaly from the oxidant to the product sulfate [*Savarino et al.*, 2000]. All other sulfate sources, including gas-phase oxidation by OH in the troposphere and primary sulfate [*Savarino et al.*, 2000; *Lee et al.*, 2002] are mass-dependent ($\Delta^{17}O = 0$). The magnitude of the transfer of the $\Delta^{17}O$ varies according to [*Savarino et al.*, 2000]

$$SO_2 + OH \rightarrow \Delta^{17}O = 0\,‰, \quad (7)$$

$$HSO_3^- + H_2O_2 \rightarrow \Delta^{17}O = 0.5 - 1\,‰, \quad (8)$$

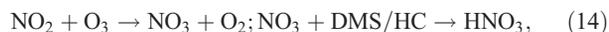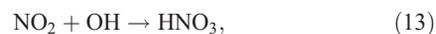$$SO_3^{2-} + O_3 \rightarrow \Delta^{17}O = 8 - 9\,‰. \quad (9)$$
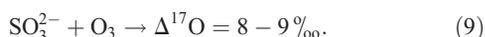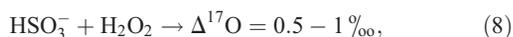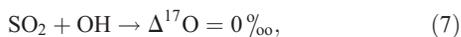
SO_2 has a mass-dependent composition throughout the troposphere due to isotopic exchange with water vapor [*Holt et al.*, 1981], which erases any source-derived isotopic signature in SO_2. Since S(IV) oxidation by O_3 (reaction (9)) is the only mechanism producing sulfate $\Delta^{17}O$ values greater than 1‰, bulk sulfate $\Delta^{17}O$ values greater than 1‰ are a robust indicator o   increased importance of O_3 in

sulfate formation. Once sulfate is formed in the atmosphere, it is very stable (million year timescales), and its isotopic composition is preserved in the ice/firn [*Lloyd*, 1968].

[10] The positive $\Delta^{17}O$ in nitrate originates primarily through NO_x oxidation by O_3 [*Michalski et al.*, 2003; *Lyons*, 2001]. The photo-stationary state of NO_x (NO and NO_2) (reactions (10)–(12)) is several orders of magnitude faster than its removal reactions (reactions (13)–(15)) [*Atkinson et al.*, 1997], so that NO_x rapidly achieves isotopic equilibrium with O_3 and RO_2/HO_2.

$$NO + O_3/HO_2/RO_2 \rightarrow NO_2 + O_2/OH/RO, \quad (10)$$

$$NO_2 + h\nu \rightarrow NO + O(^3P), \quad (11)$$

$$O(^3P) + O_2 + M \rightarrow O_3. \quad (12)$$

The $\Delta^{17}O$ value of NO_x then is a function of the relative degree of oxidation by O_3 and HO_2/RO_2. The final $\Delta^{17}O$ of HNO_3 (nitrate) is dependent upon the $\Delta^{17}O$ of NO_x plus the specific terminal reaction (reactions (13)–(15)).

$$NO_2 + OH \rightarrow HNO_3, \quad (13)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2; NO_3 + DMS/HC \rightarrow HNO_3, \quad (14)$$

$$NO_2 + NO_3 \leftrightarrow N_2O_5; N_2O_5 + H_2O_{surface} \rightarrow 2HNO_3. \quad (15)$$

Variability in $\Delta^{17}O$ of the product nitrate for a given $\Delta^{17}O$ value of NO_x is dictated by shifts in the relative importance of each terminal reaction, with OH dominated systems (reaction (13)) giving the lowest $\Delta^{17}O$ value and the O_3 dominated systems (reaction (14)) giving the highest $\Delta^{17}O$ value [*Michalski et al.*, 2003]. A photochemical box model from *Michalski et al.* [2003] attributed the observed seasonal variation of ~10‰ in $\Delta^{17}O$ of nitrate collected in La Jolla, California, to a shift from ~50% homogenous reactions (reactions (13) and (14)) during the spring to more than 90% heterogeneous reactions (reaction (15)) in winter. This study points to the importance of the specific terminal reaction in determining the $\Delta^{17}O$ value of nitrate.

