

Nitrate records of a shallow ice core from East Antarctica: Atmospheric processes, preservation and climatic implications

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Abstract

High-resolution records of nitrate (NO_3^-), oxygen isotope ($\delta^{18}\text{O}$) and non-sea salt sulphate (nssSO_4^{2-}) were studied using an ice core collected from central Dronning Maud Land in East Antarctica to identify the influence of environmental variability on accumulation of NO_3^- over the past 450 years. The results confirmed that multiple processes were responsible for the production and preservation of NO_3^- in Antarctic ice. Correlation between NO_3^- and nssSO_4^{2-} peaks revealed that sulphate aerosols released during major volcanic eruptions might have activated the production of nitric acid, which was scavenged by ion-induced nucleation in polar ice sheets. The correlation between the nitrate and $\delta^{18}\text{O}$ records further suggest that enhanced NO_3^- preservation in the ice occurred during periods of lower atmospheric temperature. Major shifts in the NO_3^- record of the ice core presently studied and its comparison with ^{10}Be record from a core collected from South Pole suggest that a reduction in solar activity influenced the NO_3^- accumulation in Antarctica through enhanced production of odd nitrogen species.

Keywords

East Antarctica, ion induced nucleation, nitrate, oxygen isotope, solar activity, sulphate

Introduction

The Antarctic continent with its vast ice cover acts as a geochemical reservoir that archives the signatures of the past atmospheric processes. Changes in the Earth's atmospheric properties can be identified in precipitating snow since it simultaneously retains the signature of the prevailing conditions. In atmospheric chemistry, nitrogen oxides (mainly NO_x) play an important role in the formation and degradation of tropospheric ozone through the catalytic cycles. Since NO_x (NO and NO_2) is closely related to NO_3^- , the NO_3^- preserved in the ice sheets could provide information on the climate change over the past several centuries (Dansgaard and Oeschger, 1989; Mayewski *et al.*, 1993, 1994). Although nitrate is being routinely measured in snow and ice cores retrieved from polar regions (Dreschhoff and Zeller, 1990; Wilson and House, 1965; Zeller and Dreschhoff, 1995; Zeller and Parker, 1979), its interpretations largely remain uncertain (Legrand *et al.*, 1999; Röthlisberger *et al.*, 2000; Savarino *et al.*, 2007; Wolff, 1995) because of contribution from multiple sources and regions. Preservation of nitrate in polar ice can also vary widely because of interconversions among different nitrogen species in the atmosphere (Jones *et al.*, 2007; Röthlisberger *et al.*, 2000; Wolff *et al.*, 2008a). Several mechanisms are proposed for accumulation and preservation of nitrate in Antarctic snow, such as (1) *in situ* biological fixation (Parker *et al.*, 1978); (2) soil denitrification (Parker *et al.*, 1978); (3) anthropogenic activity (Parker and Zeller, 1980); (4) atmospheric transport of aerosol (Parker *et al.*, 1977); (5) volcanic activity (Parker *et al.*, 1977); (6) nitrogen fixation (Parker *et al.*, 1978); and (7) ionization by cosmic and solar rays (Parker *et al.*, 1977; Zeller and Parker, 1981 and references therein). Röthlisberger *et al.* (2002) suggested that since the

factors controlling NO_3^- concentration in ice core are complex, the data interpretation is likely to involve different factors significant for different locations and time periods.

Oxidation and interconversions of nitrogen oxides in the polar atmosphere influences nitrate retention in the ice (Jones *et al.*, 2007; Röthlisberger *et al.*, 2000). Postdepositional processes may also lead to significant loss of NO_3^- by isotopic fractionation, especially where the accumulation rates are low (Blunier *et al.*, 2005; Röthlisberger *et al.*, 2002; Wolff *et al.*, 2008b). Among the processes, evaporation of HNO_3 and photolysis of NO_3^- are quite significant (Frey *et al.*, 2009). Postdepositional processes are suggested to be controlled by air temperature, UV radiation, solar irradiance, accumulation rate and snow cover (Frey *et al.*, 2009; Röthlisberger *et al.*, 2002).

