

A 15,800-year record of atmospheric lead deposition on the Devon Island Ice Cap, Nunavut, Canada: Natural and anthropogenic enrichments, isotopic composition, and predominant sources

Jiancheng Zheng,^{1,2} William Shotyk,² Michael Krachler,² and David A. Fisher¹

Received 14 November 2006; revised 5 March 2007; accepted 18 April 2007; published 21 June 2007.

[1] Using appropriate clean methods for handling and preparation, 57 ice samples from the Devon Island Ice Cap, representing the period 134 to 15,800 years before present (BP), were analyzed for Pb, Sc, and Pb isotopes (^{206}Pb , ^{207}Pb , ^{208}Pb) using ICP-SMS. The greatest Pb concentrations were found in samples dating from the Younger Dryas. Despite the large range in Pb concentrations (from 2.2 to 181 pg g^{-1}), the Pb concentrations were proportional to those of Sc until 3100 BP when the Pb/Sc ratio exceeded by a factor of 2 the natural “background” value ($\text{Pb/Sc} = 6.3 \pm 1.8$) for the first time. The uniform ratio of Pb to Sc until 3100 BP is consistent with the hypothesis that soil dust particles derived from physical and chemical weathering dominate the inputs of Pb to the atmosphere, with the magnitude of these sources climate-dependent. Isotopic analyses of Pb further support this paradigm, with the average ratio of $^{206}\text{Pb}/^{207}\text{Pb}$ (1.230) and $^{208}\text{Pb}/^{206}\text{Pb}$ (2.059) well within the range given for the Upper Continental Crust (UCC). The shift to higher Pb/Sc ratios and lower $^{206}\text{Pb}/^{207}\text{Pb}$ values starting at 3100 BP is consistent with historical records and other archival evidence of the onset of atmospheric Pb contamination caused by Pb mining and smelting in the Iberian Peninsula. Since that time, the Devon Island ice core records several other episodes of notable atmospheric Pb contamination, including those dating from Roman and medieval times, as well as the industrial period. The Pb, Sc, and Pb isotope data presented here represent the first chemical and isotopic record of the natural, “background” atmospheric inputs to the Canadian Arctic, against which modern values may be compared.

Citation: Zheng, J., W. Shotyk, M. Krachler, and D. A. Fisher (2007), A 15,800-year record of atmospheric lead deposition on the Devon Island Ice Cap, Nunavut, Canada: Natural and anthropogenic enrichments, isotopic composition, and predominant sources, *Global Biogeochem. Cycles*, 21, GB2027, doi:10.1029/2006GB002897.

1. Introduction

[2] In a recent study of atmospheric Pb in the Arctic, we reported the abundance of Pb and Sc in over 500 samples taken from a 5-m snow pit and a 65-m firn core from Devon Island, Nunavut, Canada, representing 160 years of precipitation [Shotyk *et al.*, 2005]. The temporal changes in Pb concentrations, Pb/Sc ratio, and isotopic composition of Pb all argued in favor of anthropogenic sources having dominated the atmospheric inputs to this remote region since at least 1842 AD, the oldest sample collected. Despite the decline in Pb emissions during the past decades due to the gradual phase-out of leaded gasoline additives, even in the most recent samples, however, anthropogenic inputs continue to dominate the atmospheric Pb flux. For example,

from the pit, 45 samples representing snow accumulation from 1994 to 2004 contained an average of 45.2 pg g^{-1} of Pb but only 0.43 pg g^{-1} of Sc, yielding an average Pb/Sc ratio of 105 [Shotyk *et al.*, 2005]. Given the range in Pb/Sc represented by crustal rocks (1:1 according to Wedepohl [1995]) and typical soils (5:1 according to Bowen [1979]), we estimated that ~95 to 99% of recent Pb in the snow samples was still anthropogenic. Support for this interpretation was provided by the analyses of Pb isotopes. The isotopic composition of Pb in the snow samples from 1994 to 2004 ranged from $^{206}\text{Pb}/^{207}\text{Pb} = 1.131\text{--}1.170$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.088\text{--}2.151$. Comparison with the corresponding ratios in average Upper Continental Crust (UCC) of ~1.20 and 2.07 [Stacey and Kramers, 1975; Othman *et al.*, 1989; Kramers and Tolstikhin, 1997] supports the view that Pb in recent snow samples from Devon Island is dominated by anthropogenic contributions.