[11] Physical processes such as transport fractionate in a mass-dependent manner ($\Delta^{17}O = 0$), ensuring that the $\Delta^{17}O$ values of sulfate and nitrate in a given air mass are influenced only by chemical transformation processes. Since $\Delta^{17}O$ values for O_3 are an order of magnitude larger than $\Delta^{17}O$ values for HO_x and H_2O_2, large (>1‰) $\Delta^{17}O$ values in sulfate and nitrate are a robust indicator of the importance of O_3 oxidation. Isotopic measurements of both species preserved in ice cores provide information on how the regional chemistry of sulfur and nitrogen species has varied in the past, and can provide insight into past oxidant variations.

3. Methods

[12] The Site A, Greenland ice core (70°45′N, 35°57.5′W, elevation 3145 m) represents firn samples roughly centered

around the Industrial Revolution, from the surface to a depth of 86 m corresponding to the years 1692–1976. The age-depth scale is from *Clausen et al.* [1988]. Each sample spans a length of 1–3 m, representing a resolution of approximately 10 years. The ice is decontaminated and the sulfate and nitrate extracted from the ice as described by *Alexander et al.* [2002]. Major ion analyses were performed using Dionex DX500 ion chromatographs, using the following configurations: 1) for anions, ASII columns, 6 mM NaOH eluant and 500 μL sample loop; 2) for cations, CS12a columns, 25 nM MSA eluant, and 400 μl sample loop.

[13] Bulk organics were removed from the samples before isotopic analysis by filtering through activated carbon (4–12 mesh) and running the samples through standard silica based C18 cartridges (Alltech). Nitrate and sulfate are isolated and concentrated from the complex mixture of ionic species using a Dionex 2000i ion chromatograph equipped with an AS9-HC separation column and an AMMS III to neutralize the carbonate/bicarbonate eluant. The sulfate and nitrate are then processed according to *Savarino et al.* [2001] and *Michalski et al.* [2002] and measured for the oxygen isotopic composition on a Finnigan MAT 251 isotope-ratio mass-spectrometer. Primary sea-salt sulfate has been subtracted out of the sulfate data using Na^+ measurements as described by *De Angelis et al.* [1997]. Terrestrially derived magnesium (Mg_{terr}^{2+}) can be calculated using Na^+ measurements (assuming Na^+ is entirely of marine origin as done by *De Angelis et al.* [1997]).

4. Results

[14] The 30-year running average of the $\Delta^{17}O$ of non-sea-salt sulfate ($nssSO_4^{2-}$) and nitrate (NO_3^-) from the Site A, Greenland ice core is shown in Figure 1a, along with concentration measurements from the Site A and GISP2 B [*Mayewski et al.*, 1997; *National Oceanic and Atmospheric Administration*, 1997] cores in Figures 1b ($nssSO_4^{2-}$) and 1c (NO_3^-). Our concentration measurements from the Site A core fall within the range of values from the nearby GISP2 B core (72°35′N 38°28′W), and reflect the timing and magnitude of the increases in $nssSO_4^{2-}$ and NO_3^- due to increases in SO_2 and NO_x emissions from fossil fuel burning around the turn of the century [*Mayewski et al.*, 1990]. The trends in $\Delta^{17}O$ for $nssSO_4^{2-}$ and NO_3^- are similar to each other (Figure 1a), with increasing $\Delta^{17}O$ values occurring about a half-century before the concentration increases, peaking around the year 1880, and subsequently decreasing to levels slightly above those observed between the late 1600s and 1700s. The $\Delta^{17}O$ values peak close to 3.5‰ and 30‰ for $nssSO_4^{2-}$ and NO_3^- respec-tively, a 2.5–3‰ difference between the minimum and maximum values. There is no correlation between $nssSO_4^{2-}$ and NO_3^- $\Delta^{17}O$ and Mg_{terr}^{2+} indicating the $\Delta^{17}O$ variation is not the result of changing terrestrial fluxes. Similar measurements of the $\Delta^{17}O$ of $nssSO_4^{2-}$ from the Vostok ice core over a full glacial/interglacial cycle [*Alexander et al.*, 2002] show a 3.5‰ climate variation, with minimum and maximum values at 1.3‰ and 4.8‰ respectively. Analysis of the Antarctic data showed a strong link to O_3 as the source of the $\Delta^{17}O$, and that the ratio of gas-phase (OH) over aqueous-phase (O_3) ion was greater during the
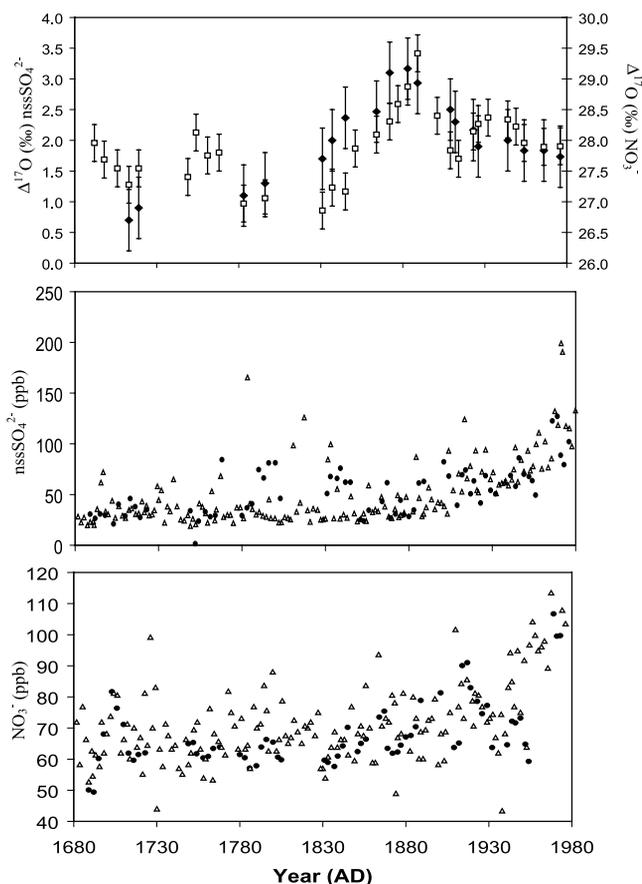

