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250 years of accumulation, oxygen isotope and chemical records in a firn core from Princess Elizabeth Land, East Antarctica

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Abstract: A 51.85-m firn core collected from site DT001 (accumulation rate 127 kgm^{-2}a^{-1}, mean annual temperature -33.1 ^{o}C) on Princess Elizabeth Land, East Antarctica, during the 1996-97 Chinese First Antarctic Inland Expedition has been analyzed for chemical composition and oxygen isotope ratio. A comparison between the seasonal variations of major ions was carried out in order to reduce the dating uncertainty, using the volcanic markers as time constrains. A deposition period of 251 years was determined. The calculated accumulation rates display an increasing trend before 1820, while after 1820, the trend of the accumulation is not obvious. Overall, temperature change in the region shows a slight increasing trend over the past 250 years. But, notably, a temperature decline of -2 ^{o}C is observed from 1860 to the present. This feature, at odds with the warming trend over the past century recorded in both hemispheres, likely reflects a regional characteristic related to the lack of a high latitude/low latitude link in the Southern Hemisphere circulation patterns. The results of the glaciochemical records of the firn core show that the mean concentrations of Cl^-, Na^+ and Mg^{2+} are similar to those reported from other sites in East Antarctica. However, the mean concentration of Ca^{2+} is much higher than that reported from other regions, suggesting the influence of the strong local terrestrial sources in Princess Elizabeth Land. There is no evidence of a positive correlation between NO_3^- concentrations and solar activity (11-year solar cycle and solar cycle length), although solar proton events may account for some of the NO_3^- peak values in the record.

Key words: firn core; $\delta^{18}O$; accumulation rate; glaciochemistry; Antarctic ice sheet
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1 Introduction

In the ongoing discussion of climate change, the mass balance of Antarctica has received increasing attention during recent decades, since its reaction to global warming will strongly influence sea-level change (Schlosser and Oerter, 2002). Many different compilations of Antarctic mass balance, using models and measurements, have been published (Giovinetto and Bentley, 1985; Bentley and Ciovinetto, 1991; Van Lipzig, 1999; Giovinetto and Zwally, 2000). However, the uncertainties are still relatively large due to the size of the continent and a lack of measurements in some parts of it. Additionally, the response of ice sheet mass balance to climate changes is slow, and it is therefore difficult to directly connect any changes in the extent and height of the ice sheet to a changing climate on short timescales (Isaksson *et al*., 1996). Snow accumulation is found to be sensitive to changes in air temperature (Giovinetto *et al*., 1990) and considered a more important factor to affect Antarctic mass balance. More recent increases in accumulation during the last 30-40 years have been reported for coastal Antarctica (Morgan *et al*., 1991),

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the interior ice sheet (Petit *et al*., 1982) as well as from the Antarctic Peninsula (Peel, 1992). However, there are some other evidences showing decreasing accumulation during the last decades. For example, the decreasing accumulation during 1927-1975 in Northern Victoria Land was reported by Maggi *et al*. (1998). Isaksson *et al*. (1996) found that the accumulation in Dronnig Maud Land was also decreasing during 1932-1991. At this point, any wider implications of these changes are difficult to assess, because glaciological data are sparse from large parts of Antarctica.

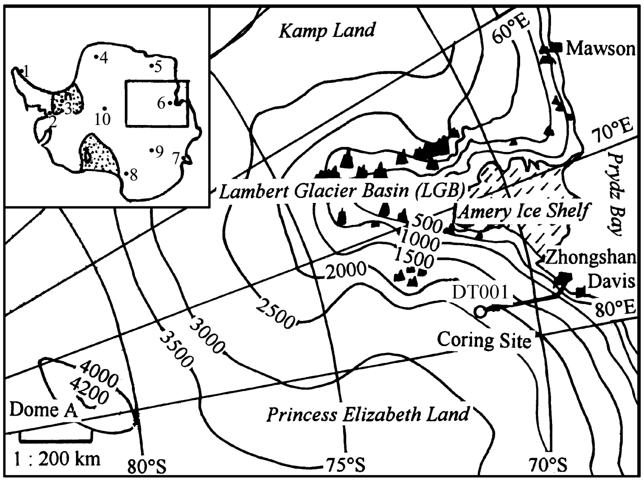

Figure 1 Map showing the route of the Chinese First Antarctic Inland Expedition during 1996-97 and location of coring sites discussed in the text
1-Dalinger Dome; 2-Siple; 3-T340; 4-Epica; 5-Mizuho; 6-DT001; 7-Law Dome; 8-Hercules Névé; 9-Dome C; 10-South Pole