[3] In our previous study, it was not possible to quantify the enrichment of Pb due to anthropogenic inputs, simply because the “natural background” Pb to Sc ratio in the ice core was unknown. Studies of atmospheric Pb contamina-

¹Geological Survey of Canada, Natural Resources Canada, Ottawa, Ontario, Canada.

²Institute of Environmental Geochemistry, University of Heidelberg, Heidelberg, Germany.

tion using peat bogs in Europe have shown that anthropogenic inputs have dominated the atmospheric Pb cycle continuously for at least 3000 years [Shotyk *et al.*, 1998]. Atmospheric Pb contamination dating from antiquity has also been found in the ice cores from Greenland [McConnell *et al.*, 2002; Rosman *et al.*, 1997; Boutron *et al.*, 1995, 1994; Candelone *et al.*, 1995; Hong *et al.*, 1994] and Antarctica [Van de Velde *et al.*, 2005; Planchon *et al.*, 2002, 2003; Hong *et al.*, 1998; Boutron and Patterson, 1983; Ng and Patterson, 1981]. Although it has been known that the past natural concentrations of Pb in ancient ice from Antarctica [Boutron *et al.*, 1994; Boutron and Patterson, 1986] and Greenland [Hong *et al.*, 1996] are highly dependent upon climatic conditions, there are no similar studies in Canadian Arctic. The evaluation of the extent of Pb contamination of atmospheric aerosols commonly uses the ratio of this metal to a conservative reference element (such as Sc) which has no significant anthropogenic source. The fundamental assumption with this approach is that the Pb/Sc ratio of natural aerosols predating the onset of atmospheric Pb contamination closely resembles the corresponding ratio in rocks and soils [Rahn, 1976]. This assumption, however, is rarely put to the test. Moreover, the Pb/Sc ratio given by Wedepohl [1995] for the Upper Continental Crust ($17/7 = 2.4$) is approximately one half that given by Bowen [1979] for uncontaminated soils (5:1); the difference between these two values may reflect the natural enrichment of Pb in soils due to natural variability across the Earth's crust, including effects of chemical weathering, volcanic events, forest fires, oceanic sources and biogenic sources. Regardless of the cause of the discrepancy between these two reference values, the question remains: which Pb/Sc ratio is representative of the natural inputs of atmospheric Pb to the Arctic? In our previous study [Shotyk *et al.*, 2005], both values (UCC and soil) were used as a first step toward estimating the proportion of anthropogenic Pb in arctic aerosols today. A more desirable approach would be to directly determine the "natural background" Pb concentrations and concentrations of conservative elements, such as Sc, (and thus Pb/Sc ratio), in ice samples dating back in time many thousands of years, and predating the onset of atmospheric Pb contamination. One advantage of this approach is the ability to also determine the extent to which the Pb/Sc ratio in Arctic aerosols varied in response to climate change during the Holocene.

