



## Seasonal variation in the input of atmospheric selenium to northwestern Greenland snow



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### HIGHLIGHTS

- The first comprehensive seasonal variation of Se in Greenland snow is presented.
- Data exhibit pronounced seasonality in the fallout of Se to Greenland.
- High Se/MSA ratios indicate a significant contribution from anthropogenic sources.
- Coal combustion in China is likely to be a major anthropogenic source.

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### ABSTRACT

Oxygen isotope ratio ( $\delta^{18}\text{O}$ ) and concentrations of Al,  $\text{Na}^+$ , methanesulfonic acid (MSA),  $\text{SO}_4^{2-}$ , and selenium (Se) in a continuous series of 70 snow samples from a 3.2-m snow pit at a site in northwestern Greenland were determined using ultraclean procedures.

Well-defined depth profiles of  $\delta^{18}\text{O}$ , Al, and sea-salt- $\text{Na}^+$  allowed the determination of chronology of the snow pit that spanned approximately 6 years from spring 2003 to summer 2009. Se concentrations were at a low pg/g level, ranging from 7.2 to 45 pg/g, and exhibited high variability with generally higher values during winter and spring and lower values during summer and fall. Very high crustal enrichment factors ( $\text{EF}_c$ ) of Se averaging approximately 26,600 for the entire time period indicate a small contribution from crust dust. High Se/MSA ratios are generally observed in the winter and spring snow layers, in which the Se concentrations were relatively high (>20 pg/g). This suggests that a significant component of the Se present in the snow layers is of anthropogenic origin. During the summer season, however, high  $\text{EF}_c$  values are accompanied with low Se/MSA, indicating an increased contribution of marine biogenic sources. Significant correlations between Se, Al, and non-sea-salt  $\text{SO}_4^{2-}$  highlight that significant inputs of Se to the snow are likely controlled by the seasonality in the transport efficiency of anthropogenic Se from the source regions to the site. Based on the seasonal changes in Se concentrations, Se/MSA, and Se/S ratios observed in the samples, the input of anthropogenic Se to the site appears to be governed by the long-range transportation of Se emitted from coal combustion in East Asian countries, especially in China.

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### 1. Introduction

Selenium (Se) is an essential element for human and animal health and plant growth (Hamilton et al., 1990; Rayman, 2000; Germ et al., 2007). However, over- and underexposure of safe dietary Se intake (17 ~ 1600  $\mu\text{g}$  Se/day) can cause significant health problems, such as selenosis and chronic Keshan disease. (Yang and Xia, 1995; Moreno-Reyes et al., 2003). Because of toxicity, Se has been widely studied

since the 1960s in various environmental samples (Anderson et al., 1961; Mosher and Duce, 1983; Cutter and Church, 1986; De Gregori et al., 2002). It is now known that the atmosphere plays an important role in the global biogeochemical cycle of Se (Wen and Carignan, 2007). In particular, atmospheric deposition of Se is considered to be an important source of contamination, because elevated concentrations of Se have been observed in remote aquatic environments and other habitats far from anthropogenic sources (Cutter and Church, 1986; Bennett, 1995; Kagawa et al., 2003; Beavington et al., 2004). As a result, significant attention has been paid to the emission, transport, and deposition of atmospheric Se (Ross, 1985; Atkinson et al., 1990; Dudzinska-Huczuk et al., 2000; Wen and Carignan, 2007).

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To date, studies of atmospheric Se have focused primarily on the spatial distribution of Se at local to regional scales using aerosols and rainwater samples (Mosher and Duce, 1983; Cutter and Church, 1986; Ellis et al., 1993; De Gregori et al., 2002; Kagawa et al., 2003; Ranville et al., 2010; De Santiago et al., 2014). These studies provided useful information to further understanding of the processes of transport and removal of anthropogenic Se from source regions. However, because there are not many studies that include time period covering more than one year, temporal changes in atmospheric Se still remains poorly understood (Ellis et al., 1993; Kagawa et al., 2003).

Studies of the occurrence of various trace elements in successively dated snow and ice layers in Greenland have allowed us to decipher the large-scale changes in the atmospheric cycles of these elements in the Northern Hemisphere (Boutron et al., 2011). Nonetheless, the only data on the occurrence of Se in Greenland were reported more than 40 years ago by Weiss et al. (1971); their data were based on samples of old and young ice and firn in Greenland representing a time period spanning from 800 BC to the 1960s. This data limitation has occurred primarily because the extremely low concentrations of Se in these materials make it difficult to overcome sample contamination during the entire analytical procedure from field sampling to final analysis (Boutron, 1995; Boutron et al., 2011). Since the pioneering work by Clair Patterson and coworkers at the California Institute of Technology (Patterson and Settle, 1976; Ng and Patterson, 1981), only a few laboratories have established adequate ultraclean procedures to minimize contamination and obtain reliable time series data on ultra-low concentrations of trace elements from polar snow and ice.

We present here a complete dataset of high-resolution short-term (intra- and inter-annual) variation in the occurrence of Se in northwestern Greenland snow dated from spring 2003 to summer 2009. This study aims to investigate the relative magnitude of natural and anthropogenic Se inputs to the snow and their variability throughout the year, governed by the large-scale atmospheric transport and the significance of natural versus anthropogenic sources. The results will help assess the extent to which Se is enriched in the Arctic atmosphere and also assist in the interpretation of long-term record of Se from Greenland snow and ice cores.

## 2. Experimental setup

### 2.1. Field sampling

Sampling was performed on June 26, 2009, at a site (77°26′81″ N, 50°56′78″ W, 2461 m a.s.l.) 3.5 km from the North Greenland Eemian Ice Drilling (NEEM) deep ice coring site in northwestern Greenland (Fig. 1). A 3.2 m snow pit was hand-dug by operators wearing clean garments and polyethylene gloves, using acid-cleaned low-density polyethylene (LDPE) shovels. Approximately 10 cm of snow was shaved away from the upwind wall using an acid-cleaned Teflon scraper. A continuous series of 70 samples was collected from the surface to a depth of 3.2 m by horizontally inserting acid-cleaned cylindrical Teflon tubes (diameter 5 cm, length 35 cm) into the snow, using an LDPE hammer. Snow samples were transferred from the tubes into acid-cleaned LDPE wide-mouthed 1000 mL bottles. It should be noted that the use of tubes with a diameter of 5 cm enabled us to collect the samples at 4.6 cm intervals because the tubes were hammered into the wall of the pit with crossing over and slight overlapping between vertical sampling lines to avoid contamination from the outside of the tubes.

