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NON-SEA-SALT SULFATE AND NITRATE VARIATIONS IN THE S25 CORE, NEAR THE COASTAL REGION, EAST ANTARCTICA

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Abstract: Non-sea-salt sulfate ($nssSO_4^{2-}$) and nitrate (NO_3^-) data in the S25 core in the coastal region on Mizuho Plateau, East Antarctica, have been analyzed. Time series of $nssSO_4^{2-}$ which is mainly derived from marine-biogenic sulfur (DMS), showed not only seasonal variations, but also 4–5 year and about 8 year variations. The result indicates that DMS emission and the transport process of $nssSO_4^{2-}$ may be affected by the Antarctic Circumpolar Wave (ACW), whose initiation is probably associated with El Niño activity. The NO_3^- concentrations in the S25 core presented about 11-year variations corresponding to the solar cycle.

1. Introduction

Ice core studies provide valuable information to reconstruct the past atmospheric environment because polar snow and ice samples contain atmospheric trace gases and aerosol constituents from the past. In the Arctic, air pollution has increased and significant increase of anthropogenic pollutants in the past century has been observed in Arctic ice cores (NEFTEL *et al.*, 1985; MAYEWSKI *et al.*, 1990). In the southern hemisphere, high latitude regions are still remote from the world's major industrial areas, and the Antarctic troposphere may be considered relatively unspoiled by human activity (ARISTARAIN *et al.*, 1982; LEGRAND, 1995; OSADA, 1996). However, the development of the stratospheric ozone (O_3) hole over Antarctica represents an example of changes in the remote atmospheric composition. NISHIKIORI *et al.* (1997) noted that photochemical oxidation in the troposphere over Antarctica might have been intensified due to depletion of stratospheric O_3 since the 1970s, based on measurements of organic materials in an Antarctic ice core. WATANABE *et al.* (1998) also pointed out an increase of a photochemical oxidant since the late 1960s.

Ionic constituents in polar ice contain sea-salts, mineral salts, organic compounds, nitrogen compounds (*e.g.* nitrate) and sulfur compounds (sulfate and methanesulfonic acid) as discussed in previous studies (DELMAS, 1992; OSADA, 1996). Sulfate (SO_4^{2-}) and nitrate (NO_3^-) ions are major impurities in polar snow and contribute to acidification (LEGRAND and DELMAS, 1988; DELMAS, 1992). Apart from sporadically volcanic

perturbations, it is considered that non-sea-salt sulfate ($nssSO_4^{2-}$) in Antarctic precipitation is mainly derived from marine biogenic activity, and $nssSO_4^{2-}$ aerosols play a major role in forcing climate change, but details of the sulfur cycle in polar regions have not been well established (CHARLSON *et al.*, 1987; ANDERSON *et al.*, 1995; LEGRAND, 1995; OSADA, 1996). There are also large amounts of NO_3^- data in ice cores, however, the data are not easy to interpret. Origins and transport processes of NO_3^- in Antarctic snow and ice are not yet well understood (WOLFF, 1995; OSADA *et al.*, 1996). It is clear that anthropogenic NO_3^- has increased the concentrations in Greenland snow, but such an increase of NO_3^- is not seen in Antarctica (WOLFF, 1995).

This paper presents $nssSO_4^{2-}$ and NO_3^- data in an ice core taken at site S25 on Mizuho Plateau, East Antarctica. Site S25 is located near the coastal region where a higher snow accumulation rate has been observed (WATANABE *et al.*, 1988), and post-depositional changes of relatively unstable chemical species, such as H_2O_2 and NO_3^-, may be suppressed in snow. Moreover, there are few melting layers in the S25 core, and strong seasonal variations of hydrogen peroxide (H_2O_2) have been observed (WATANABE *et al.*, 1998). Therefore, the S25 core may be useful for understanding past NO_3^- variations. In this paper, we discuss the historical variations of $nssSO_4^{2-}$ and NO_3^- in snow, near the coastal region, East Antarctica.