[4] The main goal of this paper is to characterize the natural atmospheric Pb inputs to the Arctic using samples dating from preanthropogenic times. Specifically, we wish to determine the abundance of Pb and Sc, and the isotopic composition of Pb, in ancient ice samples predating atmospheric Pb contamination. To do this, we have selected an ice core from the Devon Island Ice Cap, which may extend back in time $\sim 15,000$ years and includes 15 samples older than 4,000 years. In particular, we wish to address the following questions: what is the natural abundance of Pb in polar snow and ice, how variable is the concentration, and what are the dominant processes contributing to the variation? Similarly, what is the isotopic composition of this pre-industrial Pb, and how variable is the isotopic compo-

sition? Once this information is available, it should be possible to determine how much of the natural Pb was contributed by soil dust particles derived from weathering of crustal rocks. Once the "natural background" values have been determined and the geochemical processes which have given rise to them, understood, it will be possible to quantify the extent of Pb enrichments in modern snow and ice. In addition, it will be possible for the first time to reconstruct the chronology of atmospheric Pb contamination in the Canadian Arctic, and to identify the predominant anthropogenic Pb sources.

2. Materials and Methods

[5] Samples were taken from a core retrieved from the top of a satellite dome of the Devon Island Ice Cap, Nunavut, Canada (75°N ; 82°W ; 1860 m above sea level) in April–May 1999 (D1999 core). The total depth of the core was 170.6 m. The cores were stored at -20°C after drilling. Minor sublimation was observed during subsampling. A total of 57 samples were selected, to represent the period from the Second Industrial Revolution to a few thousand years before the transition of Holocene/Wisconsin. Sample lengths ranged from 7 to 15 cm and weighed between 32 and 71 grams each after decontamination. Core quality was good and no cracking inside the samples was observed during sample processing.

[6] The age/depth relationship of D1999 core is based on high-quality electrical conductivity measurements (ECM) determined in the field immediately on fresh cores. The main features identified and used as time markers are the volcanic eruptions of Katmai (1912 AD), Laki (1783 AD), an unknown ECM peak (1259 AD), ELDJA (940 AD) and the $\delta(^{18}\text{O})$ dip at the transition of the Wisconsin and Holocene, which occurred at 11.6 ka BP [Fisher, 1979; Fisher and Koerner, 2003]. These features are found in all Canadian Eastern Arctic ice cores [Zheng *et al.*, 1998] and using such horizons is the standard approach to develop a timescale [Fisher *et al.*, 1995]. With this timescale, the accumulation rate implied by the Katmai peak is close to the present-day accumulation rate. The density profile, which was used to help establish the age-depth relationship, was based on the weights and dimensions of the cores determined in the field on the fresh core. The densities (ice depth conversions) are accurate to 1%.

[7] To remove any possible contamination, every sample was individually decontaminated in a certified cold clean room of U.S. Class 1000. All sample processing and decontamination procedures in this study were carried out in a Class 100 work station. Before decontamination, the thin layer of sublimation was carefully removed from each sample with a titanium knife. After carefully removing the sublimation chips from the clean air bench, an extreme clean procedure was adapted for the entire sample processing [Zheng *et al.*, 2006]. Because all the samples were pure or nearly pure ice (only two out of 57 samples were solid firn), subsampling, processing and decontamination were efficient, effective and successful.

[8] High-purity water ($18.2 \text{ M}\Omega\text{-cm}$) used in this study was produced either from a Milli-Q RO-DI system (Milli-

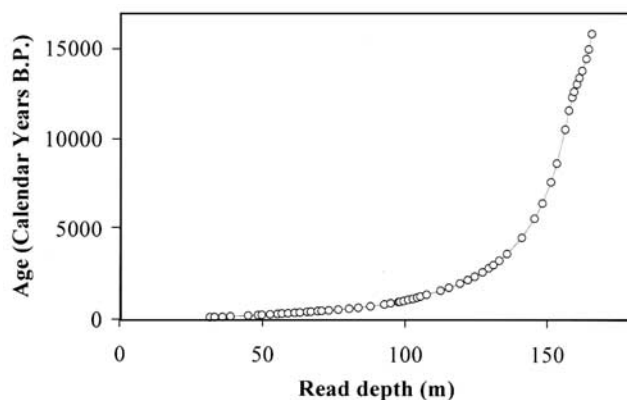


Figure 1. Relationship between depth and age for ice samples (D1999 core, Devon Island) used in this study. BP refers to calendar year 2004 AD.