Importance of nitrate-N for photosynthesis by proton events are well established (Vitt *et al.*, 2000). Some ice cores have been identified with large nitrate spikes corresponding to unusual solar events (Palmer, 2001). Inputs from continental, atmospheric and

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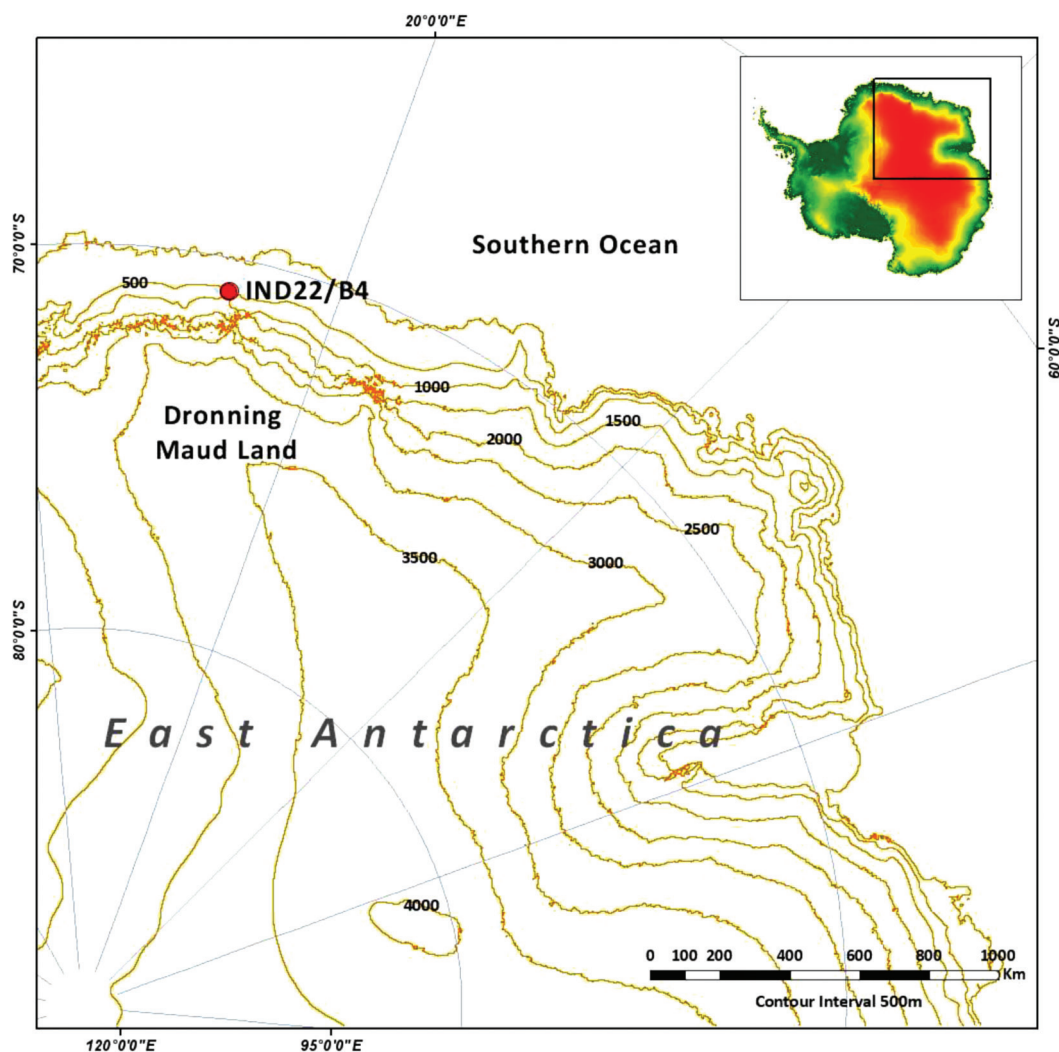