2. Sample and Methods

The ice core was taken at site S25, located at the coast of Mizuho Plateau (near Syowa Station), East Antarctica (69°01′58″S, 40°28′07″E, altitude 868 m), by the 26th Japanese Antarctic Research Expedition (JARE-26) in January 1986. The S25 core has been stored in the low-temperature room (−20°C) of the National Institute of Polar Research (NIPR). The ice core was cut in the low-temperature room, with the sampling interval of about 5 cm. About 1 cm of the ice core surface was removed in order to eliminate contaminants. After melting the cut ice, water samples were used for measurements of major ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+}) by an ion chromatograph (Dionex 2000i), as was described in detail in FUJII *et al.* (1989). Unfortunately, major ions could be measured only in the top 33 m depth. The vertical distributions for chemical elements, as well as stable oxygen isotopic ratio and electrical conductivity measurements (ECM), were obtained in 1991, and a preliminary report is now in preparation (SATOW *et al.*, in preparation).

As was mentioned above, strong seasonal variations of chemical species were observed in the S25 core. For dating of the core, we adopted the counting method of the annual cycles of chemical species (H_2O_2 and $nssSO_4^{2-}$). The mean annual net accumulation rate of snow at site S25, based on the counting, was estimated to be about 300 kg m^{-2}, showing similarity to the result of snow stake measurements (WATANABE *et al.*, 1998). Therefore, annual layer counting is a useful method for dating the S25 core.

3. Results and Discussion

3.1. Non-sea-salt sulfate

A vertical profile of the $nssSO_4^{2-}$ concentrations in the S25 core is shown with

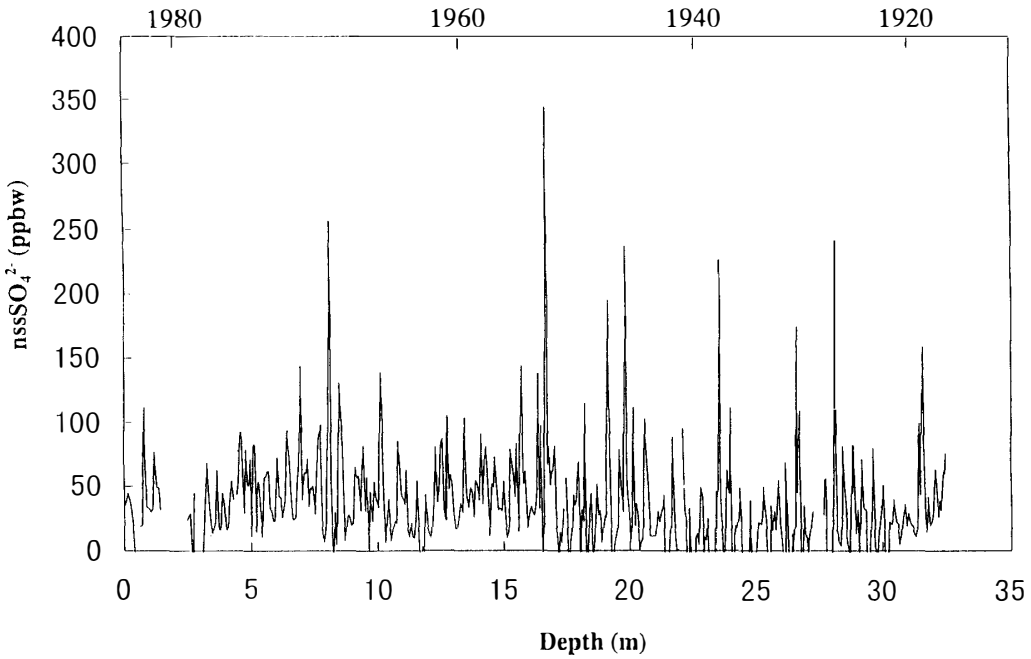

Fig. 1. Vertical profile of the nssSO_4^{2-} concentrations in the S25 core. Estimated ages are given in numbers.

