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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 ($\delta^{18}O$) and concentrations of Al, Na^+, methanesulfonic acid (MSA), 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 $\delta^{18}O$, Al, and sea-salt-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 (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 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 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.

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 μg 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

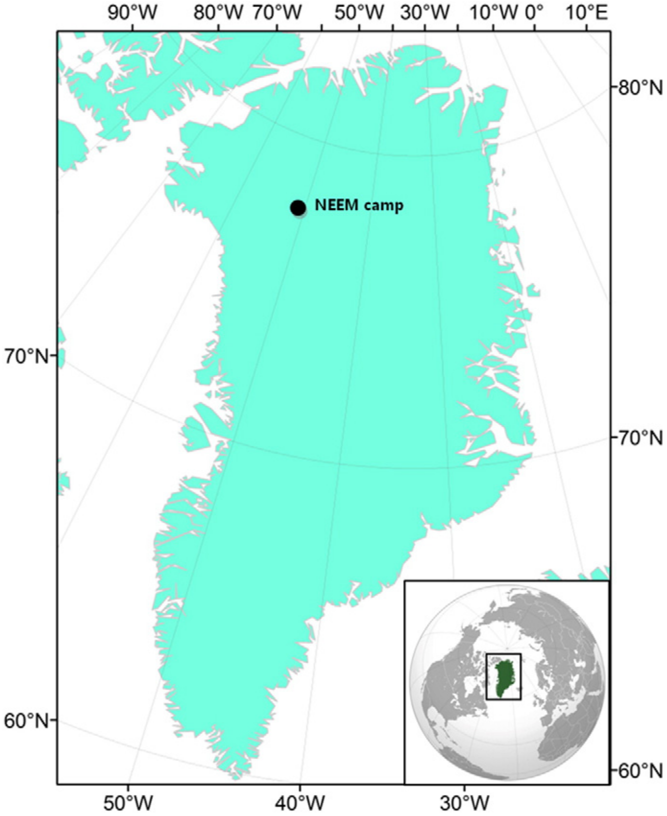

Fig. 1. Map showing the location of the snow pit sampling site in northwestern Greenland.

Se and Al concentrations in our snow samples were measured using an Element2 ultrasensitive inductively coupled plasma sector field mass 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'Ilio 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'Ilio 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}Se, ^{78}Se, and ^{80}Se have masses similar to those of argon dimmers (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}Se was used to measure Se in the snow samples. Although ^{77}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}Se/^{76}Se during Se (VI) or Se (IV) reduction (Johnson, 2011). If significant isotope fractionation of Se is mass dependent, the ^{82}Se/^{77}Se ratio would vary up to 15‰. Because a proportion of ^{77}Se in representative isotopic composition of Se could vary from 7.5% to 7.7% (Berglund and Wieser, 2011), changes in ^{82}Se/^{77}Se ratio due to isotope fractionation appear to be insignificant.

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