Figure 1. Study area and location of IND-22/B4 ice core within Dronning Maud Land

stratospheric sources also influence nitrate accumulation (Wolff, 1995; Zeller and Parker, 1981). Various hypotheses on NO_3^- and sea salt sulphate productions are still being debated, as all of them need to be corroborated (Wolff *et al.*, 2008b). So far, no detailed studies have been undertaken on the interaction between ionic species such as NO_3^- and SO_4^{2-} from the central Dronning Maud Land (DML). The present study examines the nitrate records along with SO_4^{2-} and $\delta^{18}\text{O}$ records to identify the production, deposition and preservation as well as the transport mechanisms that are involved in the burial of nitrate in central Antarctica, using an ice core from the central DML region.

Material and methods

An ice core of 62.2 m (IND-22/B4) was collected from the central DML region ($70^\circ 51.3'S$ and $11^\circ 32.2'E$; Figure 1) during the 22nd Indian Scientific Expedition to Antarctica. The annual mean temperature and snow accumulation reported at this site are $\sim -20^\circ\text{C}$ and $\sim 170 \text{ kg/m}^2$ per yr, respectively (Anschütz *et al.*, 2007). Drilling was carried out using an electromechanical drill (diameter $\sim 10 \text{ cm}$) during the austral summer of 2003. The core was preserved and transported in frozen condition (-20°C) to the National Centre for Antarctic and Ocean Research, Goa, India. Subsequently, the core samples were processed and subsampled at -15°C . As a

precaution to avoid contamination, the outer layer was chipped using microtome blades and only the inner part of the core was studied. The core samples were melted in a class 100 clean room before chemical analysis. Major ions such as nitrate (NO_3^-), sulphate (SO_4^{2-}) and sodium (Na^+) were measured from the melted ice samples using an ion exchange chromatograph (Dionex™ Model ICS-2500 equipped with EG50 Eluent generator and CD25 detector). The sample injection volume was 100 ml. Chronology of the core was obtained from volcanic stratigraphy using the non-sea-salt sulphate (nssSO_4^{2-}) records (Thamban *et al.*, 2006), and was further confirmed by tephra records (Lalraj *et al.*, 2009). Calibration was done using IV (Inorganic Ventures) high-purity standards and the concentrations are given here in micrograms per litre ($\mu\text{g/l}$). The detection limits of the RF-IC system based on bottle blanks for all ions were $<1 \mu\text{g/l}$ and the approximate blank levels of the cleaned LDPE bags were $1\text{--}5 \mu\text{g/l}$. In order to confirm the quality of measurements, chromatographic standards were analysed on a daily basis throughout the period of analysis. The estimated analytical precision based on the daily scrutiny of standards was better than 10%. The repeatability for all ions reported here based on the repeated analysis of international chromatographic standards were in the range of $5\text{--}20 \mu\text{g/l}$.

Oxygen isotopic ratios were measured using a dual inlet, Isoprime Mass Spectrometer (GV instruments, UK) using conventional