estimated age in Fig. 1. The nssSO_4^{2-} is calculated as follows:

$$(\mathrm{nssSO_4^{2-}}) = (\mathrm{SO_4^{2-}}) - (\mathrm{SO_4^{2-}/Na^+})_{\mathrm{seawater}} \cdot (\mathrm{Na^+}),$$

where (SO_4^{2-}) and (Na^+) are the observed SO_4^{2-} and Na^+ concentrations in the ice core samples, and $(SO_4^{2-})_{seawater}$ is the concentration ratio of SO_4^{2-} to Na^+ in seawater, which is 0.25 (weight ratio). The nssSO_4^{2-} concentrations in the S25 core show a range of 0–350 ppbw, and are about the same as the concentrations in other ice cores from coastal Antarctica (KOHNO *et al.*, 1996). There are sporadic negative peaks which are not shown in Fig. 1. Negative peaks which suggest the existence of excess Na^+ for unknown reasons have also been seen in the ice core drilled at site H15 (KOHNO *et al.*, 1996). The nssSO_4^{2-} concentrations show strong seasonal variations, as has already been reported in many ice cores and is very useful for dating (MOSLEY-THOMPSON *et al.*, 1991; LANGWAY *et al.*, 1994; OSADA, 1996).

There are several high nssSO_4^{2-} peaks which appear to be quasi-periodic, with a period of 4–8 years, in the S25 core (Fig. 1). High concentrations of nssSO_4^{2-} in ice cores have been sometimes treated as signs of large volcanic eruptions (LEGRAND and DELMAS, 1987; LEGRAND and FENIET-SAIGNE, 1991; KOHNO *et al.*, 1996). The volcanic signals are accompanied by high acidity and large ECM peaks (HAMMER *et al.*, 1980; CLAUSEN *et al.*, 1995; OSADA, 1996). However, the high nssSO_4^{2-} in the S25 core was not consistent with high ECM peaks, and might not have contributed to acidification (WATANABE *et al.*, 1997, 1999). The nssSO_4^{2-} data could not show the major volcanic eruptions such as Agung 1963. The Agung event could be also not be seen in the H15 core (KOHNO *et al.*, 1996).

Many samples of the S25 core show a Cl^-/Na^+ weight ratio that is lower than that

in seawater (WATANABE *et al.*, 1999). LEGRAND and DELMAS (1988) suggested that the deficit of Cl^- relative to Na^+ is mainly due to the presence of Na_2SO_4 as a result of a sea-salt alteration reaction as follows:

$$2\,NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2\,HCl.$$

The $nssSO_4^{2-}$ in the S25 core seems to exist as mainly Na_2SO_4 which does not contribute to acidification.

Volcanic signals were not detected in an ice core from the Weddell Sea sector in Antarctica because of high marine-biologically derived sulfate deposition in the coastal region (PEEL and MULVANEY, 1992). It seems difficult to detect volcanic signals in ice cores from coastal regions where marine-biologically derived SO_4^{2-} is transported actively. According to PEEL and MULVANEY (1992), $nssSO_4^{2-}$ in the ice core generally shows a strong inverse relationship with the record of annual duration of sea ice over the north-west corner of the Weddell Sea in this century, however, a large positive correlation was found over the 1970–1980 decade. The process of $nssSO_4^{2-}$ deposition onto an ice sheet may be controlled by sea ice extent and climatic variations.

To elucidate the dominant periodicity of the $nssSO_4^{2-}$ variations in the S25 core, spectral analysis by the Maximum Entropy Method (MEM) was performed. The MEM has an adantage of high resolution for a short series (HINO, 1977). Figure 2 shows the power spectrum of the time series of the $nssSO_4^{2-}$ concentrations in the S25 core. There are not only seasonal variations, but also 4–5 year variations and about 8 year variations (Fig. 2). The 4–5 year variations correspond to the ENSO (El Niño-Southern Oscillation) cycle. Perhaps $nssSO_4^{2-}$ deposition may be affected by the ENSO at site S25. LEGRAND and FENIET-SAIGNE (1991) pointed out that large methanesulfonic acid (MSA) concentrations in the South Pole firn core might have been correlated to major ENSO events over the last sixty years, and the connection between