All items used for the sampling procedure had been thoroughly cleaned in a clean laboratory following the procedures described in Hong et al. (2000). The bottles were packed in double-sealed acid-cleaned plastic bags and kept frozen until analysis.

### 2.2. Analytical procedures

Se and Al concentrations in our snow samples were measured using an Element2 ultrasensitive inductively coupled plasma sector field mass

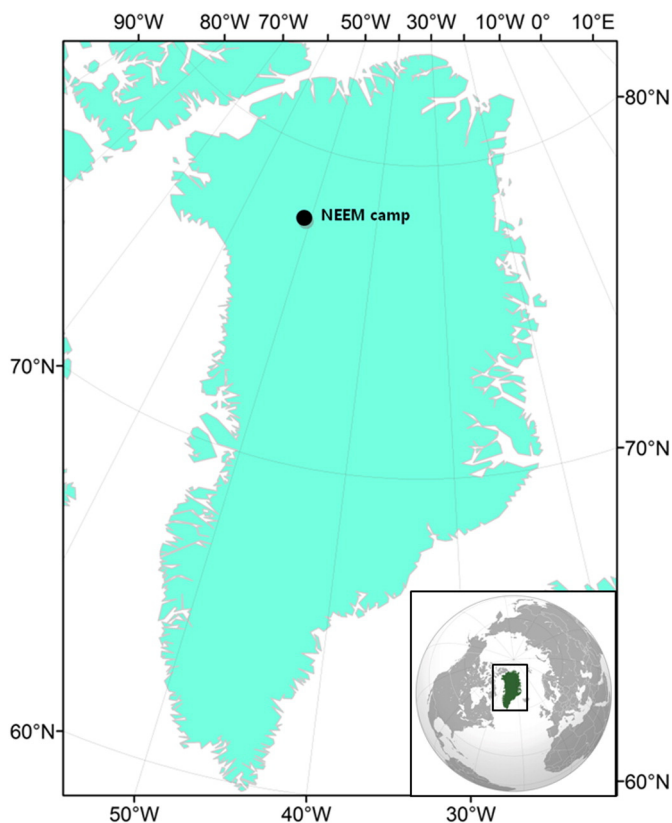


Fig. 1. Map showing the location of the snow pit sampling site in northwestern Greenland.

spectrometer (ICP-SF-MS) (Thermo Scientific, Bremen, Germany) installed in a class 10 clean booth in a class 1000 clean laboratory at the Korea Polar Research Institute. The sample introduction system of the ICP-SF-MS consists of an Apex high-sensitivity inlet system (Apex IR, Elemental Scientific Inc., Omaha, NE, USA) and Nafion® membrane desolvation module (ACM, Elemental Scientific Inc., Omaha, NE, USA). In this system, samples passing through a heated cyclonic spray chamber and a Peltier-cooled multi-pass condenser in an Apex IR are conditioned to produce intense and uniform dry aerosols (D'Illio et al., 2006). In addition, the ACM module removes residual solvent vapors from the samples using a counter-current sweep gas (Ar) flow, and thus reduces oxide levels and other interferences by the matrix (D'Illio et al., 2006). The instrumental settings and operative conditions are reported in the supporting information, Table S1.

Se forms six naturally occurring stable isotopes. Among these, the three major isotopes  $^{76}\text{Se}$ ,  $^{78}\text{Se}$ , and  $^{80}\text{Se}$  have masses similar to those of argon dimers (May and Wiedmeyer, 1998) and cannot be used for trace-level Se measurement by a conventional ICP-SF-MS (Ralston et al., 2008). The other Se isotopes also suffer from various isobaric and polyatomic interferences (May and Wiedmeyer, 1998). Therefore, the Se isotope to be used for measurement must be carefully selected. In this study,  $^{77}\text{Se}$  was used to measure Se in the snow samples. Although  $^{77}\text{Se}$  represents only 7.6% of total Se, it is no subject to isobaric interference. The magnitude of isotopic ratio shift is known to vary up to 18‰ for  $^{82}\text{Se}/^{76}\text{Se}$  during Se (VI) or Se (IV) reduction (Johnson, 2011). If significant isotope fractionation of Se is mass dependent, the  $^{82}\text{Se}/^{77}\text{Se}$  ratio would vary up to 15‰. Because a proportion of  $^{77}\text{Se}$  in representative isotopic composition of Se could vary from 7.5% to 7.7% (Berglund and Wieser, 2011), changes in  $^{82}\text{Se}/^{77}\text{Se}$  ratio due to isotope fractionation appear to be insignificant.

Potential interferences with  $^{77}\text{Se}$  measurement are  $^{40}\text{Ar}^{37}\text{Cl}$ ,  $^{36}\text{Ar}^{40}\text{Ar}^1\text{H}$ ,  $^{154}\text{Sm}^{2+}$ , and  $^{154}\text{Gd}^{2+}$  (May and Wiedmeyer, 1998). According to Vanhoe et al. (1994), 0.008% of Cl forms the  $^{40}\text{Ar}^{37}\text{Cl}$ . In this study, the interference of  $^{40}\text{Ar}^{37}\text{Cl}$  on the  $^{77}\text{Se}$  peak was experimentally

determined using a series of diluted HCl solutions (100, 200 and 500  $\mu\text{g}$  of Cl/g). No systematic increase in instrumental intensity was observed for the solutions. The interference contribution to  $^{77}\text{Se}$  was calculated to be less than 20% of the measured Se concentrations at the concentration range (4.4–175 ng/g) of  $\text{Cl}^-$  in our snow samples.