In this study we present accumulation rate and stable isotope data from a firn core from Princess Elizabeth Land (Figure 1). The chemical data of the firn core is also presented in this paper. During recent decades a steadily increasing number of studies on the chemical composition of snow and ice on polar ice sheets have been performed in order to understand environmental changes (e.g. Isaksson *et al*., 2001). Variations of the impurity concentrations recorded in the snow are commonly interpreted as changes in atmospheric composition, despite the fact that the link between the concentrations in air and those found in snow and ice is not well understood (Wolff and Bales, 1996). Thus, we need to improve our understanding of the special distribution of chemical species before we can resolve some of the questions involving origin, transport and deposition of the impurities in Antarctic snow (Isaksson *et al*., 2001).

Princess Elizabeth Land is located in the eastern side of Lambert Glacier Basin (Figure 1). The Lambert Glacier drainage basin, with a total area of more than 1.5×10^{6} km^{2}, is one of the major ice-drainage basins of the East Antarctic ice sheet (Allison, 1998). Snow accumulation in the interior of the basin drains via Lambert Glacier and its tributary ice streams to the embayed Amery Ice Shelf, and hence to the coast. The mean easterly geostrophic winds on the eastern side of the basin show greater seasonal variation in speed but less variation in direction (Allison, 1998). There have been no previous ice core investigations in Princess Elizabeth Land. Therefore, the ice core records from this region provide us valuable data to improve our understanding of the climate and the atmospheric environment over Antarctica.

2 Sampling, analysis and dating

During the 1996-97 Chinese First Antarctic Inland Expedition from Zhongshan Station to Dome A, two firn cores (one is 51.85 m long, the other is 50.32 m deep) apart from 2 meters were drilled at DT001 (71°51'S, 77°55'E; 270 km inland and 2325 m a.s.l.) on Princess Elizabeth Land (Figure 1). All cores were drilled and handled in the field with stringent contamination-control procedures (Li *et al*., 1999). The 51.85-m firn core was transported to the cold chamber (-15 °C) in the Cold and Arid Regions Environmental and Engineering Research Institute, Chinese Academy of Sciences (CAS) where it has been prepared for analyzing chemical composition and oxygen isotope ratio. The other firn core was carried to the cold chamber (-15 °C) in Chinese Institute of Polar Research where the density and stratigraphic features of the firn core were studied carefully (Wen *et al*., 2001). The ice core drilling, sampling and analysis are discussed elsewhere in detail. (Li *et al*., 1999; Zhang *et al*., 2002)

Ice core dating is the basis of ice core research. There have been lots of studies on the seasonal