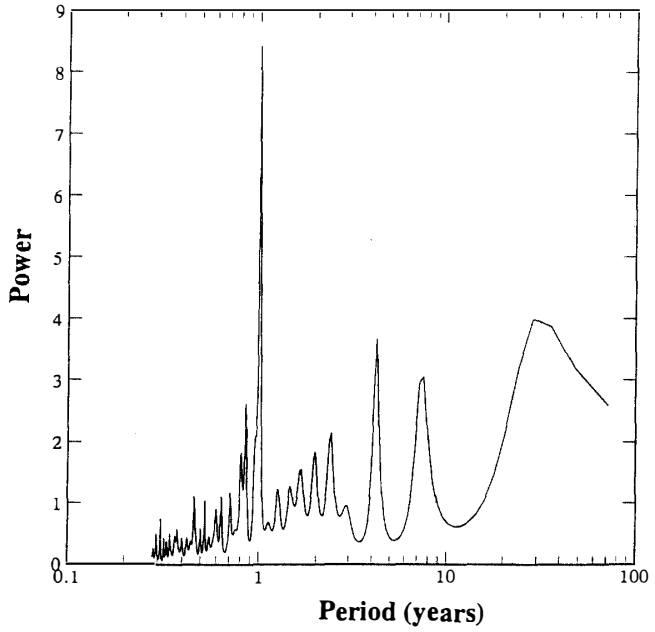

Fig. 2. Power spectrum of the time series of the $nssSO_4^{2-}$ concentrations in the S25 core.

ENSO and high DMS emissions at high southern latitudes was discussed in terms of atmospheric and oceanic circulation. LEGRAND (1995) noted that such enhanced DMS concentrations at high southern latitudes during El Niño years possibly result from higher wind speed at the sea surface which could lead to more efficient air-sea exchange of DMS. The study of MSA, which is also produced by DMS oxidation, provides more direct information about the marine-biogenic sulfur in Antarctic ice cores because MSA is not a product of volcanic eruption (LEGRAND and FENIET-SAIGNE, 1991; PEEL, 1995). However, no significant link between high MSA concentrations and ENSO events was observed in an ice core drilled on Dolleman Island on the east coast of the Antarctic Peninsula (PASTEUR *et al.*, 1995). WELCH *et al.* (1993) discussed the relationship between the MSA content of snow deposited in a coastal Antarctic region and the sea ice extent over the two last decades. Unfortunately, we could not measure MSA concentrations in the S25 core, however, significant $nssSO_4^{2-}$ from volcanic eruptions in the past century has not been detected in the S25 core, as mentioned above.

Recently, WHITE and PETERSON (1996) performed data analysis of anomalies in sea level pressure, meridian wind stress, sea surface temperature (SST), sea surface height and sea ice extent over the Southern Ocean, and indicated that these anomalies propagated eastward with the circumpolar flow, with a period of 4–5 years and taking 8–10 years to encircle the pole. This system of coupled anomalies is called the Antarctic Circumpolar Wave (ACW) and the initiation of the ACW is probably associated with El Niño activity (WHITE and PETERSON, 1996; JACOBS and MITCHELL, 1996). Especially, variations of sea ice extent, sea surface temperature and wind speed can control the amount of DMS production and emission in the coastal region (LEGRAND and FENIET-SAIGNE, 1991; LEGRAND, 1995). The transport and deposition processes of $nssSO_4^{2-}$ which is an oxidation product of DMS, may be affected by meteorological factors. The highly $nssSO_4^{2-}$ peaks in the S25 core may be due to high SST (and sea ice decline) around Syowa Station or strong northerly wind. As a result, the ACW would control not only climate systems but also bio-geochemical cycles, and $nssSO_4^{2-}$ data in an ice core from a coastal region (such as the S25 core), seem to present 4–5 year and about 8 year variations.

3.2. Nitrate

Figure 3 shows a vertical profile of the NO_3^- concentrations in the S25 core. The concentrations vary between 5 to 70 ppbw, and are in the same range of NO_3^- as that displayed by the H15 core (KOHNO *et al.*, 1996), but are significantly lower than those in the ice cores from inland Antarctica (EDDY, 1977; ZELLER and PARKER, 1981; LEGRAND and KIRCHNER, 1990; LANGWAY *et al.*, 1994). However, the NO_3^- concentrations in the S25 core are also about the same as the concentrations in snow at Dome C located in inland Antarctica (LEGRAND and DELMAS, 1988). Because post-depositional modification of NO_3^- in snow is significant at low accumulation, the interpretation of NO_3^- may still be difficult (WOLFF, 1995). In the S25 core, there is no significant increasing trend of NO_3^- in the top meter (Fig. 3), which has been observed in snow samples at low accumulation sites (MAYEWSKI and LEGRAND, 1990; DE ANGELIS and LEGRAND, 1995). The high snow accumulation rate at site S25, would suppress the chemical degradation and diffusion of NO_3^- in snow and ice.