Under the Apex-ACM sample introduction system, the double-charged ion level determined by  $\text{Ba}^{2+}/\text{Ba}$  reached 10% (Table S1). This indicates that the interferences of double-charged ions such as  $^{154}\text{Sm}^{2+}$  and  $^{154}\text{Gd}^{2+}$  can be significant for  $^{77}\text{Se}$ .  $^{154}\text{Sm}$  comprises ~23% of the total Sm. To correct for the spectral interference of  $^{154}\text{Sm}^{2+}$  on  $^{77}\text{Se}$ , a correction factor was empirically calculated with five (20, 40, 60, 80, and 100  $\mu\text{g}/\text{g}$ ) Sm single-element solutions. During the measurement of Se in the snow samples, the intensities of  $^{154}\text{Sm}$  were simultaneously measured. The  $^{154}\text{Sm}^{2+}$  interferences were then calculated using the correction factor and subtracted from the  $^{77}\text{Se}$  intensities. In most samples, the interference of  $^{154}\text{Sm}^{2+}$  did not exceed 10% of the  $^{77}\text{Se}$  intensities. However, several samples exhibited a significant influence from the  $^{154}\text{Sm}^{2+}$  interferences, up to 46% of the  $^{77}\text{Se}$  intensity. This reinforces the need to correct for  $^{154}\text{Sm}^{2+}$  interference in  $^{77}\text{Se}$  measurements by ICP-SF-MS using the Apex-ACM system. In contrast, the abundance of  $^{154}\text{Gd}$  is only 2.2% of total Gd. Considering that the amounts of Sm and Gd in the continental crust, the largest natural source for both elements, are similar, the interference of  $^{154}\text{Gd}^{2+}$  on  $^{77}\text{Se}$  would be negligible compared to that of  $^{154}\text{Sm}^{2+}$ .

Snow samples were melted at room temperature inside a class 10 clean bench in a class 1000 clean room. Approximately 10 mL aliquots were extracted for Se measurement. All analytical samples, including blank and standard solutions, were acidified to 1%  $\text{HNO}_3$  (w/w) with Fisher “Optima” grade ultrapure nitric acid. Standard solutions for external calibration were prepared from a 10  $\text{mg L}^{-1}$  multi-element ICP-MS stock solution (IV-ICP-MS-71A, Inorganic Ventures). High-purity water was obtained by double distillation of de-ionized water produced by a Milli-Q water system (Millipore, Bedford, MA, USA).

The detection limits of Al and Se were estimated to be three times the standard deviation of 20 replicate analyses of blank solution and were 7.6 and 6.9  $\mu\text{g}/\text{g}$ , respectively. A NIST SRM 1643e diluted to the concentration level of the snow samples was measured in every 10 samples for quality control of the data. National Institute of Standards and Technology Standard Reference Materials (NIST SRM) 1643e Al and Se measurements were  $158.3 \pm 29.0$  and  $11.17 \pm 1.01$   $\mu\text{g}/\text{kg}$  (mean  $\pm \sigma$ ,  $N = 9$ ), in agreement with the certified values of  $138.3 \pm 8.4$  for Al and  $11.68 \pm 0.13$   $\mu\text{g}/\text{kg}$  for Se.

Oxygen isotope ratios ( $\delta^{18}\text{O}$ ) in the snow samples were determined with wavelength scanned-cavity ring spectroscopy (L1102-I, Picarro Inc., Sunnyvale, CA, USA). Each sample was injected 6 times, and the results of the first three injections were excluded to avoid any memory effect from the previous sample. A reference material, Greenland Ice Sheet Precipitation (GISP), was measured every 5 samples. The uncertainties in  $\delta^{18}\text{O}$  were less than 0.2‰.

Soluble ions such as  $\text{Na}^+$  and  $\text{SO}_4^{2-}$ , and methanesulfonic acid (MSA) were measured in the snow samples using ion chromatography (ICS2100 with IonPac CS12 analytical column for  $\text{Na}^+$ ; and ICS2000 with IonPac AS15 analytical column for  $\text{SO}_4^{2-}$  and MSA; Dionex Corporation, Sunnyvale, CA, USA). The detection limits of  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ , and MSA were 0.01, 0.08, and 0.49  $\text{ng}/\text{g}$ , respectively.

### 3. Results and discussion

#### 3.1. Age dating of the snow samples

The snow samples were dated using the depth profiles of  $\delta^{18}\text{O}$ , Al and  $\text{Na}^+$ . Seasonal variation in  $\delta^{18}\text{O}$  responding to atmospheric temperature was reported from various sites in Greenland (Steffensen, 1985; Beer et al., 1991; Hastings et al., 2004). In general,  $\delta^{18}\text{O}$  becomes less negative during the summer season and more negative during the winter season. In our snow samples, maxima in  $\delta^{18}\text{O}$  were observed at

41.1–45.7, 91.4–96.0, 141.7–146.3, 196.6–201.1, 260.6–265.1, and 297.1–301.6 cm, while minima were found at 27.4–32.0, 73.1–77.7, 114.3–118.8, 164.6–169.1, 233.1–237.7, and 278.9–283.4 cm depth intervals (Table S2 and Fig. 2).