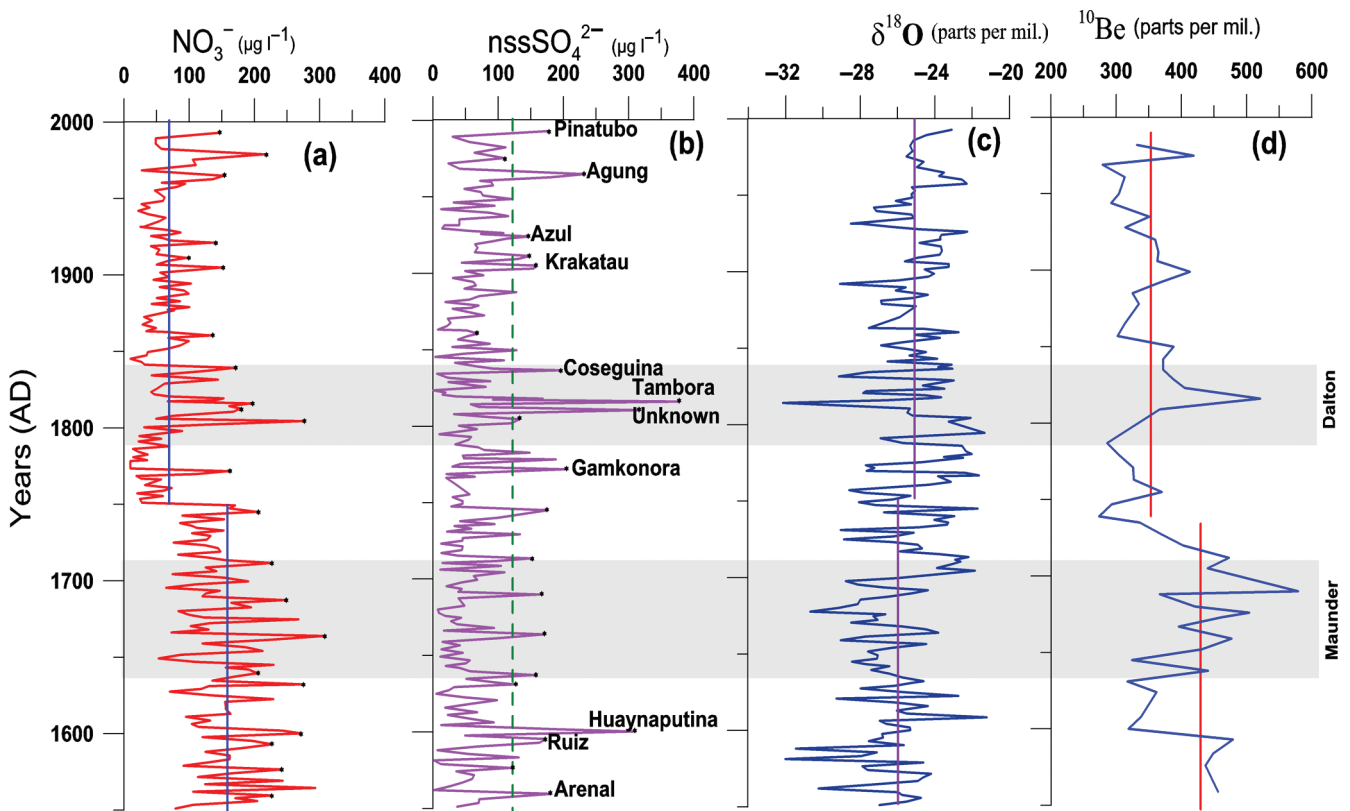


Figure 2. Concentration profiles of (a) nitrate (NO_3^-), (b) non-sea-salt sulphate (nssSO_4^{2-}), (c) oxygen isotope ratio ($\delta^{18}\text{O}$) of the IND-22/B4 ice core, and (d) South Pole ^{10}Be proxy data for solar variability. Star symbols in NO_3^- and nssSO_4^{2-} profile denote major correlation in peaks between the two. Lines in NO_3^- , $\delta^{18}\text{O}$ and ^{10}Be represent the average values of pre- and post-AD 1750

method of equilibrating sample water with CO_2 following Epstein and Mayeda (1953). All measurements were calibrated using Vienna Standard Mean Ocean Water (VSMOW) and Standard Light Antarctic Precipitation (SLAP). The external precision (1σ) of $\delta^{18}\text{O}$ measurements obtained using a laboratory standard (CDML1) was $\pm 0.05\text{‰}$. Density estimated using weight and volume of the individual core sections was used to calculate the accumulation rates. The calculated average annual accumulation rate of present ice core was 109 kg/m^2 per yr.