Figure 1. (top) Thirty-year running average of $nssSO_4^{2-}$ (solid diamonds) and NO_3^- (open squares) $\Delta^{17}O$ (‰) measurements as a function of year from the Site A, Greenland ice core. Reproducibility for the $\Delta^{17}O$ measurements is 0.5‰ and 0.3‰ for the $nssSO_4^{2-}$ and NO_3^-, respectively, for sample sizes in the range of 2 to 5 μmol. (middle) $nssSO_4^{2-}$ (ppb) from the Site A (solid circles) and GISP2 (open triangles) ice cores plotted relative to the age of the sample. (bottom) Same as middle panel except for NO_3^- (ppb). GISP2 concentration data provided by the National Snow and Ice Data Center, University of Colorado at Boulder, and the WDC-A for Paleoclimatology, National Geophysical Data Center, Boulder, Colorado, and published in the work of *Mayewski et al.* [1997]. The timescale for GISP2 is from *Meese et al.* [1994].

last glacial maximum than the surrounding interglacial periods. Because S(IV) oxidation by H_2O_2 can only give a maximum $\Delta^{17}O$ of 1‰ for sulfate, the observed values from both ice cores robustly reflect the importance of ozone oxidation in the $\Delta^{17}O$ $nssSO_4^{2-}$ trend.

5. Records of Preindustrial Biomass Burning

[15] In order to determine the cause of the observed trend in the $\Delta^{17}O$ of Site A $nssSO_4^{2-}$ and NO_3^-, we have compared our measurements with other proxies of atmospheric composition during the same time period in Greenland ice. Studies have shown that a mixture of ammonium and formate in Greenland ice close to the molar ratio is

indicative of boreal biomass-burning events [*Legrand et al.,* 1992; *Legrand and De Angelis,* 1995, 1996; *Savarino and Legrand,* 1998]. We compare our isotope data with data from *Savarino and Legrand* [1998], who report high-resolution ammonium and formate profiles in firn and ice samples from Summit (central Greenland). They compute an index of fire based on both absolute and relative concentrations of ammonium and formate in the firn at annual resolution (see *Savarino and Legrand* [1998] for details). Their results show a period of enhanced biomass burning between 1830 and 1930 AD. A comparison of their fire index data, plotted as a 30-year running average (similar to the $\Delta^{17}O$ measurements), with our $\Delta^{17}O$ measurements of $nssSO_4^{2-}$ and NO_3^- (Figure 2) reveals a correlation between the fire index data and $nssSO_4^{2-}$ ($R^2 = 0.56$) and NO_3^- ($R^2 = 0.46$) $\Delta^{17}O$ values. *Savarino and Legrand* [1998] were able to correlate their data with increases in charcoal from lake sediments [*Gajewski,* 1985] in northeastern United States. *Whitlow et al.* [1994] also report ammonium records from the 20D and GISP2, Greenland ice cores that show an increased spike frequency between 1830–1910 attributed to increased biomass-burning activity in North America during this time.