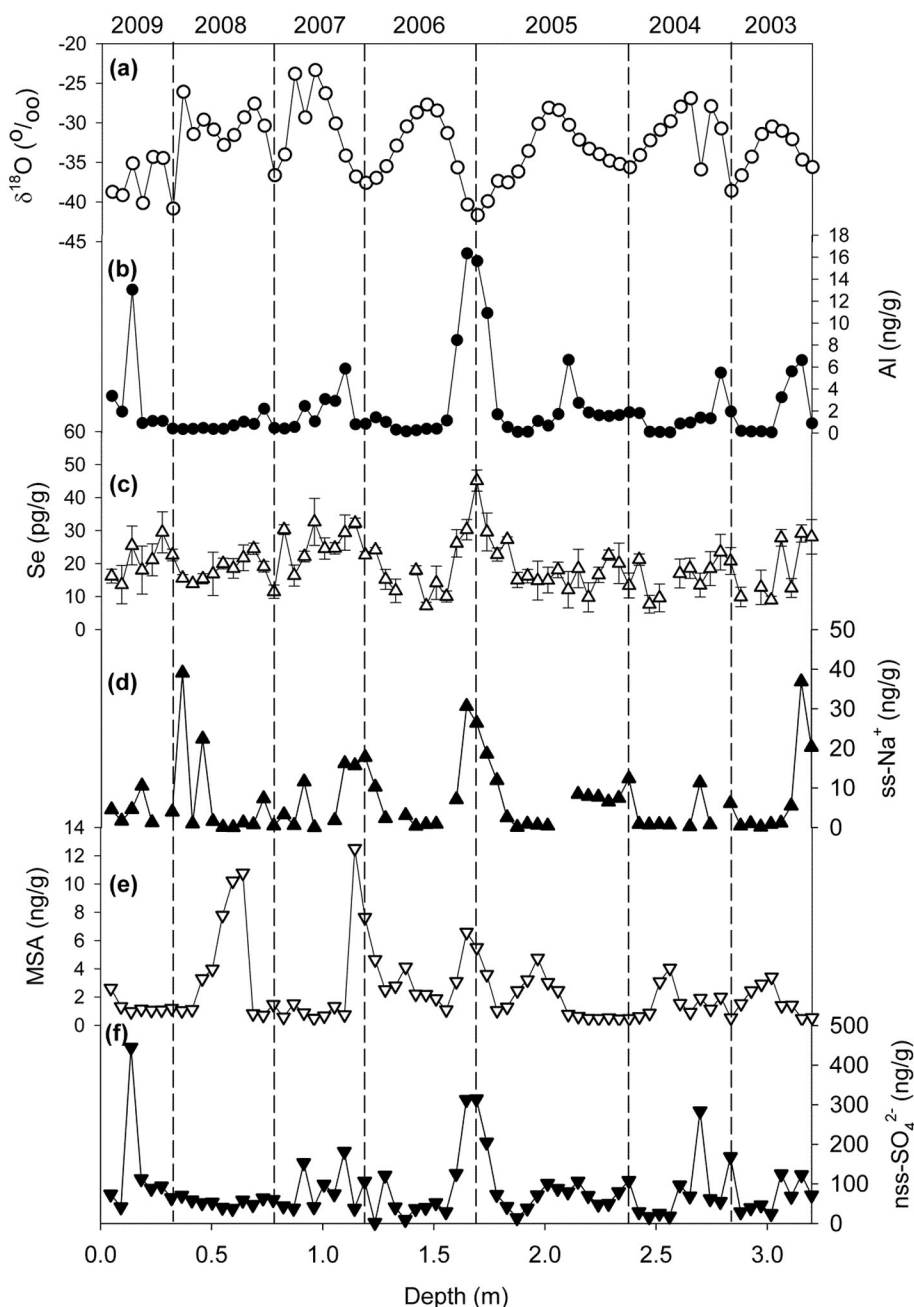
Atmospheric Al concentrations in Greenland usually exhibit strong peaks in spring associated with Asian dust episodes (Candelone et al., 1996; Barbante et al., 2003). In this study, pronounced Al peaks were observed at 9.1–13.7, 160.0–164.6, 205.7–210.3, and 306.3–310.9 cm and relatively weak peaks at 68.6–73.1, 105.1–109.7, and 274.3–278.9 cm (Table S2 and Fig. 2). The peaks generally occurred in snow layers deposited slightly later than winter as defined by  $\delta^{18}\text{O}$  minima, indicating that these depth intervals corresponded to spring. Seasonal variation in  $\text{Na}^+$  concentration derived from sea salt are characterized by winter–spring maxima and mid-summer minima in interior Greenland aerosols and snow (Mosher et al., 1993; Dibb et al., 2007). After subtracting the Na concentration from crustal dust using the Al concentrations in each sample (Wedepohl, 1995), the sea-salt- $\text{Na}^+$  ( $\text{ss-Na}^+$ ) concentrations in our snow samples exhibit strong peaks in the transition from winter to spring as inferred from  $\delta^{18}\text{O}$  and Al, except for the 32.0–36.6 cm and 41.1–45.7 cm depth intervals. Similar poorly defined peaks for chemical species were previously reported in a central Greenland snow profile (Mayewski et al., 1990; Barbante et al., 2003).

Combining the depth profiles of  $\delta^{18}\text{O}$ , Al, and  $\text{ss-Na}^+$  concentrations, our snow samples could be dated from spring 2003 to summer 2009, as shown in Fig. 2. Our dating assignment was in close agreement with the age of snow samples recovered in July 2009 from a 2 m snow pit at a site ~1 km from ours (Kuramoto et al., 2011).

#### 3.2. Characteristics of the data

Se concentrations ranged from 7.2 to 45  $\mu\text{g}/\text{g}$  with a mean value of 20  $\mu\text{g}/\text{g}$  (Table S2 and Fig. 2). Compared to the scarce available data previously obtained from wet deposition samples, it appears that the extremely low Se concentrations in our snow samples from northwestern Greenland are in accordance with those observed in Greenland ice and firn from Camp Century (Table 1). Based on the relatively constant Se concentrations and the relationship between Se and S in Greenland glacial samples, Weiss et al. (1971) claimed that there was no evidence for anthropogenic input of Se from fossil fuel combustion in Greenland until the 1960s. However, it should be noted that reliable data of various trace elements in polar ice samples only began to emerge after ultraclean decontamination procedures for contamination control for the entire procedure from field sampling to laboratory analysis were pioneered by Clair Patterson and coworkers at the California Institute of Technology (Patterson and Settle, 1976; Ng and Patterson, 1981; Boutron et al., 1998). This means that the data of Weiss et al. (1971) could be erroneous due to inadequate contamination control. Considering that the natural emission rates of Se and Pb are estimated to be similar (Nriagu, 1989), this assumption regarding the effects of contamination is supported by the fact that the Se concentration (25.5  $\mu\text{g}/\text{g}$ ) measured in 800-year-old Greenland ice was an order of magnitude higher than the Pb concentrations (2.5–4.0  $\mu\text{g}/\text{g}$ ) in Greenland ice from 723 to 985 years BP, during which anthropogenic Pb inputs were already significant (Hong et al., 1994). The effects of contamination will be more convincingly confirmed when a reliable long-term Se record from Greenland snow and ice is obtained using ultraclean procedures.

It is interesting to observe that, as shown in Table 1, the high Se concentrations in some of our samples are comparable to the mean concentration of Se in precipitation samples collected from Bermuda, the mid-ocean region of the western Atlantic Ocean. Se concentration in rainwater in Bermuda is known to reflect contributions from both marine (natural) and continental (anthropogenic) sources (Cutter and Church, 1986). Therefore, it appears that enhanced Se concentrations in the NEEM snow pit samples are linked to anthropogenic inputs. The mean concentration of Se in our samples is 9 to 11 times lower than



**Fig. 2.** Depth profiles of (a)  $\delta^{18}\text{O}$ , (b) Al, (c) Se, (d) ss-Na<sup>+</sup>, (e) MSA and (f) nss-SO<sub>4</sub><sup>2-</sup> concentrations determined in our 70 snow samples. The dotted lines indicate the minima of  $\delta^{18}\text{O}$  values representing the winter season.

that in rainwater samples collected at various sites close to anthropogenic sources (Table 1). Such large differences in Se concentration between the remote northwestern Greenland snow samples and rainwater samples from continental sites may be due to differences in distance from the anthropogenic sources.