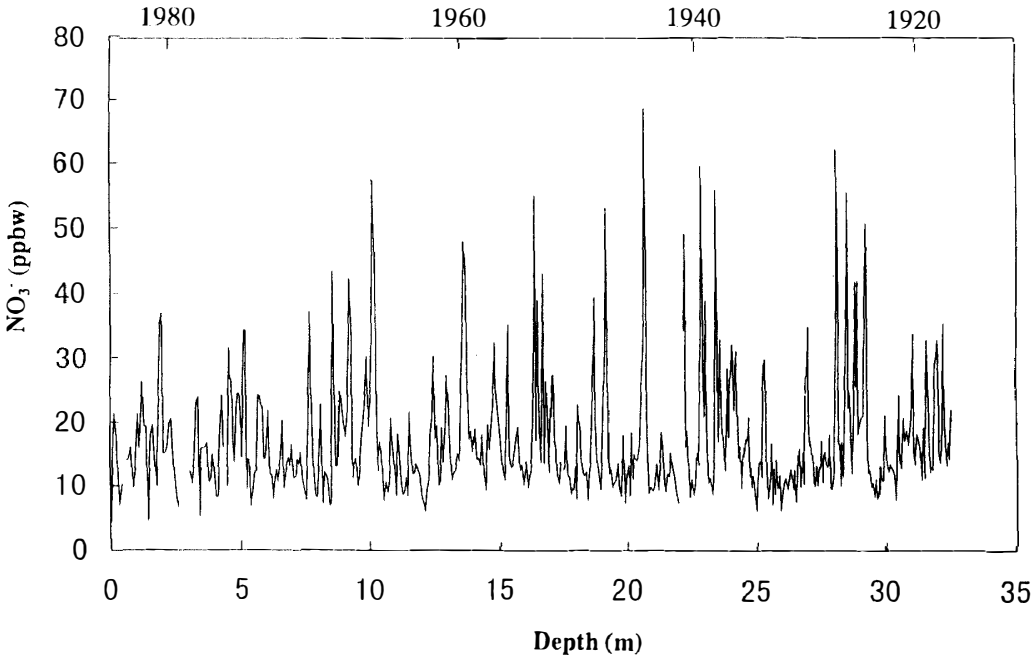

Fig. 3. Vertical profile of the NO_3^- concentrations in the S25 core.

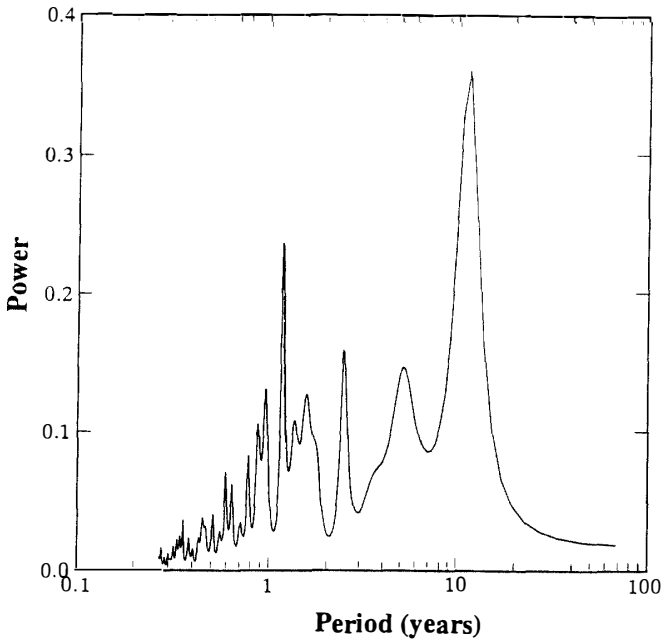

Fig. 4. Power spectrum of the time series of the NO_3^- concentrations in the S25 core.

