Greenland NEEM ice core records of trace metals during the 1710~1970

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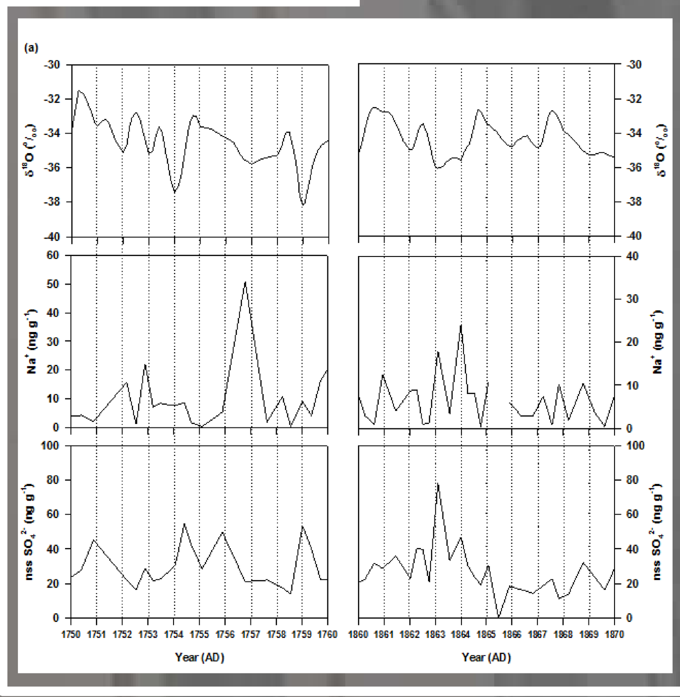
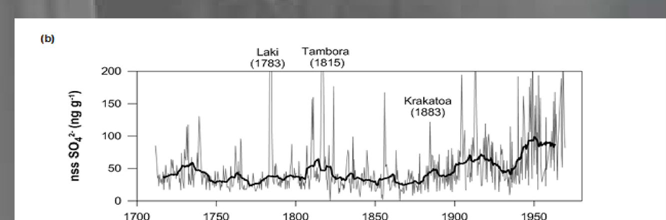
Abstract

In this research, we present high resolution record of Al, As, Ba, Cd, Co, Cr, Mn, Mo, Pb, Rb, Sr and V from Greenland NEEM ice core samples covering the period from 1710 to 1970. To our knowledge, long-term trends of these elements except Cd and Pb have never been reconstructed from Greenland ice cores at such a high resolution. The ice core records of the trace metals concentrations are characterized by large fluctuations. The ratios between maximum and minimum concentrations range from 69 for Sr to 1596 for As indicating a stark variation in concentration with depth. To help understanding long-term changes in atmospheric trace metals, individual data points were averaged for a decadal period. The main features of long-term changes are all categorized into three groups. Al, Ba, Mn, Rb, Sr and V show no distinct peaks in their concentrations over the whole period. Meanwhile, Cr and Mo concentrations are largely peaked from the mid-1830s to the mid-1850s and steadily increase for the 20th century. For As, Cd and Pb, two concentration peaks are appeared around 1800 AD and 1900 AD. The different patterns in the periods reaching peaks in concentrations are likely due to the primary anthropogenic sources for the different element. Our first comprehensive and reliable time series for various trace metals from Greenland NEEM ice core provide valuable insights into significant enrichments of these elements due to human activities from the early-19th to the mid-20th century.