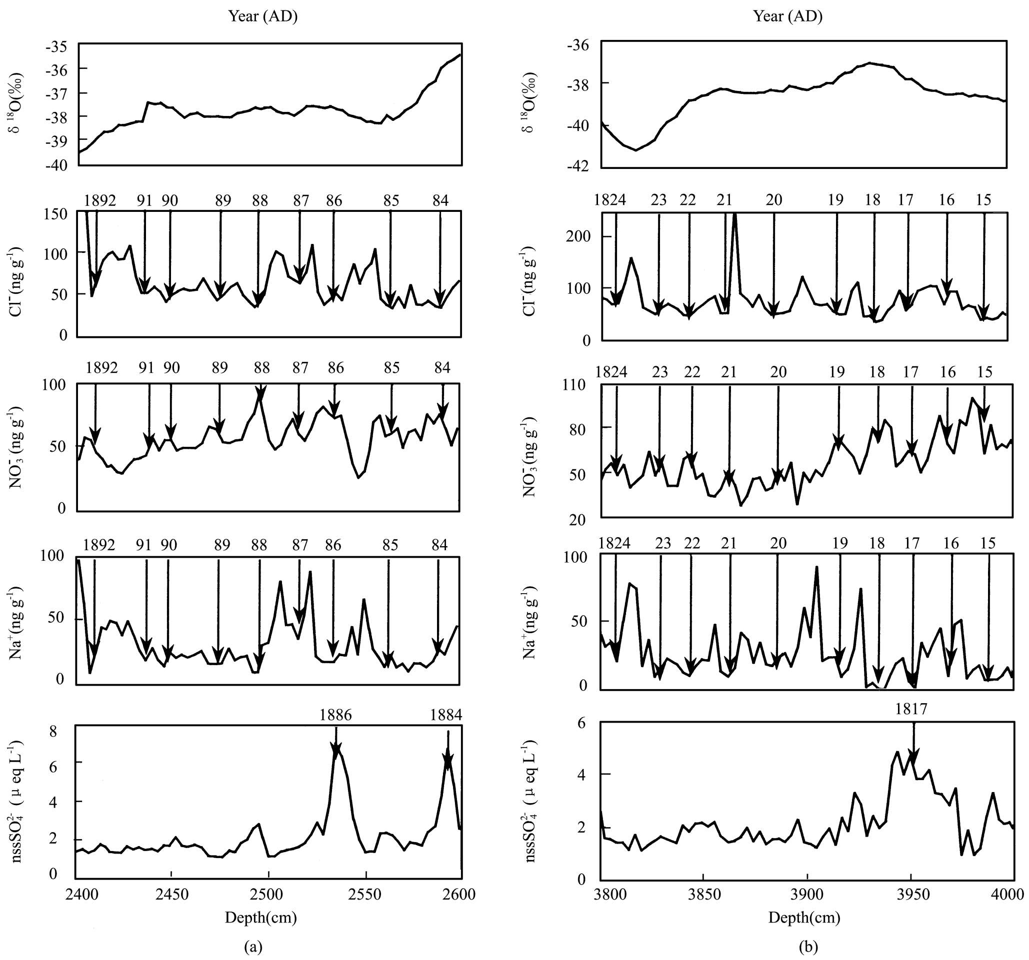

Figure 2 $\delta^{18}O$, Cl^- , NO_3^-, Na^+ and $nssSO_4^{2-}$ profile from firn core at DT001 covering depths: a. 24-26 m, b. 38-40 m

variations of major chemical species in the Antarctic snow and firn (Mosley-Thompson *et al.*, 1993; Whitlow *et al.*, 1992). In order to date the firn core accurately, we paid special attention to seasonal variations in major ions from snow and firn recovered from Princess Elizabeth Land, Antarctica (Li *et al.*, 1999; Qin *et al.*, 2000). Our results show that variations in sea-salt ions (Cl^- and Na^+) and NO_3^- reasonably represent seasonal variations. Therefore, the firn core was dated on the basis of well-preserved $\delta^{18}O$ (smoothed below 3 meters), NO_3^-, Cl^- and Na^+ seasonal cycles counted to establish the depth-age relationship with high accuracy. The accumulated errors, attributable to a few ambiguous seasonal cycles, are estimated to be only ±3 years at the end of the record. The 51.85-m firn core record extends for 251 years (AD 1745-1996). The accuracy of our dating is confirmed by two proofs: 1) the major volcanic eruptions such as Tambora (AD 1815), Krakatoa (AD 1883) and Tarawera (AD 1886) were dated in the firn core at 1817, 1886 and 1884, respectively, as expected (Figure 2); and 2) the 50.32-m firn core carried to Chinese Institute of Polar Research was dated in terms of density and stratigraphic features and contains 243 years which is consistent with our dating (Wen *et al.*, 2001).

3 Accumulation and isotope records

The accumulation rates and the mean annual $\delta^{18}O$ values calculated after multi-parameter dating appear in Figure 3 against time. Decadal means of accumulation and $\delta^{18}O$ in DT001 firn core appear in Table 1.

The mean annual accumulation rate for the entire period is 127 $kgm^{-2}a^{-1}$.

The annual accumulation record from core DT001 shows large interannual variability throughout the whole sequence (Figure 3), which is not uncommon for an accumulation record (Isaksson *et al*., 1996). Processes such as redistribution by wind tend to be very local, and it is therefore more reliable to look at trends over longer time periods rather than at values from individual years. The accumulation in DT001 core displays an increasing trend before 1820, while after 1820, the trend of the accumulation is not obvious. The accumulation in this core shows an increasing trend between 1940 and 1996 (Xiao *et al*., 2004), which is consistent with the results of the firn core from Wilks Land (Goodwin, 1991), but conflicts with the results from Dronning Maud Land, Mizuho Plateau and Kamp Land (Isaksson *et al*., 1996; Oerter *et al*., 1999; Satow and Watanable, 1990). Therefore, accumulation time series from a single site, such as in this case, should be viewed cautiously and large-scale (e.g. regional) interpretations should be avoided without additional supporting evidence. It is, however, interesting to note that there appears to be a period of low accumulation around 1965 followed by a rapid increase which coincides with many other ice core records from Antarctica (e.g. Isaksson *et al*., 1996).