Results and discussion

The NO_3^- profile of the IND-22/B4 ice core revealed concentrations varying between 10 and $306 \mu\text{g/l}$, with an average value of $107 \mu\text{g/l}$ (Figure 2a). The NO_3^- profile clearly showed large-scale variability with high values (average $151 \mu\text{g/l}$) before AD 1750 and low values (average $75 \mu\text{g/l}$) thereafter. The $\delta^{18}\text{O}$ record of the ice core during the past ~ 450 years fluctuated between -21.2 and -32.1 (average -25.5 ; Figure 2c). Since the ratios of $\delta^{18}\text{O}$ in snow/ice generally indicate the temperature of condensation, ice cores have been used for reconstruction of past climatic changes (Dansgaard *et al.*, 1989; Grootes *et al.*, 2002). The major negative spikes of isotope data were coinciding with high NO_3^- values (Figure 2a and c), thereby indicating a positive correlation between temperature and NO_3^- accumulation ($r^2=0.36$; $n=210$).

In Antarctica, the NO_3^- records exhibit a seasonal variation with minimum during winter and maximum during summer (Mulvaney and Wolff, 1993). It has been opined that insolation during summer causes maximum sublimation that results in an increase of nitrate

in the snow surface (Dreschhoff and Zeller, 1990; Laird *et al.*, 1987). Based on the odd nitrogen concentrations at atmosphere, it was suggested that NO_3^- concentrations in ice are ultimately controlled by solar activity (Dreschhoff and Zeller, 1990; Laird *et al.*, 1987; Palmer, 2001; Zeller and Dreschhoff, 1995; Zeller and Parker, 1981). Nitrate peaks corresponding to intense solar events are distinguishable from meteorologically derived nitrate peaks (Shea *et al.*, 1993). The nitrate signals in the ice sheets are possibly associated with dissociation of energetic particles derived from solar and geomagnetic events (Dreschhoff and Zeller, 1990; Dreschhoff *et al.*, 1993; Laird *et al.*, 1987; Palmer, 2001; Zeller and Dreschhoff, 1995; Zeller and Parker, 1981). The dominant processes influencing NO_3^- concentration in Antarctic ice are snow accumulation rate and temperature of the site (Legrand and Mayewski, 1997). The average accumulation rate derived for the present core is $\sim 109 \text{ kg/m}^2$ per yr, which is comparable with an earlier study in the coastal DML region that revealed large spatial variability (Anschütz *et al.*, 2007). Such moderate accumulation rates can prevent high loss of nitrate by photolysis of NO_3^- (Röthlisberger *et al.*, 2002). The spatial and temporal variability in snow accumulation may be due to the large-scale variations in precipitation owing to cyclonic activities along the coastal areas of DML (Schlösser and Oerter, 2002).

Based on compilations of NO_3^- data from more than 50 Antarctic sites covering various temperature and accumulation regimes, it has been suggested that temperature is also a key parameter in determining NO_3^- concentration preserved in Antarctic snow and ice, with lower temperature resulting in higher NO_3^- concentration being preserved in the snow (Röthlisberger *et al.*, 2000). The high concentration of HNO_3 found at low temperature also indicates its

increased accumulation in snow during cold events (Abbatt, 1997; Wolff and Mulvaney, 2000). Thermodynamically, an increase in temperature facilitates the release of HNO₃ from the ice surface (Abbatt, 1997). The HNO₃ accumulation in ice is initiated when the acid concentration in fresh snow exceeds the levels in the cloud. Thus, activities of HNO₃ by co-condensation, riming and adsorption determine the intensity of nitrate accumulation in the ice. Furthermore, the NO₃⁻ distribution in snow is influenced by air temperature, humidity and the initial concentration of HNO₃ in the atmosphere (Thibert and Domine, 1998). The low temperature also leads to better preservation of HNO₃ in the ice as it reduces the exchange between ice and atmosphere.