### 3.3. Seasonal variation in atmospheric Se, MSA, and nss-SO<sub>4</sub><sup>2-</sup>

Fig. 2 illustrates the depth profiles of Se, MSA, and nss-SO<sub>4</sub><sup>2-</sup> concentrations measured in the NEEM snow pit samples. Non-sea salt-SO<sub>4</sub><sup>2-</sup> concentrations were calculated from the following equation:

$$[\text{nss-SO}_4^{2-}] = [\text{SO}_4^{2-}]_{\text{total}} - (\text{SO}_4^{2-}/\text{Na}^+)_{\text{seawater}} \times \text{ss}[\text{Na}^+], \quad (1)$$

where  $[\text{SO}_4^{2-}]_{\text{total}}$  is the total concentration of SO<sub>4</sub><sup>2-</sup> in our snow samples and  $(\text{SO}_4^{2-}/\text{Na}^+)_{\text{seawater}}$  is the concentration ratio (0.12) of SO<sub>4</sub><sup>2-</sup>/Na<sup>+</sup> in seawater (Kuramoto et al., 2011). According to our calculations, the sea salt SO<sub>4</sub><sup>2-</sup> did not exceed 10% of the total SO<sub>4</sub><sup>2-</sup> in most of the samples. This agrees well with the fraction of marine sulfate measured in aerosols over the Greenland ice sheet (Jaffrezo et al., 1994).

Se concentrations generally increased during the winter and spring, and decreased during summer and fall (Fig. 2). Pronounced seasonal variation has been previously observed for various trace elements in Greenland snow and ice with different patterns of variation for different elements due to the diversity of the sources (Candelone et al., 1996; Boutron et al., 1998; Barbante et al., 2003). The only previous data on seasonal variation in Se were recorded by Weiss et al. (1971) in Greenland firn samples corresponding to the period from fall 1964 to summer 1965; these indicated an elevated concentration of Se in the

**Table 1**

Comparison of Se concentrations in NEEM snow pit samples with previous data determined from wet deposition samples from various sites. The mean concentration is given in parentheses.

Site	Description	Se conc. (pg/g)
NEEM <sup>a</sup>	This study	7.2–45 (20)
Camp Century <sup>b</sup>	Greenland old ice (800 B.C.)	25.5
Camp Century <sup>b</sup>	Greenland and Antarctic ice (1815–1960)	7.6–22 (11.6)
Camp Century <sup>b</sup>	Greenland firn samples (1964–1965)	(9.1)
	1964 (fall)	5.1
	1964 (December)	9.7
	1965 (winter)	14
	1965 (spring)	8.0
	1965 (summer)	8.7
Bermuda <sup>c</sup>	Mid-ocean region in the western Atlantic Ocean (1983–1984)	(30)
Lewes <sup>c</sup>	Urban area 30 km from coal fired power plant, U.S. (1983–1984)	(174)
Valparaíso <sup>d</sup>	Various sites near copper smelter and coal fired power plant, Chile (1997–1999)	7.4–1308 (225)

<sup>a</sup> This study.

<sup>b</sup> Weiss et al., 1971.

<sup>c</sup> Cutter and Church, 1986.

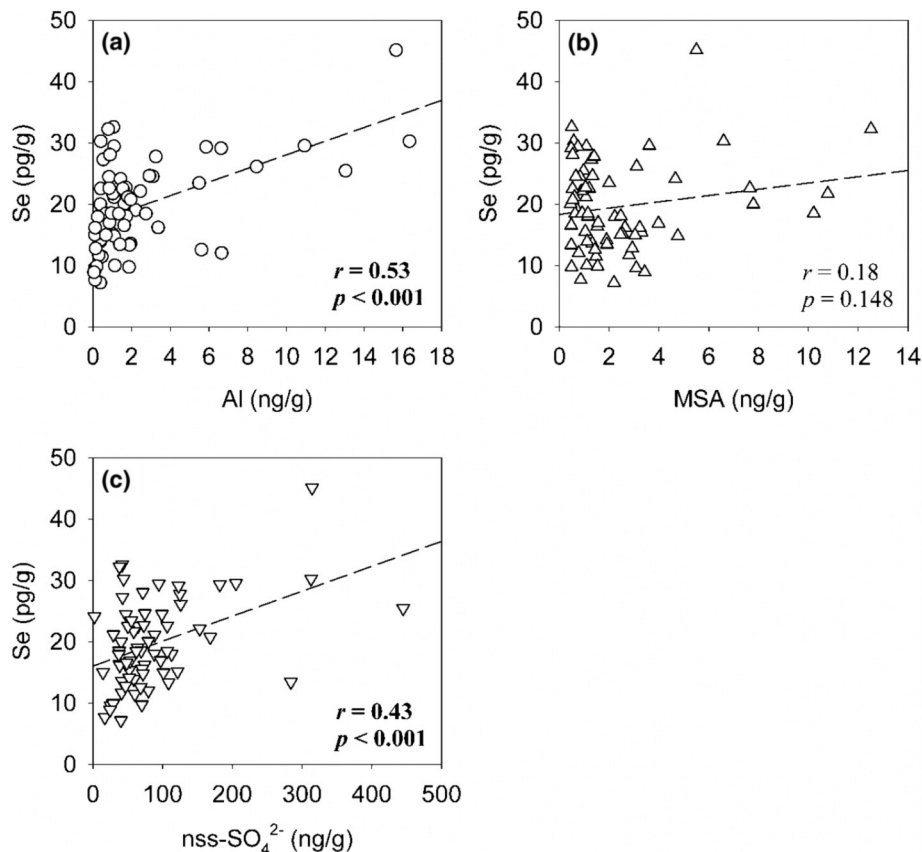
<sup>d</sup> De Gregori et al., 2002.

winter layer (Table 1). Although a suspected contamination problem in that study makes it difficult to compare the seasonal patterns with our dataset, the relatively high winter concentrations observed in both our study and earlier data suggest a pattern.