Table 1 Comparison of decadal accumulation and $\delta^{18}O$ values in the DT001 firn core, the rates of change in accumulation and $\delta^{18}O$ since 1745 are also listed

Time period	Mean accumulation rate $kgm^{-2}a^{-1}$	Deviation from average $kgm^{-2}a^{-1}$	Mean $\delta^{18}O$‰	Deviation from average ‰
1745-1749	100	-27	-37.01	0.47
1750-1759	109	-18	-38.64	-1.16
1760-1769	106	-21	-37.97	-0.49
1770-1779	117	-10	-38.15	-0.67
1780-1789	115	-12	-39.07	-1.59
1790-1799	128	1	-38.25	-0.77
1800-1809	129	2	-37.60	-0.12
1810-1819	146	19	-38.54	-1.06
1820-1829	125	-2	-37.77	-0.29
1830-1839	121	-6	-36.97	0.51
1840-1849	140	13	-36.70	0.78
1850-1859	128	1	-35.83	1.65
1860-1869	144	17	-34.48	3.00
1870-1879	142	15	-36.97	0.51
1880-1889	122	-5	-37.14	0.34
1890-1899	131	4	-37.82	-0.34
1900-1909	122	-5	-36.81	0.67
1910-1919	149	22	-35.27	2.21
1920-1929	114	-13	-36.81	0.67
1930-1939	122	-5	-36.77	0.71
1940-1949	135	8	-38.89	-1.41
1950-1959	131	4	-37.70	-0.22
1960-1969	93	-34	-38.67	-1.19
1970-1979	142	15	-38.44	-0.96
1980-1989	155	28	-37.35	0.13
1990-1996	134	7	-37.57	-0.09
1745-1996	127	+0.0727$kgm^{-2}a^{-1}$ (rate of change)	-37.48	+0.0022‰a^{-1} (rate of change)

Overall, the stable isotope record from DT001 firn core suggests an increasing trend of 0.0022‰a^{-1} (significant at the 99% level) during the past 250 years. However, an $\delta^{18}O$ decline trend is observed from 1860 to the present. The $\delta^{18}O$ record and the instrumental surface air temperature record at Davis meteorological station display the same variations (Xiao *et al*., 2004), which shows the variation of the $\delta^{18}O$ in the DT001 firn core may represent the temperature change in the region.

In order to further study the overall decreasing trend of $\delta^{18}O$ during the period AD 1860-1996, the comparison between DT001 oxygen isotope record and hemispheric and global temperature averages by year for the period 1856-1998, relative to 1961-1990 (Jones *et al*., 1999) was made (Figure 4). From Figure 4 we can see that the oxygen isotope temperature in Princess Elizabeth Land shows a prominent decreasing trend which conflicts with the Northern Hemispheric and Global, especially Southern Hemispheric surface temperature changing trends over the past 150 years. The preliminary results of the oxygen isotope temperature in the firn core collected from site DT085 (73°22'S, 77°01'E and 2577 m a.s.l.) on Princess Elizabeth Land, East Antarctica, during 1997-98 Chinese Second Antarctic Inland Expedition show similar decreasing trend during the same period (Dr. Xiao communication, unpublished data). There are more ice cores from Antarctica showing increasing isotope temperature trends in the past 150 years (Isaksson *et al*., 1996; Isaksson *et al*., 1999; Stenni *et al*., 1999). For example, the isotope temperature increase of about 0.8 °C in Dronning Maud since AD 1865 was reported by Isaksson *et al*. (1996). However, some other ice core records show a decrease in isotopically derived temperature (Mosley-Thompson, 1992) and Aristarain *et al*. (1990) reported a temperature decline of -2 °C from 1850 to present conditions in Antarctic Peninsula.

If the experiential δ-T formula in Princess Elizabeth Land, $\delta^{18}O = 0.70T - 11.36$ (Qin *et al*., 2000), is used, the decrease in temperature is about -1.8 °C (significant at the 99% level) in Princess Elizabeth Land, comparable to that found in the Antarctic Peninsula.