An important aspect of variability in NO₃⁻ concentration in ice core records is the effect of H₂SO₄ from volcanic eruptions. Volcanic eruptions during the Holocene showed that H₂SO₄ concentrations enhanced immediately after the nitrate concentrations peak (Röthlisberger *et al.*, 2000; Wolff, 1995), indicating that during recrystallisation, nitrate accumulation succeeds sulphate deposition. In order to examine this relationship, the nitrate and nssSO₄²⁻ records were compared. The nssSO₄²⁻ [(nssSO₄²⁻) = (SO₄²⁻) - 0.252(Na⁺)] record yielded a significant correlation with nitrate records ($r^2=0.31$; $n=210$), suggesting a close relation in their depositional characteristics (Figure 2a and b). The nssSO₄²⁻ anomalies (Figure 2b) in the ice core have been interpreted as the aerosol anomalies related to major volcanic events in the past (Thamban *et al.*, 2006). It is well known that volcanic eruptions emitting SO₂ and other gases have a large impact on atmospheric chemistry. The SO₄²⁻ could provide nucleation centers forming multi-ion complexes with HNO₃ in the stratosphere. The NO₃⁻ deposition in the polar ice caps is considered to result from stratospheric-tropospheric exchange of clouds (Adachi *et al.*, 1992), where HNO₃ is sequestered as NO₃⁻ into the snow. The undersaturation of aerosol ionic particles for the nucleation is commonly referred to as ion-induced nucleation (Adachi *et al.*, 1992). Arnold (1980) suggested that presence of other ions in the atmosphere could lead to large multi-ion complexes that mutually coalesce. It was suggested that ionization in the polar atmosphere induced nucleation of H₂SO₄ vapor at an altitude of 30–35 km (Arnold, 1982; Hofmann and Rosen, 1982, 1983), which eventually lead to an increase in the concentration of HNO₃ in the ice through the formation of multi-ion complexes within snow precipitation. In addition, increase in H₂SO₄ shifts the reaction $H^+ + NO_3^- \rightleftharpoons HNO_3$ towards the right-hand side, leaving elevated levels of HNO₃ in the ice. Nitric acid either is rained out as free acid or reacts with ammonia (Talbot *et al.*, 1992). Within the snow/ice, the main fraction of NO₃⁻ is HNO₃ because of its easy scavenging property and its association with ammonia (Legrand *et al.*, 1996). It is presumed that similar processes had taken place in the study region in the past leading to enhanced NO₃⁻ during periods of anomalous SO₄²⁻ deposition.

While correlation between $\delta^{18}O$ (a proxy for temperature) and nssSO₄²⁻ records appears to explain some of the significant variations in NO₃⁻ records, a drastic reduction in nitrate values corresponding to AD 1750 as well as the large spike corresponding to AD 1800 can not be attributed to them. The atmospheric odd nitrogen (molecules which contain an odd number of nitrogen atoms) is considered to be precursors for the NO₃⁻ deposition in polar ice (Vitt *et al.*, 2000). In fact, the atmospheric HNO₃ is the second most important mineral acid implicated in the acid rains and nitrate accumulation in the ice sheets. The deposition of odd nitrogen (sum of all oxidised form of nitrogen) in snow/ice mainly depends

on the rate of production of nitrogen oxide molecules in the atmosphere. The odd nitrogen production in the middle and upper atmosphere is through reactions of O₂ and N₂ by solar and geomagnetic charged particles (Dreschhoff and Zeller, 1990; Vitt and Jackman, 1996; Zeller and Parker, 1981; Zeller *et al.*, 1986).