In Fig. 3, a significant correlation coefficient ( $r = 0.53$ ) is observed for Se and Al concentrations in the snow. This seems to be associated with the atmospheric Se transport mechanisms. According to Wen

and Carignan (2007), most of the atmospheric Se emitted from natural and anthropogenic sources is in the form of volatile species such as dimethyl selenide (DMSe), dimethyl diselenide (DMDSe), elemental selenium ( $S^0$ ), hydrogen selenide ( $H_2Se$ ), and selenium dioxide ( $SeO_2$ ). Because these volatile species are very unstable, they are readily condensed or adsorbed onto atmospheric aerosols to be transformed into particulate phase in the atmosphere (Wen and Carignan, 2007). Then the secondary particulate Se formed by gas-particle conversion can be transported long distances through atmospheric pathways (Ellis et al., 1993; Wen and Carignan, 2009). This atmospheric transport mechanism of Se may explain the observation of elevated Se concentrations together with elevated Al (dust aerosol) concentrations observed in some of the samples.

In contrast to Se, MSA concentrations in the NEEM snow pit samples generally increased during summer and fall (Fig. 2). This seasonal variation is consistent with the changes in atmospheric MSA concentration observed in the Greenland ice sheet (Jaffrezo et al., 1994). Because MSA is produced by the oxidation of dimethyl sulfide (DMS), its seasonal cycle is dominated by the marine biogenic production of DMS, which is correlated with insolation (Li et al., 1993). Therefore, the atmospheric MSA concentration over the ice sheet begins to increase as early as April, but large increases occur in June and July corresponding to a shift in the source region from the Arctic Basin to North Atlantic Ocean (Jaffrezo et al., 1994). Marine biogenic emissions are known to be a dominant natural source of Se in the atmosphere (Nriagu, 1989). As shown in Fig. 3, there is no significant correlation ( $r = 0.18$ ) between Se and MSA concentrations, suggesting that the contribution from marine biogenic source might be insignificant for at least part of Se concentrations determined in our samples. In the present study, the snow samples from 109.7–118.9 and 160.0–169.1 cm exhibited high MSA concentrations despite representing winter seasons (Fig. 2). This appears to be associated with episodic changes in the air circulation. Occasional high



**Fig. 3.** Changes in Se concentration as a function of (a) Al, (b) MSA, and (c)  $nss-SO_4^{2-}$  concentration determined in our 70 snow samples. Dotted lines represent linear regression lines. The correlation coefficients that are significant at 99% confidence levels are shown in bold.

concentrations of MSA during the late fall were also observed in aerosol samples over Greenland as a result of long-range transport from mid-latitudes where the seasonal variation in MSA is less pronounced, with some production taking place in winter (Jaffrezo et al., 1994).

Seasonal variation in  $\text{nss-SO}_4^{2-}$  was characterized by significant increases in the transition from winter to spring, with relatively high concentrations over the whole year of 2007 (Fig. 2). This pattern is generally similar to that of Se. In Fig. 3, it is observed that a comparatively significant correlation ( $r = 0.43$ ) associates  $\text{nss-SO}_4^{2-}$  with Se. As mentioned above,  $\text{nss-SO}_4^{2-}$  accounts for more than 90% of the total  $\text{SO}_4^{2-}$  in most of the samples, so the seasonal variation in  $\text{nss-SO}_4^{2-}$  reflects that of the total  $\text{SO}_4^{2-}$ . An increase in  $\text{SO}_4^{2-}$  concentrations during the transition from winter to spring has also been reported for various sites in Greenland (Weiss et al., 1971; Jaffrezo et al., 1994; Bigler et al., 2002; Dibb et al., 2007; Kuramoto et al., 2011). This has been primarily attributed to the strong influence of anthropogenic inputs (Jaffrezo et al., 1994; Dibb et al., 2007; Kuramoto et al., 2011).

Overall, in our data, the seasonal variation in Se was observed to be of a generally similar pattern to that of Al and  $\text{nss-SO}_4^{2-}$ , whereas a contrasting pattern was displayed by MSA (Fig. 2). Considering that elevated Al and  $\text{nss-SO}_4^{2-}$  concentrations in Greenland snow reflect crustal and anthropogenic contributions, it can be inferred that the deposition of Se over the Greenland ice sheet is most likely controlled by the combined effect of anthropogenic emissions of Se and their transport efficiency from the source regions to the site.

#### 3.4. Natural versus anthropogenic contributions to the atmospheric Se over Greenland

According to global and regional emissions inventories for trace elements (Nriagu and Pacyna, 1988; Nriagu, 1989; Pacyna and Pacyna, 2001), the present-day atmospheric cycle of Se is governed by both natural and anthropogenic contributions. The natural sources include crustal dust, volcanoes, sea salt spray, forest fires, and continental and marine biogenic activity (Nriagu, 1989), and the anthropogenic sources are stationary fossil fuel combustion, non-ferrous metal production, iron and steel production, cement production, and waste disposal (Pacyna and Pacyna, 2001). Globally, marine biogenic sources account for ~80% of the total atmospheric Se emissions from natural sources (Mosher and Duce, 1987), while fossil fuel combustion accounts for ~90% of the total anthropogenic Se emissions (Pacyna and Pacyna, 2001). However the distribution of atmospheric Se is known to be highly heterogeneous over the Earth's surface (Wen and Carignan, 2007).

In this study, the contribution from rock and soil dust to atmospheric Se over Greenland was evaluated using the crustal enrichment factors ( $\text{EF}_c$ ). The calculation of  $\text{EF}_c$  for Se is as follows:  $\text{EF}_c = [\text{Se}/\text{Al}]_{\text{snow}} / [\text{Se}/\text{Al}]_{\text{crust}}$ , where  $[\text{Se}/\text{Al}]_{\text{crust}}$  refers to the concentration ratios in the mean upper continental crust (Wedepohl, 1995). If a sample has an  $\text{EF}_c$  value close to unity, this indicates that the Se in that sample originates primarily from rock and soil dust. Conversely, an  $\text{EF}_c$  value much larger than unity indicates a significant contribution from other natural and/or anthropogenic sources.