Making a comprehensive view of the isotope records of the ice cores from the coastal regions of Antarctica (Figure 5), we can see that, the isotope temperature records of the ice cores from Epica (75°00'S, 2°00'E and 2900 m a.s.l.), Mizuhio (70°42'S, 44°20'E and 2230 m a.s.l.), Law Dome (66°44'S, 112°50'E and 1390 m a.s.l.) and Hercules Név é (73°06'S, 165°28'E and 2960 m a.s.l.) show a warming trend in the past 150 years, however, the records from Sipe (75°55'S, 84°15'W and 1054 m a.s.l.), Dalinger Dome (64°12'S, 57°40'W and 1640 m a.s.l.), T340

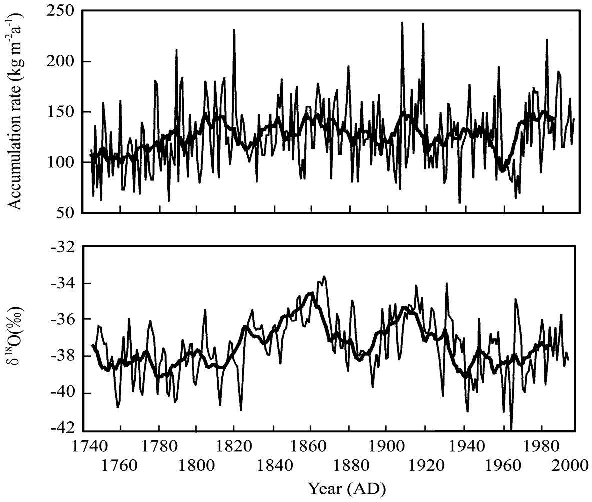

Figure 3 Annual average (thin black lines) and 11-year running mean (thick black lines) of accumulation and $\delta^{18}O$ for the DT001 firn core from Princess Elizabeth Land, Antarctica from 1745 to 1996

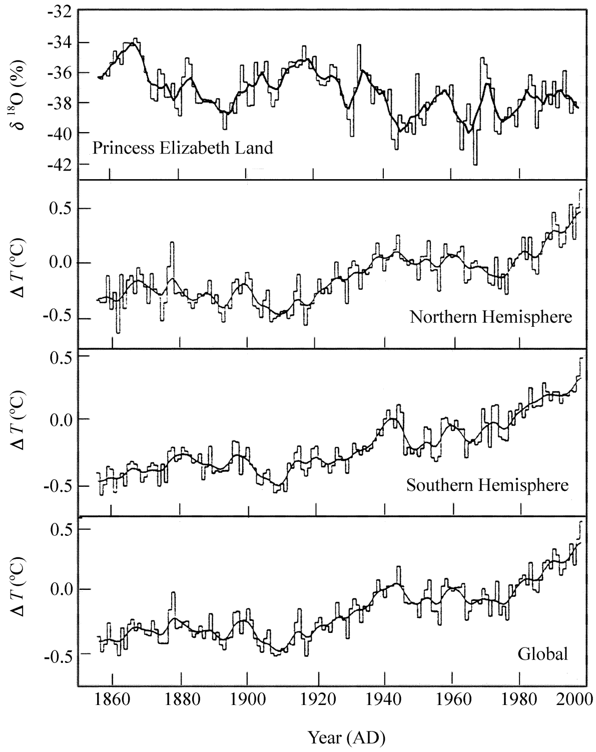

Figure 4 Comparison between the DT001 oxygen isotope record and the hemispheric and global temperature averages by year for the period 1856-1998, relative to 1961-1990 (Jone *et al*., 1999). The smooth line highlights variations on decadal time scale (10-year Gaussian filter)

(78°60'S, 55°00'W) and DT001 show a declining trend of temperature. The reason may be as follows: there is a lack of high latitude/low latitude link particularly due to the nature of the Southern Hemisphere atmospheric circulation. It does not favor strong north-south energy exchanges, due to the relatively small meridional amplitude of the long waves and to the strong circum-polar circulation around Antarctic continent. Princess Elizabeth Land is located in the east of Lambert Glacier Basin. Studies show that the topography of the basin, which extends more than 800 km inland, strongly influences the surface climate of the region (Allison, 1998). Therefore, the reason for the decreasing trend of oxygen isotope temperature in Princess Elizabeth Land over the past 150 years may be the impacts of the unique atmospheric circulation patterns in Southern Hemisphere and the topography in Princess Elizabeth Land.

As regards the bottom section of the firn core, the isotope record suggests "colder" environmental conditions (more negative $\delta^{18}O$ values) at Princess Elizabeth Land for the period AD 1745-1820. This colder period seems to correspond to the so-called Little Ice Age (LIA) episode, even though particular care must be taken in using this term with a global meaning.