The power spectrum (by MEM) of the time series of the NO_3^- concentrations in the S25 core is shown in Fig. 4. There exists large power around 11 years that correspond to the solar cycle (while there is no predominant spectral peaks of the time series of the $nssSO_4^{2-}$ around 11 years (Fig. 2)). LAIRD *et al.* (1982) has already reported that NO_3^- deposition in South Pole snow exhibited a significant relationship with sunspot numbers. It has been suggested that the specific mechanism for the

relationship might have been through production of NO_X by solar cosmic rays or solar proton events (SPE) in the upper and middle atmosphere (ZELLER *et al.*, 1986; LAIRD *et al.*, 1988). There have been negative opinions about the importance of solar modulation of the NO_3^- signal in snow and ice (LEGRAND and DELMAS, 1986; LEGRAND *et al.*, 1989; LEGRAND and KIRCHNER, 1990). LEGRAND and DELMAS (1986) suggested that lightning at tropical or mid latitudes was the most likely source of Antarctic NO_3^-. However, our result in the S25 core may support the paper of LAIRD *et al.* (1982).

Nitrate from the stratosphere has been discussed as one of the main sources (WOLFF, 1995). The stratospheric source has been estimated to provide about one third of the NO_3^- to high latitude precipitation (LEGRAND and KIRCHNER, 1990). There are two ways in which NO_3^- can be transported from the stratosphere to the troposphere. One is stratosphere-troposphere exchange of air, the other is deposition of polar stratospheric clouds (PSCs) particles consisting of nitric acid trihydrate (NAT) ice (WOLFF, 1995). Type 1 PSCs consisting of NAT ice are produced when the temperature falls to around 193K in the stratosphere, while Type 2 PSCs (mainly water ice) are formed at lower temperature (WOLFF, 1995). If they grow large enough, PSCs particles may deposit from the stratosphere, and HNO_3 may eventually reach the ice surface (FARMER *et al.*, 1987; SALAWITCH *et al.*, 1989; FAHEY *et al.*, 1990; IWASAKA and HAYASHI, 1991). The NO_3^- records in ice cores may provide information on polar stratospheric temperatures (LEGRAND and KIRCHNER, 1988; WOLFF, 1995).

Nitric acid constituting NAT ice is produced by N_2O oxidation (by O atoms) in the stratosphere. As the amount of O atoms available for the reaction depends on stratospheric O_3 concentrations, HNO_3 formation may be affected by O_3 concentrations. A previous study (CHRISTIE, 1973) showed that column O_3 (mainly in the stratosphere) variation had a clear 11-year cycle before 1950; therefore, HNO_3 variation might also have an 11-year cycle. There is another possibility; that the HNO_3 may take its source in the upper and middle atmosphere where NO_X productivity is much influenced by the 11-year solar variability. CALLIS and NATARAJAN (1986) suggested that NO_X formed in the upper stratosphere and the mesosphere are transported to the lower stratosphere. If the process is important, it is quite possible that the NO_3^- concentration in the ice core has 11-year variation.

To pick up the 11-year variation, we applied a 9–13 years bandpass filter, as proposed by MURAKAMI (1979), to the NO_3^- data. The filter is available to reduce short term fluctuations shorter than 9 years and long term trends longer than 13 years. The age distributions for the filtered NO_3^- concentrations in the S25 as well as for the sunspot number are shown in Fig. 5. We also found that the H_2O_2 variation in the S25 core had the 11-year cycle (WATANABE *et al.*, 1998). The bandpass filtered H_2O_2 concentrations in the S25 core and the sunspot numbers (WATANABE *et al.*, 1998) are also displayed in Fig. 5. The comparison indicates that the peaks of H_2O_2 slightly precede those of solar activity with regard to phase; however, the maximum concentrations of NO_3^- occur when the sunspot numbers are highest or decreasing. The phase delay (1–3 years) of NO_3^- behind the solar variability may be due to a time lag between NO_X production by solar activity and HNO_3 deposition on the ice surface. The NO_X produced in the middle atmosphere would be converted into HNO_3 constituting NAT ice, and the HNO_3 must be transported to the ice surface. The transport processes may