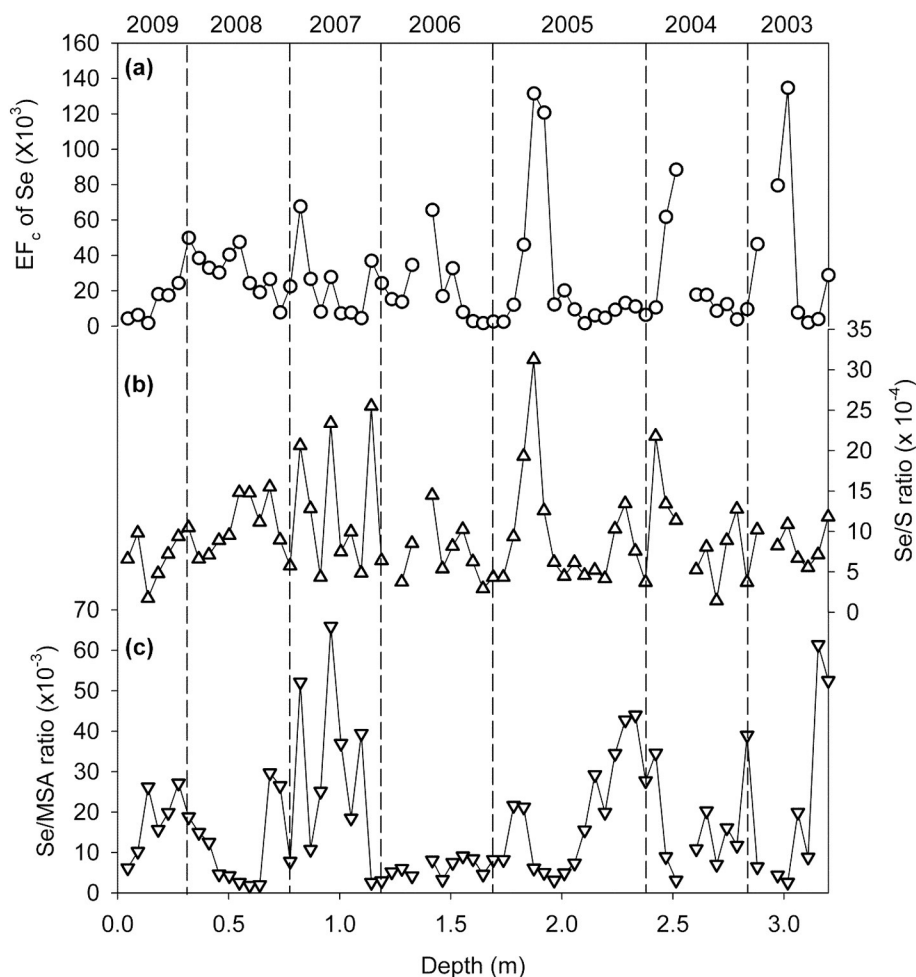
The  $\text{EF}_c$  values of Se determined in this study ranged from 1630 to 134,692 with the mean value of 26,584 (Fig. 4). Such high  $\text{EF}_c$  values indicate a small contribution of crust dust to atmospheric Se. A high enrichment of atmospheric Se relative to crust dust has been previously observed in various sites around the world ranging from urban to remote Antarctic areas (Chiou and Manuel, 1986; Xie et al., 2006; Weller et al., 2008; Ranville et al., 2010). However, the main sources for atmospheric Se differ among sites. In the Antarctic region, atmospheric Se is primarily attributed to natural sources such as marine bioactivities (Weller et al., 2008) or volcanic emissions (Cunningham and Zoller, 1981). On the other hand, in the Northern Hemisphere, high  $\text{EF}_c$  values of atmospheric Se are primarily due to industrial emissions, even in the open ocean of North Pacific (Ranville et al., 2010).

In our snow pit profiles, peaks of  $\text{EF}_c$  values were observed at 27.4–32.0, 54.9–59.4, 77.7–82.3, 91.4–96.0, 109.7–114.3, 137.1–141.7, 182.9–187.4, 224.0–228.6, 246.9–251.4, 297.1–301.7 and 315.4–320.0 cm depth intervals (Fig. 4). Interestingly, they were generally coincident with high Se/sulfur (S) ratios. The Se/S ratio is known to be useful for identifying the anthropogenic source of atmospheric Se (Hashimoto et al., 1970; Chiou and Manuel, 1986; Kagawa et al., 2003). Coal and petroleum, the two major representatives of fossil fuel, have different Se/S ratios (Hashimoto et al., 1970). The Se/S ratios of these fuels were reported to be  $11 \times 10^{-4}$  (Chiou and Manuel, 1986) or  $4\text{--}6 \times 10^{-4}$  for coal (Hashimoto et al., 1970) and  $0.3\text{--}1.0 \times 10^{-4}$  for petroleum (Hashimoto et al., 1970). In contrast, to date, very little data have been published on Se/S ratios from the marine biosphere. The only data was provided by Kagawa et al. (2003), who estimated the Se/ $\text{nss-SO}_4^{2-}$  ratio of marine algae to be  $0.8 \times 10^{-4}$  by combining the Se/MSA and MSA/ $\text{nss-SO}_4^{2-}$  ratios of marine air mass during winter season (Ellis et al., 1993; Matsumoto et al., 1998). However, according to Matsumoto et al. (1998), the MSA/ $\text{nss-SO}_4^{2-}$  ratios exhibited large seasonal variations, and the mean value of summer and autumn was three times higher than that of winter and spring. Considering this seasonal variation of MSA/ $\text{nss-SO}_4^{2-}$  ratio, the Se/S ratios corrected from the value of  $0.8\text{--}2.4 \times 10^{-4}$  for Se/ $\text{nss-SO}_4^{2-}$  were  $2.5\text{--}7.5 \times 10^{-4}$ , which makes it difficult to discriminate between the Se/S ratios of marine algae and fossil fuel sources. Therefore, to assess the relative contributions from natural and anthropogenic sources to Se in our snow pit samples, we used the Se/MSA ratio of  $8.8\text{--}9.4 \times 10^{-3}$  that was reported for a marine biogenic source in the western Atlantic Ocean (Ellis et al., 1993).

The Se/S and Se/MSA ratios determined in our samples are shown in Fig. 4. The Se/MSA ratios ranged from  $2.0 \times 10^{-3}$  to  $66 \times 10^{-3}$ . The large range of Se/MSA ratios indicates pronounced inter- and intra-annual changes in the sources of atmospheric Se reaching northwestern Greenland. Although the Se/MSA ratios showed inter-annual variation, high Se/MSA ratios were generally observed in the winter and spring snow layers, in which the Se concentrations were relatively high. This implies that a significant part of the Se present in the snow layers is primarily attributable to anthropogenic inputs. This is also supported by the fact that the mean value ( $17 \times 10^{-3}$ ) of the Se/MSA ratios in our samples was a factor of ~2 higher than that from a marine biogenic source (Ellis et al., 1993). During the summer of 2003, 2004, 2006 and 2008, however, relatively high  $\text{EF}_c$  values and Se/S ratios were accompanied by low Se/MSA ratios close to that of marine biogenic sources (Fig. 4). This indicates that the marine biogenic sources also contributed to the enrichment of atmospheric Se, especially during the summer season.