A better understanding of the climatic significance of the isotope variation recorded in DT001 core requires a comparison with other Antarctic ice core records. Previous ice core records from East Antarctica (Mosley-Thompson *et al.*, 1992), such as Law Dome (Morgan, 1985), Hercules Névé (Stenni *et al.*, 1999) and the South Pole (Mosley-Thompson *et al.*, 1985), suggest similar colder conditions in the time period encompassing the LIA. The smoothed δD record observed in the 905 m ice core drilled at Dome C (Benoist *et al.*, 1982) also suggests cooler conditions from AD 1200 to 1800. The Hercules Névé and Law Dome profiles resemble more closely the DT001 record, with the coldest conditions from 1750 to 1850.

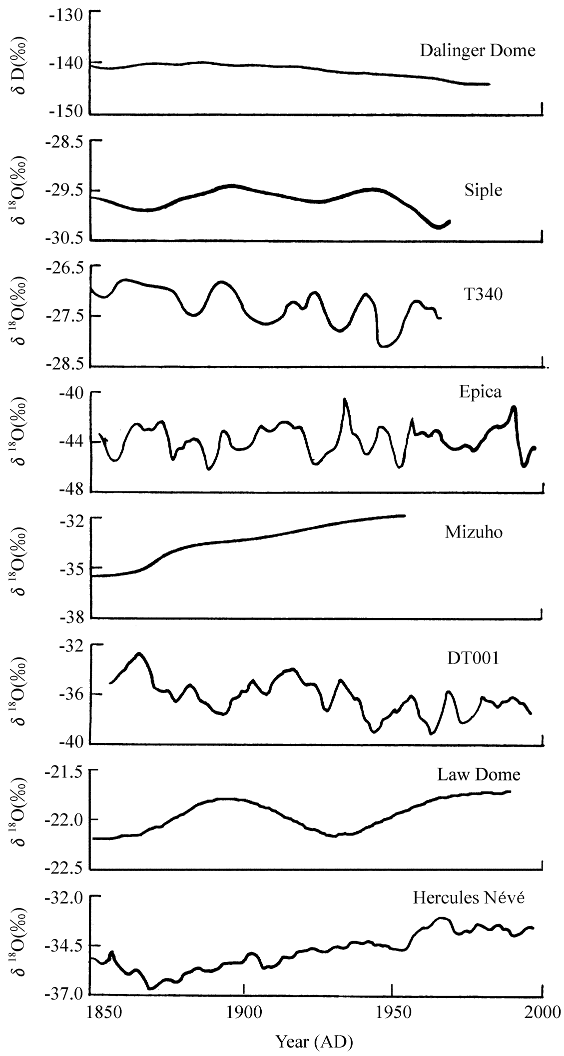

Figure 5 The Antarctic isotope records in the past 150 years: Dalinger Dome (cubic spline with $\sigma = 1\times10^{-3}$, Aristarain *et al.*, 1990), Siple (48-year Gaussian filter, Mosley-Thompson, 1992), T340 (48-year Gaussian filter, Mosley-Thompson, 1992), Epica (20-year moving average, Isaksson *et al.*, 1996), Mizuho (48-year Gaussian filter, Mosley-Thompson, 1992), DT001 (11-year smoothed), Law Dome (30-year smoothed, Morgan and Ommen, 1997), Hercules Névé (11-year smoothed, Stenni *et al.*, 1999)

The positive empirical relationship between temperature and snow accumulation is widely used in discussions of greenhouse warming and sea level changes (e.g. Oerlemans, 1982). It is also interesting to note that the variations of $\delta^{18}O$ are partly in phase with those of accumulation rate recovered from DT001 firn core. That is, the increasing temperature is accompanied with increasing precipitation, and vice versa (Figure 3 and Table 1).

4 Chemical composition records

Mean concentrations of Cl^-, Na^+, Mg^{2+}, $nssMg^{2+}$, Ca^{2+}, $nssCa^{2+}$, NO_3^- and $nssSO_4^{2-}$ are reported in Table 2.