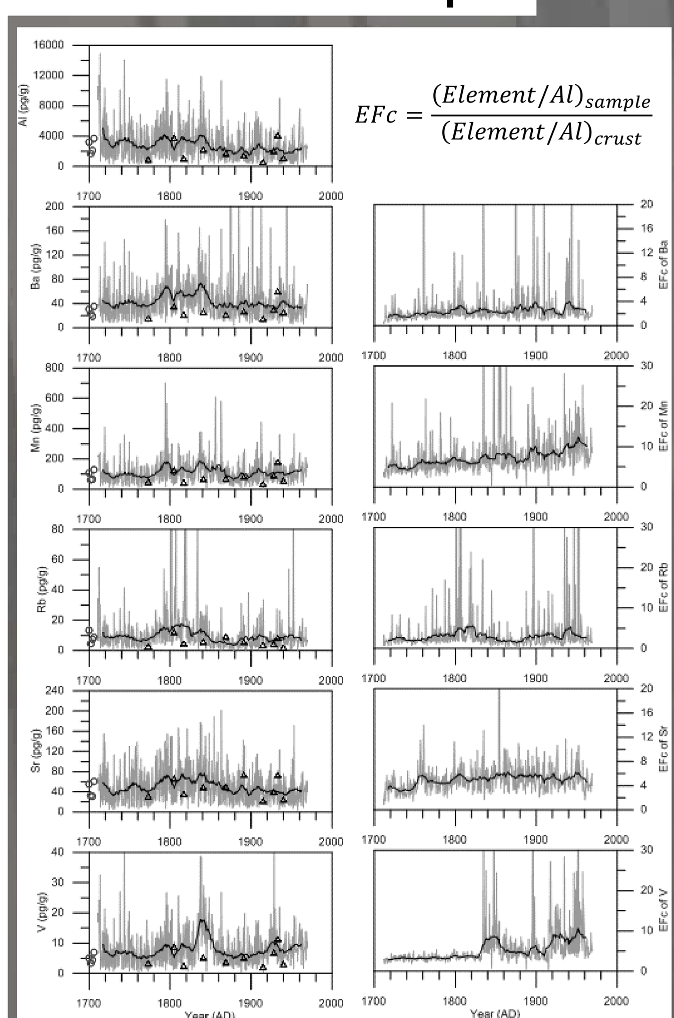
Age dating





The Neem 2009S1 ice core was primarily dated by counting annual layers using seasonal variations of $\delta^{18}O$, Na^+ and $nssSO_4^{2-}$ (left). According to Kuramoto et al. (2011), both Na^+ and $nssSO_4^{2-}$ concentrations in NEEM snow pit samples peaked in winter to spring. We also matched large peaks in $nssSO_4^{2-}$ to major volcanic events (up). Dating uncertainty was estimated to be ±0 year at 1783 based on the Laki volcanic eruption. The age of bottom was 1711 AD.

Result – Group I



$$EFc = \frac{(Element/Al)_{sample}}{(Element/Al)_{crust}}$$

Figure. Concentrations and crust enrichment factors (EFc) of trace metals in NEEM 2009S1 ice core. Thick lines represent 25 point running averages. Open triangles and circles represent the concentrations of the trace metals recovered from the Summit ice core samples and the NEEM deep ice core samples corresponding to 9328~9603 years before 2000 AD, respectively.

The first group includes Al, Ba, Mn, Rb, Sr and V. These elements commonly show slight increases in concentrations from the late 18th century to the mid-19th century and no significant changes during the 20th century. Also, the concentration levels during 1700~1970 were similar to those at the early Holocene. The first group elements also show mean EF values less than 10 over whole period. According to Wedepohl (1995), Al and Ba are highly enriched in crust dust, and thus they have been used as the proxies for crust dust inputs. Regarding Mn and V, it was estimated that soil-derived dust accounts of over 50% of total natural emissions (Pacyna et al., 1995). In addition, anthropogenic emissions of Mn only accounted 10% of total amount even during 1980s (Nriagu 1989). The information for the global budgets of Rb and Sr has not been precisely reported yet. However, they present in crustal material at concentrations of several-hundred ppm which are comparable to Mn and Ba (Wedepohl 1995). Also, both central Greenland ice core and European Alpine ice core records showed that Rb and Sr enhancement by anthropogenic emissions only began after 1950s and dominant source for those elements during pre-industrial era was natural curst dust (Burton et al. 2006; Burton et al. 2007). Considering all these, the first group elements are most likely to originate mainly from natural soil dust.