pore Corporation, USA) or from a Milli-Q-Element system (Millipore, Milford, MA, USA) designed for inorganic ultra trace analysis. The nitric acid used was trace metal grade for bottle precleaning and BASELINE[®] grade (double distilled) (Seastar Chemicals Inc., Canada) or freshly double distilled for final bottle cleaning, blank test, detection limit determination and sample acidification. Impurities in the BASELINE[®] grade HNO₃ were certified by the manufacturer to be <1 pg g⁻¹ for Pb. For sample acidification (max 0.4%), contributions of the Pb from the acid would be <0.004 pg g⁻¹ or <4 fg g⁻¹, which is negligible [Krachler *et al.*, 2005; Zheng *et al.*, 2006]. Both RO-DI water and HNO₃ acid were tested for Pb and Sc when sample analyses were carried out.

[9] The Teflon beakers (Teflon PFA, Chemware, VWR Canlab, Canada) and HDPE sample bottles (Nalgene[®], Fisher Scientific, Canada) used for sample melting and storage were cleaned using cleaning procedures described elsewhere [Zheng *et al.*, 2006; Krachler *et al.*, 2004a, 2004b, 2005]. The Teflon beakers were reused for each batch of up to 18 samples for processing and melting. Before using for each batch, the beakers were thoroughly decontaminated again by soaking them in 0.5% BASELINE[®] grade HNO₃ for at least 24 hours. For all the handling and processing of beakers, tools, bottles and plastic bags, polyethylene gloves were employed. Titanium chisels and saws for sample cleaning and decontamination were all precleaned with 5% BASELINE[®] HNO₃ and 18.2 MΩ-cm high-purity water.

[10] Analyses of samples for this study were performed using an Element 2 ICP-SMS (Thermo Electron, Bremen, Germany) equipped with a guard electrode [Krachler *et al.*, 2004a, 2004b, 2005] at the Institute of Environmental Geochemistry, University of Heidelberg, Germany. A Merck multielement standard solution was used to calibrate the instrumental response. As no polar ice reference material for trace elements is currently available, a riverine water reference material (SLRS-4 by the National Research Council of Canada, Ottawa) was used for quality control purposes. A microvolume autosampler (ASX 100, Cetac Technologies, Omaha, Nebraska) and a high-efficiency sample introduction system (APEX IR, Elemental Scientific

Inc., Omaha, Nebraska, USA) was used with or without the combination of X-cone for both elemental concentration and Pb isotopic ratio measurements, depending on the element concentrations [Krachler *et al.*, 2004b]. For Pb isotope measurements (²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb), the isotopic standard reference material NIST 981 (Standard Reference Material 981 Common Lead Isotopic Standard, National Institute of Standards and Technology, USA) was analyzed before and after each sample to correct for mass discrimination effects. An analytical procedure for Pb isotope ratio measurements developed by Krachler *et al.* [2004a] was adopted for this study.

[11] Using the high-efficiency sample introduction system (APEX IR) [Krachler *et al.*, 2005], the limits of detection (LODs), calculated using the 3σ criterion, were 0.06 pg g⁻¹ for Pb and 0.005 pg g⁻¹ for Sc. These were determined using measurements of 20 replicates of independently prepared blank solutions, 0.4% HNO₃, prepared with freshly double distilled HNO₃ and determined at the start of sample measurements. Analyses of 8 replicate blanks composed of 0.4% HNO₃ (prepared from BASELINE[®] grade HNO₃ when samples of ancient ice were processed) showed that the combined background concentrations from the HNO₃, RO-DI water, sample bottles and the test tubes were 0.15 pg g⁻¹ for Pb and 0.03 pg g⁻¹ for Sc: these values were at least 5 to 10 times lower than the lowest value in the 57 ancient ice samples. Analyses of Pb in riverine reference water material SLRS-4 at regular intervals during the analyses (84 ± 3 pg g⁻¹, N = 8) matched well with its certified value (86 ± 7 pg g⁻¹). For Sc, because there is no adequate certified water reference material available currently, we compared the measured values in SLRS-4 from this study (10.7 ± 0.2 pg g⁻¹, N = 8) with the value of 11.3 ± 0.6 pg g⁻¹ reported in previous studies [Krachler *et al.*, 2005]. Using the APEX IR sample introduction system, the precision of the Pb isotope ratios of both ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb was ~0.2% for samples containing low pg g⁻¹ concentrations of Pb. For samples with concentrations higher than 50 pg g⁻¹, measurement precision for both ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb was better than 0.15% [Krachler *et al.*, 2004a].