The NO₃⁻ record of IND-22/B4 core revealed good similarity with the ¹⁰Be record of South Pole ice core record (Figure 2a and d). The ¹⁰Be levels in the ice core from Antarctica had been used as a proxy record of solar irradiance (Bard *et al.*, 2000; Raisbeck *et al.*, 1990). ¹⁰Be is a cosmogenic isotope produced by galactic cosmic rays. Since cosmic rays are affected by the interplanetary magnetic field, the rate at which ¹⁰Be is produced reflects changes in solar activity (Beer *et al.*, 1990). A more active sun would result in low ¹⁰Be concentrations. The residence time for ¹⁰Be in the atmosphere being not more than few years, it can be used to study solar magnetic cycle. Hence, ¹⁰Be is the best indicator of solar activity and production of odd nitrogen (Dreschhoff and Zeller, 1990; Zeller *et al.*, 1986). Some of the ¹⁰Be deposited are archived within the annual snow layers and hence, cosmogenic ¹⁰Be can be used to reconstruct the history of solar activity. Raisbeck *et al.* (1987) found that ¹⁰Be flux in Vostok ice core from Antarctic depends on solar variability rather than geomagnetic variability over the last 150 ka.

Comparison of the South Pole ¹⁰Be and NO₃⁻ records of ice core demonstrates an excellent similarity between the two (Figure 2a and d). There are several major peaks in the nitrate data, which are similar to ¹⁰Be spikes. The drastic increase in nitrate before and after AD 1750 (151 and 75 $\mu\text{g/l}$, respectively) was similar to the ¹⁰Be spikes (410 and 350 parts per mil, respectively) in the South Pole ice core for the corresponding periods (Bard *et al.*, 2000), suggesting that solar activity is a major source of NO₃⁻ in atmosphere. The ¹⁰Be flux in ice cores was also exhibiting variations related to unusual solar activity (Beer *et al.*, 1990; Mayewski *et al.*, 2005; Steig *et al.*, 1996). Major periods of reduced solar activity (and increased ¹⁰Be) such as the Dalton Minimum (~AD 1790–1830) and Maunder Minimum (~AD 1640–1710) were characterised by relatively enhanced concentration of NO₃⁻ in the present ice core (Figure 2). This indicates that NO₃⁻ accumulation in Antarctica is mainly controlled by the changes in production rate of NO_x in the upper atmosphere, which are in turn, modulated by the solar activity. The present study reveals a strong correlation ($r^2 > 0.5$; $n=145$) between increased nitrate concentrations in Antarctic ice and ¹⁰Be production caused by solar activity.

Nitrate-ions generated in the Earth's atmosphere from nitric oxide are captured by aerosols and are deposited in the polar ice. Hence, the NO₃⁻ values in the ice core indicate some of the atmospheric disturbances during that period. A large portion of NO₃⁻ is oxidized to HNO₃ and incorporated in snow crystals together with NO₃⁻ from tropospheric sources. Since the nitrate concentration correlates positively with solar activity, it is likely that its origin is the result of ionization by ultraviolet or charged particles emitted from the sun in the upper atmosphere over Antarctica. Hence, from the study it is deduced that the nitrate content in the Antarctic snow was not only influenced by the temperature and availability of condensation nuclei, but also by the rate at which odd nitrogen species was produced by solar activity.

Conclusion

Nitrate records along with sulphate and oxygen isotope records in the ice core revealed that the temporal variability in nitrate

records in Antarctic ice core are influenced by complex processes of production, accumulation and preservation of atmospheric odd nitrogen species. We propose that the scavenging of nitric acid in atmosphere by the non sea-salt sulphate forming multi-ion complex could be a mechanism influencing the deposition of nitrate in Antarctic snow. The relatively cooler periods (more negative $\delta^{18}\text{O}$ values in ice core) were characterized by high nitrate deposition in the ice core, suggesting a temperature control in the accumulation of nitrate in snow/ice. The prominent variations in NO_3^- profile before and after AD 1750 correlate well with the ^{10}Be records from Antarctica, suggesting the influence of solar activity on the NO_3^- accumulation in snow. The nitrogen species produced through solar activity would ultimately define the NO_3^- deposition in association with scavenging of SO_4^{2-} ions, that may preferentially preserve NO_3^- in Antarctic snow during relatively cooler conditions. Although the present study provides improved understanding of some of the processes involved in NO_3^- accumulation in Antarctica, further studies are required to quantify the processes involved in the nitrate accumulation and preservation in snow within spatially distinct areas in Antarctica.

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