Result – Group III

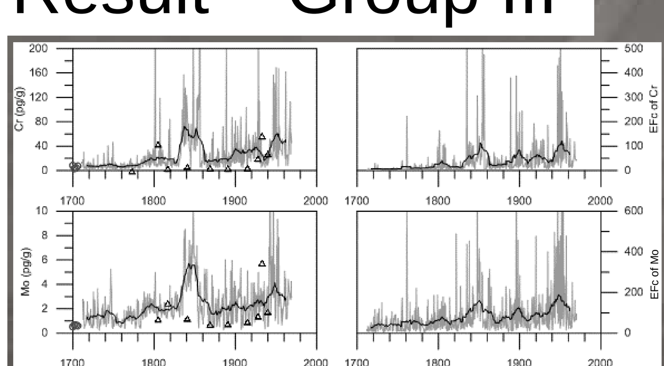


Figure. Concentrations and crust enrichment factors (EFc) of trace metals in NEEM 2009S1 ice core. Thick lines represent 25 point running averages. Open triangles and circles represent the concentrations of the trace metals recovered from the Summit ice core samples and the NEEM deep ice core samples corresponding to 9328~9603 years before 2000 AD, respectively.

The third group elements including Cr and Mo show large increases in concentrations not only during the 20th century but also during 1830s~1860s (left). The abrupt increases in the mid-19th century was also found in continuous profile of Mo presented from the Swiss peat bog samples (Krachler and Shotyk, 2004). In addition, Cr and Mo concentrations in both NEEM 2009S1 ice core and Swiss peat bog increased 4~5 times during the 19th century (Krachler and Shotyk 2004). This similarity between Swiss peat bog and Greenland ice core records implies hemispheric scale changes in atmospheric input of these elements as well as the second group elements.

The EFc values of Cr and Mo also increased during the mid-19th century up to 200. According to Krachler and Shotyk (2004), the enrichment of Mo in the Swiss peat bog since the beginning of the Industrial Revolution might be caused by the rising importance of anthropogenic sources. However, no natural and/or industrial emission record able to enhance those elements were reported for that period. In order to trace the sources for the large increases of Cr and Mo for the mid-19th century, further study about emission factor and transport are necessary.

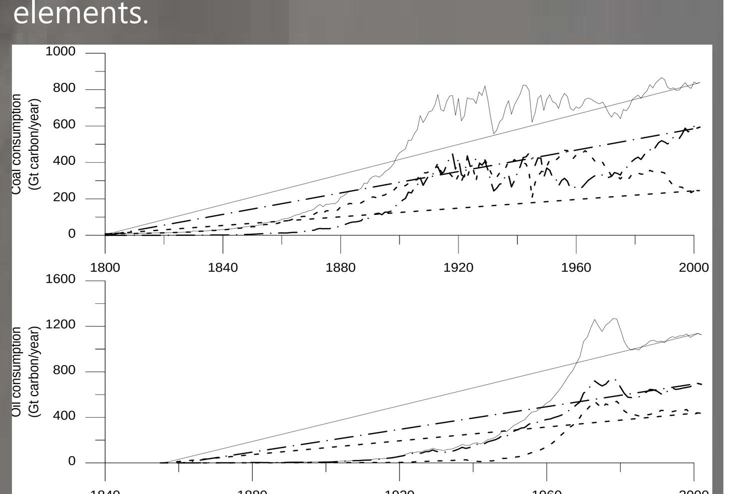
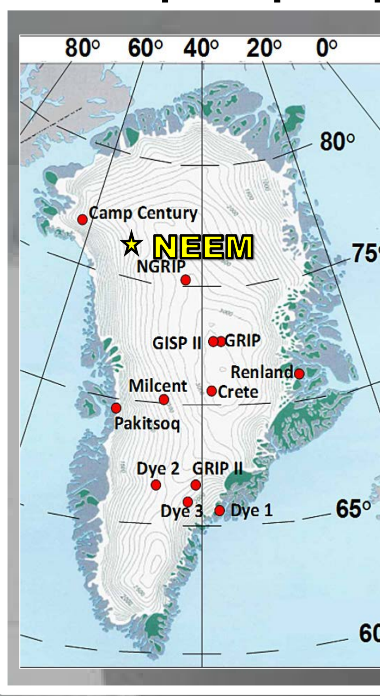
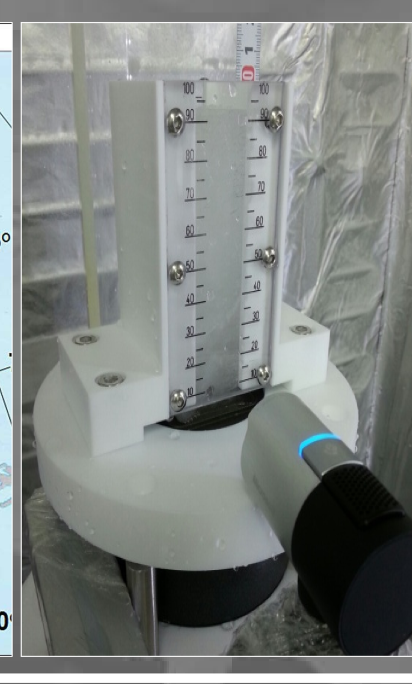