3. Results and Discussion

3.1. Timescale for the Ancient Ice Cores

[12] The timescale developed for the D1999 core is shown in Figure 1. The age in calendar year refers to 2004 AD. With this timescale, ages for the 57 samples for this study were assigned (Table 1). Considering the combined inaccuracy resulting from sample lengths, ECM measurements and the nonlinearity of the age-depth relationship, the total dating error of the timescale is estimated to be less than 2.5% for the first 200 years, approximately 3% for the time period between 200 BP and 1200 BP, and 10% for the time period from 1200 BP to 8000 BP. For samples with ages older than 8000 years (especially those older than the δ¹⁸O transition between the Wisconsin and Holocene), the inaccuracy of age assignments could be even larger because there are no confirmed markers to control the dating quality for this time period. Moreover, there could also be some net loss of ice due to melting. For example, a

Table 1. Pb Concentrations, Pb Isotope Ratios and Pb Ratios to Al, Sc, and V in 57 Samples Taken From D1999 Core^a

Age, years BP	Pb, $\mu\text{g g}^{-1}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	Pb/Al, $\times 10^{-3}$	Pb/Sc	Pb/V
134	19.8	1.179	2.066	66.9	141	22.7
145	50.7	1.227	2.028	40.9	128	14.8
163	19.1	1.182	2.077	9.5	37.7	3.5
183	29.7	1.183	2.071	17.1	40.2	5.3
230	9.7	1.185	2.069	18.7	66.3	7.2
258	14.4	1.185	2.052	11.8	37.5	4.7
269	10.5	1.185	2.075	6.9	15.0	2.2
294	16.2	1.170	2.091	9.9	34.8	4.5
317	13.1	1.185	2.067	7.8	19.4	2.4
331	9.6	1.200	2.064	5.6	17.6	2.0
350	9.0	1.193	2.049	11.2	33.3	3.6
373	14.4	1.187	2.068	15.8	48.1	6.3
390	8.1	1.167	2.049	9.7	29.8	3.6
417	5.5	1.189	2.078	7.0	19.1	2.5
430	7.4	1.186	2.034	8.9	19.9	2.1
456	3.3	1.178	1.986	6.5	22.8	2.6
471	4.1	1.201	2.062	5.7	13.1	1.5
501	19.1	1.176	2.070	8.8	25.5	3.4
543	7.3	1.182	2.050	8.1	21.8	2.9
597	6.1	1.195	2.034	4.0	12.2	1.8
648	7.8	1.173	2.090	10.1	32.1	3.9
725	6.2	1.193	2.015	1.4	8.4	0.9
833	3.6	1.188	2.043	3.1	8.9	1.2
893	6.1	1.198	2.038	4.3	8.7	1.3
975	4.7	1.197	1.998	4.1	10.0	1.3
994	3.0	1.187	2.064	3.9	10.3	1.4
1041	7.1	1.195	2.032	4.8	11.2	1.6
1105	4.4	1.171	2.033	4.4	13.3	1.7
1178	8.9	1.196	2.051	8.6	20.9	2.6
1253	5.6	1.215	2.052	4.1	11.9	1.5
1319	3.8	1.198	2.035	6.5	14.7	2.0
1412	2.2	1.213	2.033	4.1	9.3	0.9
1646	5.1	1.204	1.999	3.2	9.2	1.3
1811	4.7	1.189	2.073	7.3	20.1	2.5
2057	5.5	1.176	2.024	6.3	19.3	2.3
2256	3.1	1.212	2.044	4.0	9.8	1.4
2451	2.2	1.237	2.037	2.5	5.5	0.7
2706	3.4	1.198	2.058	4.1	12.2	1.4
2929	4.5	1.187	2.066	5.2	13.0	1.8
3115	4.5	1.171	2.140	7.9	18.1	2.0
3364	4.6	1.173	2.084	4.9	10.2	1.3
3743	4.8	1.191	2.065	4.6	12.8	1.6
4652	4.5	1.235	2.044	3.7	6.7	0.8
5705	5.9	1.342	1.862	2.5	7.8	1.0
6540	3.0	1.261	2.002	2.3	5.5	0.7
7671	5.4	1.216	2.050	3.5	8.4	1.2
8651	6.7	1.228	2.042	3.2	7.7	1.1
10372	17.3	1.168	2.198	1.1	5.2	0.9
11301	17.0	1.194	2.152	2.5	8.6	1.1
12240	181	1.221	2.052	1.6	4.8	0.5
12551	83.3	1.209	2.101	1.4	4.8	0.5
12977	20.0	1.216	2.055	1.1	4.3	0.4
13316	10.6	1.220	2.071	1.6	4.8	0.6
13723	12.8	1.237	2.073	3.5	9.1	1.3
14394	12.2	1.221	2.069	2.2	6.5	1.0
14936	3.2	1.258	2.056	1.1	3.9	0.5
15815	4.3	1.175	2.076	8.2	17.3	2.9