[16] *Holdsworth et al.* [1996] refer to the biomass-burning event that began just prior to the Industrial Revolution (~1850) as the Pioneer Agricultural Revolution (PIAGREV) in North America, citing ammonium, elemental carbon, and microparticle ice core measurements as indicators, along with direct air and ice core CO_2 concentration measurements and $\delta^{13}C$ data from tree cores. Data from *Mayewski et al.* [1993] show that just after 1900 AD, when ammonium concentrations decline to their pre-PIAGREV levels, sulfate and nitrate concentrations in the ice begin to increase, indicating a switch from biomass burning to predominantly fossil fuel burning. The decrease in biomass-burning activity coincides with the beginning of active fire suppression in 1910 in northern North America [*Whitlow et al.,* 1994]. In addition, acidification of the atmosphere since 1900 from fossil fuel burning emissions of SO_2 and NO_x may be accentuating the decrease of ammonium aerosols deposited in Greenland ice through scavenging as suggested by *Whitlow et al.* [1994].

[17] It is generally thought that North America is the main source of continental aerosols in central Greenland due to the westerly circulation of storm tracks. Indeed, *Dibb et al.* [1996] showed that a 1994 biomass-burning plume from the Hudson Bay lowlands region of Canada was transported to Summit, Greenland in 3–4 days resulting in large enhancements in ammonium and formate concentrations in gasphase, aerosol and snow samples. The $\delta^{18}O$ ice record from Summit, Greenland [*Dansgaard et al.,* 1993], which is a proxy for meteorological conditions influencing central Greenland, shows little variability during the past 10,000 years. This suggests that unchanged meteorological conditions can be assumed for the Holocene [*Fuhrer et al.,* 1996], and that the source region for soluble impurities such as sulfate, nitrate, ammonium and formate in the ice remains constant. Climate variability such as the North Atlantic Oscillation and average Greenland coastal temperature during the Holocene has been shown to correlate with $\delta^{18}O$ in Greenland ice [*White et al.,* 1997], and shows no correlation with our Site A $\Delta^{17}O$ da $^2 < 0.02$) further suggesting that
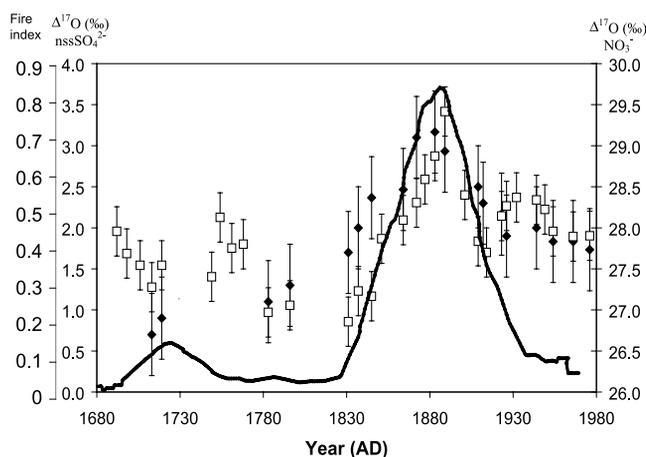

Figure 2. The $nssSO_4^{2-}$ (solid diamonds) and NO_3^- (open squares) 30-year running average $\Delta^{17}O$ (‰) data from the Site A core plotted with the fire index series (solid line) (also a 30-year running average) from *Savarino and Legrand* [1998] from Summit, Greenland (see text). The fire index is a function of both formate and ammonium concentration measurements.

the observed variations in ice impurities cannot be attributed to changing meteorological conditions.