Figure. Industrial records of coal and oil consumption inferred from CO_2 emissions after 1800 AD. Dashed lines, dot and dashed lines and straight lines represent industrial records of Europe, North America and the sum of Europe and North America, respectively.

Since the late 19th century, the EFc values of Cr and Mo showed relatively steady increases. These features rather similar to the coal consumption records of Europe and North America (up). According to Nriagu (1988), the largest anthropogenic source for Cr and Mo is coal combustion. Therefore, it can be inferred the changes of atmospheric Cr and Mo for the 20th century were mainly attributed by coal consumption.

Sample preparation





In 2009, the 136 m long ice core was recovered from NEEM camp at the northwest Greenland (77.45˚N, 51.06˚W, 2450 m a.s.l.) (Left 1). The ice core was cut into every 55 cm section. Each section of upper 90m (NEEM2009S1, hereafter) was vertically cut off in a form of square pillar (4 cm x 4 cm), and then melted on the 23℃ hot melting head through which inner and out layer samples were separated (Left 2). One ice core section is again distributed into 4~5 discrete samples depending on depth. The length of each sample ranges from 8 to 18 cm. All melted sample were kept in frozen until measurement.

Analysis

	Detection Limit	This study	Measured
	(pg/g)	(ng/g)	
Al	92.3	30.0±5.9	33.9±2.2
As	0.27	0.55±0.04	0.57±0.08
Ba	1.23	13.3±1.0	14.3±0.5
Cd	0.09	0.0079±0.0017	0.0063±0.0014
Co	0.10	0.057±0.006	0.053±0.012
Cr	1.09	0.263±0.024	0.252±0.012
Mn	0.53	2.15±0.18	2.12±0.10
Mo	0.21	0.197±0.013	0.215±0.018
Pb	0.93	0.18±0.03	0.17±0.026
Rb	0.12	1.41±0.09	
Sr	0.53	42.28±3.13	40.72±0.32
V	0.06	0.377±0.044	0.352±0.006

The concentrations of the trace metals in NEEM 2009S1 ice core samples were measured by ICP-SF-MS (Element2, Thermo) (up left). In order to improve instrumental signal intensities, Apex desolvation nebulizer (Apex-HF, ESI, Omaha, U.S.) and Nafion® membrane desolvation module (ACM, ESI, Omaha, U.S.) was used for sample introduction. All sample handling and analytical operations were performed in class 10 clean booth set in class 1000 clean laboratory. The analytical samples were melted at room temperature just before measurement and acidified to 1% with Fisher Optima grade HNO_3. In addition, rhodium (Rh) was spiked as an internal standard. For the confirmation of data reliability, SLRS6 reference material diluted to sample concentration levels was repeatedly measured during the sample measurement (up right).