Table 2 Mean concentrations of major ions for the DT001 firn core from Princess Elizabeth Land, East Antarctica, estimated to cover the time 1745-1996

Site	Cl^- ng g^{-1}	Na^+ ng g^{-1}	Mg^{2+} ng g^{-1}	$nssMg^{2+}$ ng g^{-1}	Ca^{2+} ng g^{-1}	$nssCa^{2+}$ ng g^{-1}	NO_3^- ng g^{-1}	$nssSO_4^{2-}$ ng g^{-1}
DT001 core								
Mean	63	43	10	5.1	54	52	61	82
Std dev.	28.8	24.5	8.8	5.6	48.2	46.3	22.4	39.9
Min.	5	1	0	-2	1	-1	10	5
M ax.	263	197	77	49	497	492	164	340
LGB72 pit[1] 1.8m in depth	96	78	19	9	51	48	66	62
LGB10 pit[2] 2.5m in depth	91	51	7.2	1.1	55	53	132	48
Epica core[3] 1865-1991	35.6	13.5	2	0.3	1.2	0.7	54.4	58.1
South Pole[4] 1955-1988	34.1	11.1	2.8		4.2		98.8	
Dome C[5] 1760-1980	69	22					15	

Note: [1]Zhang *et al*. (1999), [2]Qin *et al*. (2001), [3]Isaksson *et al*. (2001), [4]Whitlow *et al*. (1992), [5]Legrand and Delmas (1988).

The results of the $nssSO_4^{2-}$ record for DT001 firn core are reported elsewhere (Zhang *et al*., 2002). In this paper the Cl^-, Na^+, Mg^{2+}, Ca^{2+} and NO_3^- records are discussed.

In our core, 49% of the magnesium and 4% of the calcium are of sea-salt origin, in agreement with snow-pit data from the same area, but the ratio of the $ssCa^{2+}$ is much lower than that from other sites.

Figure 6 shows that the variation trends of major ion concentrations are not obvious. Temporal variations in sea salts are thought to be associated with changing intensity of surface winds near the ocean surface (Petit *et al*., 1981). The temporal variability of Cl^- and Na^+ through this record is not large, except for some high concentration spikes (Figure 6). The sea salt records show clear seasonal variations, with winter peaks (Li *et al*., 1999), as at other ice core records from coastal regions of Antarctica (Curran *et al*., 1998). Table 2 shows that the mean concentrations of Cl^- and Na^+ are similar to those reported from other areas in East Antarctica. However, mean concentrations of Ca^{2+} are much higher than those reported from other regions, and this anomaly phenomenon may be related to the local terrestrial sources, for there are many bare mountains around Lambert Glacier Basin. The higher ratio of the $nssCa^{2+}$ in the snow and firn may suggest the influence of the strong local terrestrial sources in Princess Elizabeth Land.

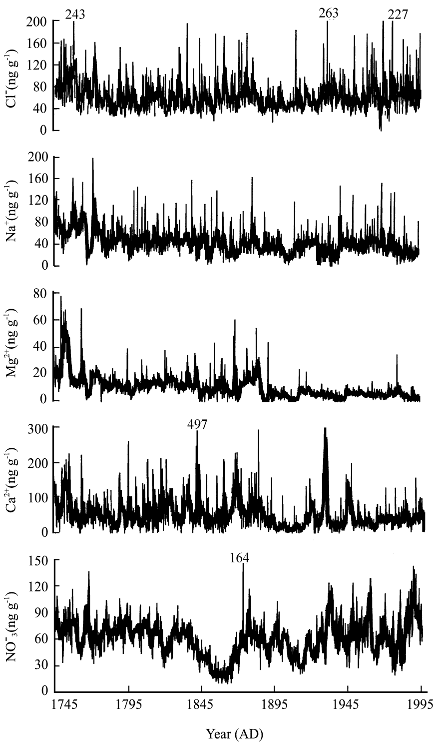

Figure 6 The ion-concentration records of Cl^-, Na^+, Mg^{2+}, Ca^{2+} and NO_3^- for the DT001 firn core (thin black line). The records are running smoothed with eleven-point moving average (thick black line)

There are a lot of concentration data of NO_3^- in the Antarctic snow, but the sources of NO_3^- in the Antarctic snow are still disputed. Some articles show the concentrations of NO_3^- in the Antarctic snow are related to solar activities (Zeller and Parker, 1981; Dreschhoff and Zeller, 1990, 1998; Shea *et al*., 1999; Palmer *et al*., 2001), while other studies reveal no evidence of a positive correlation between solar activity and NO_3^- content of south polar snow (Legrand and Kirchner, 1990; Legrand and Delmas, 1986; Herron, 1982; Mosley-Thompson *et al*., 1991). So special attention is given to the study of NO_3^- in the DT001 firn core.