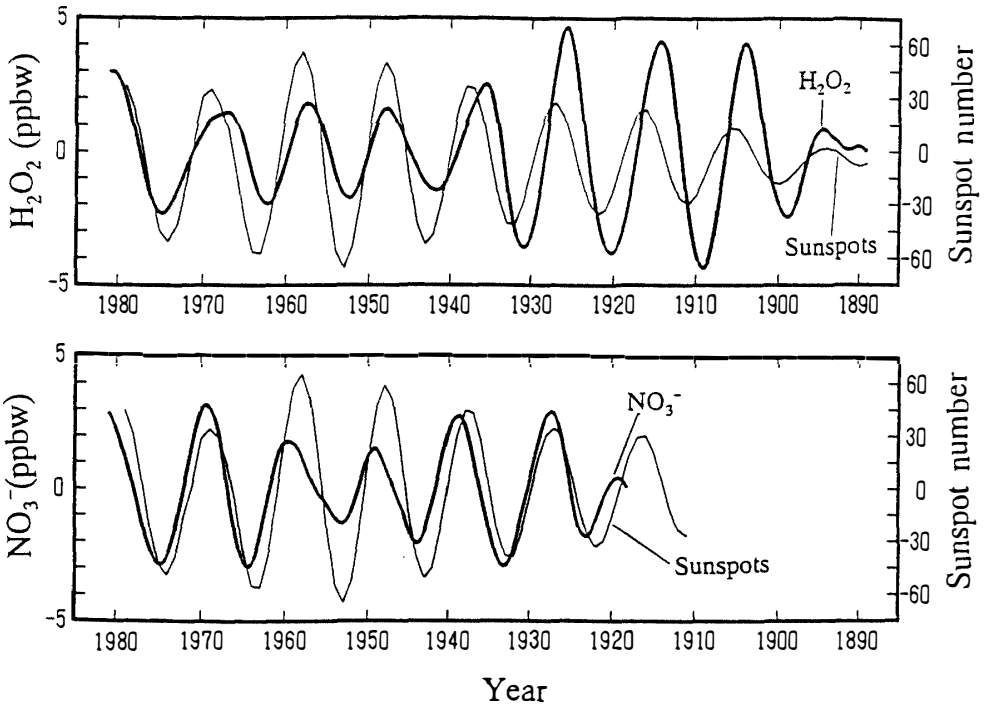

Fig. 5. Bandpass filtered (9–13 year) H_2O_2 concentrations in the S25 core and the sunspot numbers (WATANABE et al., 1998) (upper panel), and NO_3^- concentrations in the S25 core and the sunspot numbers (lower panel).

take 1–3 years. However, we cannot deny the possibility that the time lag may be due to the dating error of the ice core.

The amplitude of NO_3^- variations were small in the 1950s–1960s, while solar activity was highest in this century (Fig. 5). The concentrations of NO_3^- in snow are dependent on not only NO_X productivity but also transport processes. Even if abundant NO_X is produced by strong solar activity, high HNO_3 may not be transported to the troposphere or an ice sheet if conditions prevent that NAT ice from being formed. Perhaps, stratospheric temperatures might be high and NAT ice formation depressed due to high solar activity in the 1950s–1960s. Therefore, the NO_3^- variations might have been small in the 1950s–1960s.

There are also significant spectral peaks at not only about 1 year but also approximately 2.4 years corresponding to the QBO (Quasi-Biennial Oscillation) cycle (Fig. 4). The QBO is a strong oscillation of the mean zonal wind and temperature of the tropical stratosphere, and seems to influence polar stratospheric temperatures (LABITZKE and VAN LOON, 1994). As a result, the transfer processes of NO_3^- onto the ice sheet may be affected by the QBO.

4. Summary

Chemical data analysis on ice obtained at site S25, near the coastal region on Mizuho Plateau, East Antarctica, has been performed. The $nssSO_4^{2-}$ concentrations in the S25 core present not only strong seasonal variations, but also 4–5 year and about 8

year variations. The 4–5 year and 8 year cycles of the ice core nssSO_4^{2-} indicates that the emission and transport process of marine-biogenic sulfur may be affected by the Antarctic Circumpolar Wave (ACW). The result indicates that the ACW would control not only climate systems but also bio-geochemical cycles.

Time series of NO_3^- concentrations in the S25 core showed about 11-year variations corresponding to the solar cycle, while there has been considerable controversy about the importance of solar modulation of the NO_3^- signal in Antarctic snow and ice (LEGRAND and DELMAS, 1986; LAIRD *et al.*, 1988; WOLFF, 1995). In this paper, we discuss the possibility that polar snow has recorded the 11-year cycle of NO_3^-.

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