Result – Group II

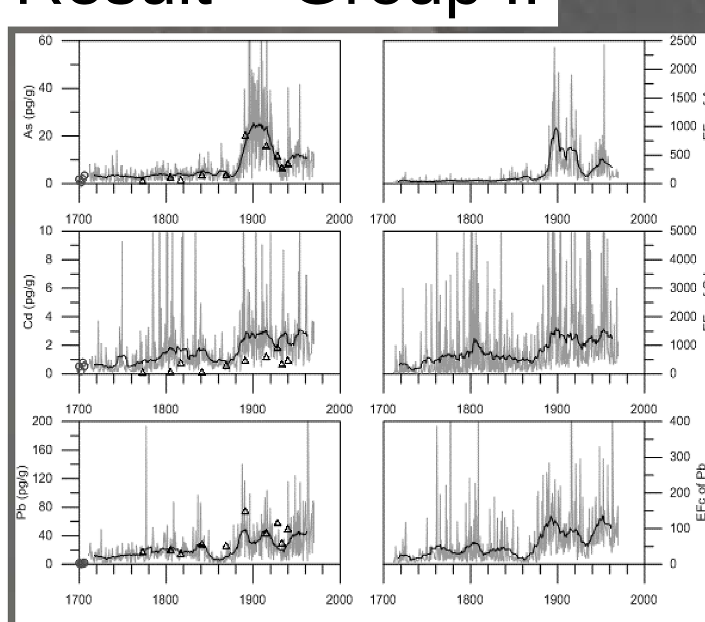


Figure. Concentrations and crust enrichment factors (EFc) of trace metals in NEEM 2009S1 ice core. Thick lines represent 25 point running averages. Open triangles and circles represent the concentrations of the trace metals recovered from the Summit ice core samples and the NEEM deep ice core samples corresponding to 9328~9603 years before 2000 AD, respectively.

The second group elements are As, Cd and Pb. They are all characterized by the large increases in the concentrations during 1880~1920 AD (left). These features well meet the Cd and Pb records of ACT2 ice core recovered from southern Greenland (McConnell and Edwards 2008). In addition, the dramatic increases in concentrations from the late 19th century to the early 20th century were also found in the European peat bog profiles of As and Pb (Shotyk et al. 1996). According to Shotyk et al. (1996), peat bog has preserved historical records of atmospheric deposition of As and Pb. Therefore, similar patterns of As and Pb records from both Greenland ice core and European peat bog may represent that the large increases in atmospheric inputs of those elements occurred in hemispheric scale from the late 19th century to the early 20th century.

The averaged EFc values for these elements were much higher than unity ranging from several dozens to several hundred even during the 18th century. Also, the EFc values of As, Cd and Pb rapidly increased around 1900 AD. During the 20th century, they decreased during 1920~1930s and then increase again after 1940s.

Interestingly, these features are also found in the global non-ferrous metal production records (right). This strongly suggests that enhanced anthropogenic emissions – especially non-ferrous metal production – during the 20th century largely contributed enrichment of these elements.

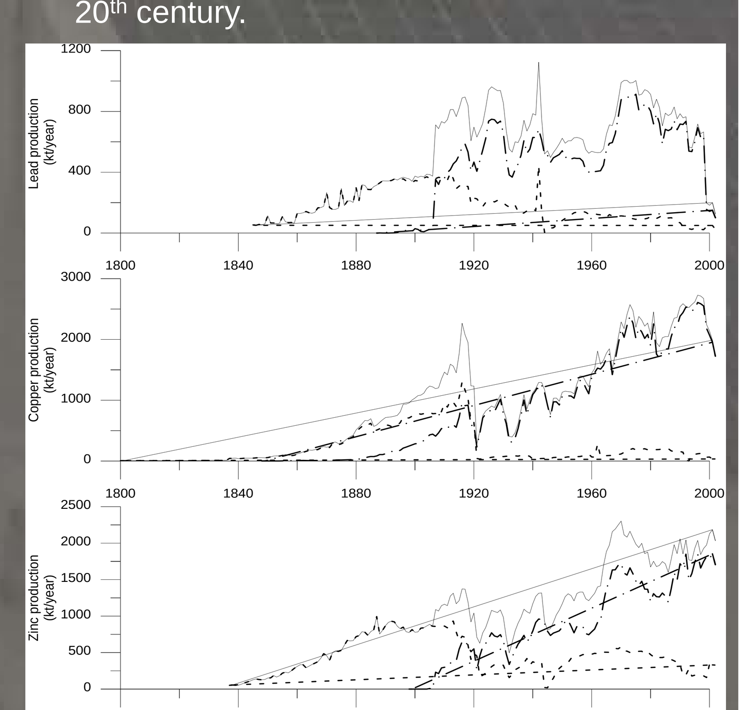


Figure. Industrial records of lead, copper and zinc production after 1800 AD. Dashed lines, dot and dashed lines and straight lines represent industrial records of Europe, North America and the sum of Europe and North America, respectively.

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