Cross spectral analysis for the NO_3^- concentration reveals that the variation of NO_3^- concentration does not show a significantly rhythmical variation with a periodicity of about 11 years. Comparing the NO_3^- content in the DT001 firn core and the reconstructed solar cycle length during the past 250 years reveals no evidence of a positive correlation between NO_3^- concentrations and solar cycle length. In order to study the relationship between the NO_3^- peak values in the record and solar proton events, we use events listed by Shea *et al*. (1999) covering the period 1942-1995 and augment these with the July 1928 white-light flare (Dreschhoff and Zeller, 1990) (Table 3). Figure 7 shows the nitrate concentrations in the firn core for 1920-1996. From Figure 7 it is possible that most of the higher peaks do appear in proximity with solar proton events listed in Table 3. However, some of the solar events are not evident in our record, also, several large nitrate peaks appear which are not readily associated with any solar proton events.

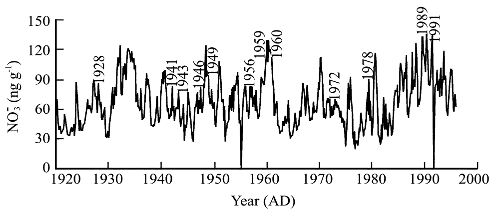

Figure 7 Nitrate record and solar proton events, 1920-1996

Table 3 List of solar events used in this study

Event(s)[a]	Year	Ref.
15/7	1928	2
1/3; 18/9	1941	1
28/2; 7/3	1942	1
28/3; 25/7	1946	1
19/11	1949	1
23/2	1956	1
10-12/5; 17/7	1959	1
4/5; 15/11	1960	1
7/8	1972	1
7/5	1978	1
12-18/8; 29/9; 30/10	1989	1
26/3	1991	1

a Day/month of events in that calendar year.
References: 1-Shea *et al*. (1999);
2-Dreschhoff and Zeller (1990)

So, as for the relationships between NO_3^- concentrations in Antarctic ice sheet and solar activities, we cautiously propose that although solar activities (11-year solar cycle, and solar cycle length) do not contribute to the background of content of NO_3^- in south polar snow, most of solar proton events may account for some of the NO_3^- peak values in snow and ice in Antarctica. However, it is impossible to provide a record of the solar proton events based on the NO_3^- concentrations (Palmer *et al*., 2001) in Antarctic ice sheet due to the following reasons: First, the origins of the NO_3^- in Antarctic ice sheet are more complicated. Second, there are various sporadic phenomena such as the solar proton events, supernovae, meteor falls, volcanic eruptions and nuclear tests may lead to the high values of NO_3^- in Antarctic ice sheet (Rothlisberger *et al*., 2000; Legrand and Kirchner, 1990; Rood *et al*., 1979; Holdsworth, 1986). Third, the concentrations of NO_3^- deposited in Antarctic ice sheet may have changed due to post-depositional processes (Neubauer and Heumann, 1988; Legrand *et al*., 1996; Wagnon *et al*., 1999).

5 Conclusions

The reported 250 years of accumulation, $\delta^{18}O$ and chemical profiles in a firn core from Princess Elizabeth Land provide additional data for a better understanding of the climate and the atmospheric environment over Antarctica. The accumulation rates display an increasing trend before 1820, while after 1820, the trend of the accumulation is not obvious. Temperature in the study region decreased after 1860 compared to the background of the whole South Hemispheric warming. Such regional behavior requires conformation from other ice cores in the Princess Elizabeth Land. However, despite this limited geographical significance, this first 250-year climatic record from Princess Elizabeth Land has one implication of broad interest. If the DT001 record is included in the compilation of Southern Hemisphere historical records, it will for the earliest part of the record (before 1880) have a significant impact on the hemispheric averages, as there are only a few records available. However, due to the first firn core from

Princess Elizabeth Land, East Antarctica, the accumulation, oxygen isotope and chemical composition records should be viewed cautiously and large-scale (e.g. regional) interpretations should be avoided without additional supporting evidence. Fortunately, during 1997-98 and 1998-99 Chinese National Antarctic Research Expedition, three firn cores were drilled in Princess Elizabeth Land (Qin *et al*., 2000). Most of the laboratory analyses of the cores are still in progress, and the expected results may be helpful to explain for the overall climate and atmospheric environment in this region.

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