6. Impact of Biomass Burning on the $\Delta^{17}O$ of Sulfate and Nitrate

[18] A schematic of chemical processes that could lead to an increase in $\Delta^{17}O$ of sulfate and nitrate due to biomass-burning emissions is shown in Figure 3. The $\Delta^{17}O$ values of $nssSO_4^{2-}$ from the Site A core during the PIAGREV, which are all greater than 1‰, can only be the result of increases in S(IV) oxidation by O_3. Pre-PIAGREV $\Delta^{17}O$ sulfate values indicate a range of 0–10% of $nssSO_4^{2-}$ formed through O_3 oxidation (reaction (9)), while peak PIAGREV $\Delta^{17}O$ $nssSO_4^{2-}$ values indicate a range of 20–40% O_3 oxidation. A regional increase in O_3 concentration due to biomass-burning emissions is a likely source of this increase in S(IV) oxidation by O_3 during the PIAGREV. Studies on emissions from boreal forest fires are limited in scope relative to studies of burning in the tropics. *Goode et al.* [2000] performed in situ trace gas measurements using FTIR in smoke plumes from large boreal forest fires in interior Alaska. Although measurements well inside a plume did not have detectable O_3, near the edge of a plume they observed an enhanced O_3 formation rate of 50 ppbv/hr. *Browell et al.* [1994] observed >20% increase in O_3 concentrations in aged biomass-burning plumes from Canada and Alaska, influencing about 25% of the free troposphere below 4 km. *Andreae et al.* [1988] sampled biomass-burning plumes and haze layers in the central Amazon Basin. Their measurements showed elevated levels of ozone in the biomass-burning-derived haze layers that contributed significantly to the regional ozone budget, and that most of the ozone production is the result of photochemical oxidation of NMHC produced from biomass burning. *Duncan et al.* [2003] used a 3-D model of tropospheric chemistry and transport to assess the affect of the 1997 Indonesian wild-
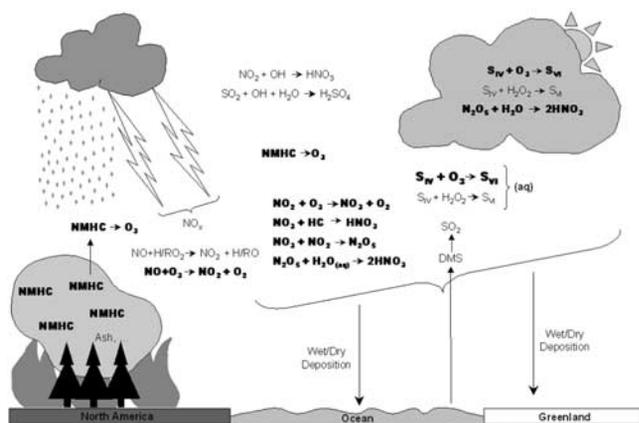
Figure 3. Schematic of chemical processes leading to sulfate and nitrate production. Chemical mechanisms responsible for the observed increase in $\Delta^{17}O$ of sulfate and nitrate as a result of biomass-burning emissions are shown in bold (HC = hydrocarbon). NMHC $\rightarrow$ O_3 is an abbreviation for the following: NMHC + OH + O_2 $\rightarrow$ RO_2 + H_2O; RO_2 + NO $\rightarrow$ NO_2; NO_2 + hv $\rightarrow$ NO + O; O + O_2 $\rightarrow$ O_3.

fires, showing that biomass burning results in a 10% elevation in the O_3 column and a 20% decrease in OH concentrations over much of the tropical Indian Ocean region. Both measurement and modeling studies support our assertion that the $\Delta^{17}O$ fluctuations observed for $nssSO_4^{2-}$ in the Site A ice core are likely due to increases O_3 production via biomass burning.

[19] This assertion is also supported by the simultaneous increase in the $\Delta^{17}O$ of Site A NO_3^-. Biomass-burning emissions can elevate NO_3^- $\Delta^{17}O$ values by shifting the mixing ratios of the relevant oxidants. If O_3 concentrations were increased relative to HO_x, this would favor the O_3 pathway for NO oxidation thus increasing the $\Delta^{17}O$ values in NO_2 (and thus HNO_3). Increasing the $\Delta^{17}O$ values in NO_3^- may also result from an increase in the NO_3-hydrogen abstraction pathway (reaction (14)). High ozone conditions favor the formation of the nitrate radical (NO_3) and biomass-burning plumes are enriched in species such as aldehydes and reactive hydrocarbons that are highly reactive with NO_3. High ozone levels also favor the heterogeneous HNO_3 formation pathway (reaction (15)) by increasing the mixing ratios of NO_2 and NO_3. This is especially relevant in the North Atlantic because colder temperatures increase the proportion of N_2O_5 in the NO_2 + NO_3 $\leftrightarrow$ N_2O_5 equilibrium due to its large temperature dependence. The peak $\Delta^{17}O$ value of 29‰ is consistent with complete heterogeneous hydrolysis at mid latitudes [*Michalski et al.*, 2003], but this value could also be attained with OH + NO_2 + M reactions (reaction (13)) being offset by abstraction reactions (reaction (14)) in an approximately 2:5 fashion.