The Se/S ratios determined in our samples varied between  $1.4 \times 10^{-4}$  and  $31 \times 10^{-4}$  with a mean value of  $9.4 \times 10^{-4}$  (Fig. 4). This mean Se/S ratio was well within the range of Se/S ratios reported from coal but higher than that for petroleum (Hashimoto et al., 1970; Chiou and Manuel, 1986). However, the Se/S ratios observed in the snow layers with relatively high  $\text{EF}_c$  values were generally higher than  $15 \times 10^{-4}$  (Fig. 4). This means that the primary source of the atmospheric Se reaching the site might have a Se/S ratio higher than the Se/S ratio reported for coal. According to Ren et al. (1999), the mean concentration of Se in Chinese coal is 6.2 ppm. This is more than two times higher than that (2.8–3.1 ppm) in U.S. coal (Chiou and Manuel, 1986; Ren et al., 1999). However, the average sulfur content of coal in China is also 2.8 times higher than that in U.S. coal (Hong et al., 1993; Chiou and Manuel, 1986). Therefore, the Se/S ratios in both U.S. coal and Chinese coal are not distinguishable.

Here, it should be noticed that if anthropogenic Se and S were deposited on the Greenland snow, they probably reflected the Se/S ratios of flue gas from anthropogenic sources, not the raw materials. According to Wen and Carignan (2007), during coal combustion, about 30% of Se is partitioned into the vapor phase and the rest 70% of Se into the particulate phase which is effectively removed from the



**Fig. 4.** Depth profiles of (a)  $EF_c$  values, (b) Se/S and (c) Se/MSA ratios. The dashed line indicates the minima of  $\delta^{18}O$  values representing the winter season.

emission by the electrostatic filters within combustion plants. On the other hand, desulfurization efficiency of scrubbers used in coal fired power plants can be >90% (Xu et al., 2000; US EPA, 2006). Considering removal efficiencies of both Se and S within power plants, it can be inferred that the Se/S ratios of flue gas emitted from coal combustion might be 3 times higher than those in coals. Therefore, the Se/S ratios of flue gas calculated from those of coals,  $8.4\text{--}11 \times 10^{-4}$ , are  $25\text{--}33 \times 10^{-4}$  (Chiou and Manuel, 1986; Hong et al., 1993; Ren et al., 1999). These values well match with the high Se/S ratios observed in Greenland snow samples (Fig. 4).

According to Chiou and Manuel (1986), several potential Se sources including volcanic ash ( $16 \times 10^{-4}$ ), soil ( $45 \times 10^{-4}$ ) and bottom ash from power plants ( $150 \times 10^{-4}$ ) also exhibit the Se/S ratios higher than  $15 \times 10^{-4}$ . However, these potential inputs appear to be limited by several factors. First, as mentioned above, the remarkably high  $EF_c$  values of these snow samples confirm that soil cannot be the primary source for atmospheric Se. Also, volcanic ash can hardly explain the high Se/S ratios observed in the snow samples with high  $EF_c$  values because the several highest Se/S ratios observed in those snow samples were markedly higher than the Se/S ratio of volcanic ash. Finally, Se can only be transported over a long distance through the atmosphere, so it would be difficult for bottom ash to reach remote areas such as Greenland (Wen and Carignan, 2007). Taken together, the highly elevated Se/S ratios observed in the snow samples with high Se/MSA ratios most likely reflect the contributions of anthropogenic emissions from coal combustion.

Recently, the long range transport of trace elements emitted from coal combustion in Asian countries has become the major source of

atmospheric trace elements over the Arctic (McConnell and Edwards, 2008). In addition, Asian countries have been reported to account for ~40% of the total Se emission of ~3500 t in 1995 (Pacyna and Pacyna, 2001) and China is the largest consumer of coal in the world, accounting for ~40% of global coal consumption between 2003 and 2009 (BP statistical review of world energy, 2010). According to a 44-year record of 10-day back trajectories of air masses reaching Greenland (Kahl et al., 1997), 58% of air masses originate from East Asia during winter and 65% pass over East Asia/North Pacific during spring, while only 20% of the trajectories show transport from East Asia during summer. Interestingly, the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios observed in an unpublished work on Pb isotopes in our samples point to Chinese coal as a major contributor to anthropogenic Pb in the winter and spring snow layers (in preparation).

Consequently, it appears that the intra-annual variations in the Se/MSA and Se/S ratios observed in our samples are due to the seasonal changes in the inputs of natural Se from the marine biosphere and the long-range transport of anthropogenic Se from East Asian countries, especially China.

#### 4. Conclusion

This study provides the first comprehensive data on Se concentrations in recent snow at a site in northwestern Greenland. Data indicate pronounced seasonality in Se concentrations, with generally elevated concentrations in the winter and spring snow layers. Concentrations of Se are moderately correlated with Al and  $\text{nss-SO}_4^{2-}$ , demonstrating that the input of Se to the snow is likely controlled by the seasonality in the transport efficiency of atmospheric Se from the source regions

to the site. High  $EF_c$  values of snow samples indicate that the contribution of crust dust to the atmospheric Se was always negligible. The Se/MSA ratio used as an indicator for possible anthropogenic contributions is characterized by strong seasonality with an increase during winter and a decrease in summer. Considering the relative high Se concentrations during winter, a significant part of the Se present in our snow samples is attributed to contributions from anthropogenic sources. Two episodic increases in Se concentrations with low Se/MSA ratios at 109.7–114.3 and 274.3–278.9 cm are most likely related to the deposition of Se derived from marine biogenic emissions, suggesting that a biogenic source on the ocean surface could occasionally be important in interior Greenland. The Se/S ratio which is informative for differentiating anthropogenic Se between coal and petroleum sources, together with the Se concentration and the Se/MSA ratio, reflects a large contribution of anthropogenic Se emitted from coal combustion in East Asian countries, especially in China.

It would be worthwhile to investigate past changes in Se over time periods of decades to centuries to increase our understanding of the temporal behavior of atmospheric Se controlled by natural and anthropogenic processes and mechanisms in the remote Arctic atmosphere.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2015.04.082>.

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