[20] We note that biomass-burning emissions could increase the $\Delta^{17}O$ value of $nssSO_4^{2-}$ and NO_3^- by increasing aerosol loading and surface area, which would favor the heterogeneous formation pathways. However, aqueous-phase ozone oxidation of S(IV) species is highly pH dependent, with O_3 ox   only being important above

a pH value of about 5.6, and H_2O_2 oxidation dominating below this pH. Measurements of precipitation influenced by biomass-burning emissions in various areas [*Cachier and Ducret*, 1991; *Balasubramanian et al.*, 1999; *Sanhueza*, 1991; *Andreae et al.*, 1988] show low pH values (pH < 5). This acidity is attributed to a mixing of mineral acids (HNO_3 and H_2SO_4) and organic acids (formic and acetic acids) primarily due to chemical production within the plumes. The low pH of these aerosols limits S(IV) oxidation by O_3 and would result in correspondingly low $\Delta^{17}O$ values in the product sulfate in contrast to our observations. The dominant source of sulfate and nitrate to Greenland is thought to be oxidation of marine biogenic sulfur (DMS) [*Patris et al.*, 2002] and volcanic SO_2 [*Legrand*, 1995] and oxidation of NO_x originating from lightning, soil emissions, and stratospheric mixing [*Wolff*, 1995]. Direct transport of sulfate and nitrate generated in continental biomass-burning events to central Greenland does not appear to be significant compared to natural background levels (as also noted by *Wolff* [1995]). The impact of biomass-burning plumes on oxidant levels appears to affect the oxidation pathways of natural SO_2 and NO_x produced downwind of the biomass-burning plume. This is consistent with increases in O_3 formation near the edge of the plume as observed by *Goode et al.* [2000], and the large spatial extent of O_3 column increases calculated by *Duncan et al.* [2003] from Indonesian wildfires.

[21] The magnitude of the increase in O_3 concentrations is difficult to estimate based solely on the measured $\Delta^{17}O$ values. This is because the $\Delta^{17}O$ pathways depend not only on the relative concentration of oxidants but also the dynamics of the reactions such as the amount of gas versus aqueous-phase oxidation, the pH values of the aqueous-phase, the branching ratios of the terminal reactions for nitrate formation, relative concentrations of all oxidants, as well as SO_2 and NO_x concentrations. $\Delta^{17}O$ measurements of sulfate and nitrate collected near boreal fires coupled with modeling studies will help to quantitatively interpret these $\Delta^{17}O$ measurements in terms of variations in atmospheric oxidant chemistry.

7. Conclusions

[22] Biomass burning has long been recognized to be a source of trace species such as CO, NO, CH_4 that can have large impacts on the oxidation capacity of the atmosphere [*Crutzen and Andreae*, 1990]. The present results indicate that biomass burning in North America has a significant impact on the oxidation pathways of sulfate and nitrate in this region in the preindustrial atmosphere during the PIAGREV. A more detailed model than that of *Michalski et al.* [2003], including transport and details of biomass-burning plumes such as oxidant formation/destruction and aerosol loading and pH is required to investigate the use of sulfate and nitrate $\Delta^{17}O$ as a quantitative indicator of paleo-oxidant levels.

[23] Models currently assume that increases in fossil fuel burning emissions at the turn of the century will have a significant impact on the oxidation capacity of the atmosphere. However, they generally do not consider this additional anthropogenic biomass-burning source when adjusting the spatial patterns and magnitude of biomass-

burning emissions prior to the Industrial era. Our results indicate that, at least for the high northern latitudes, biomass burning seems to have impacted the oxidation of sulfur and nitrogen species in the atmosphere on a large scale. This change in the latitudinal distribution of biomass burning from high to low latitudes and forest fire intensity during the PIAGREV should be taken into account in model simulations estimating changes in the oxidation capacity of the atmosphere since the Industrial Revolution, particularly when using high northern latitude paleo-archives as a metric for model evaluation.

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