^aBP refers to calendar year 2004 AD. Data in bold were used to calculate Pb and Sc natural concentration backgrounds, and ratios of Pb/Sc, $^{206}\text{Pb}/^{207}\text{Pb}$, and $^{208}\text{Pb}/^{206}\text{Pb}$.

similar melting situation was found in ice cores drilled on the Agassiz ice cap, Nunavut, Canada [Fisher *et al.*, 1995].

[13] The Devon Island ice core reveals an outstanding peak in Pb concentrations ($181 \mu\text{g g}^{-1}$) at a depth of 158.7 m (Figure 2) which, according to the age-depth model shown in Figure 1, corresponds to 12,240 yr BP (Table 1). This

anomalous Pb value, however, is proportional to that of Sc ($38 \mu\text{g g}^{-1}$) and the Pb/Sc ratio (4.8) at this same depth (Table 1) is consistent with soil values. Clearly, therefore, the D1999 core provides a record of greatly elevated fluxes of atmospheric soil dust. For comparison with the Devon Island ice core, a pronounced peak in both Pb and Sc

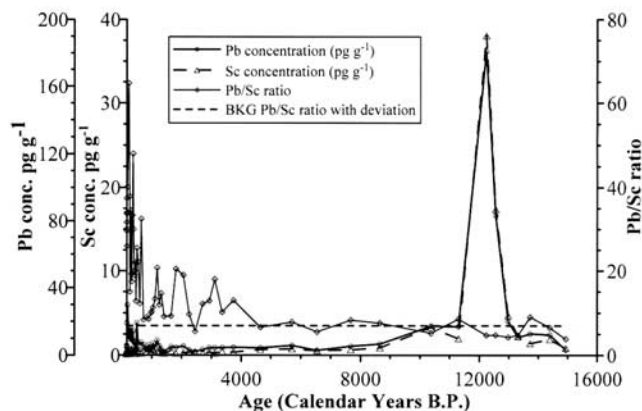


Figure 2. Variations of Pb and Sc concentrations and Pb/Sc ratios in samples older than 160 BP. Note that the x axis starts at 160 BP. BP refers to calendar year 2004 AD.

concentrations was also found in an ombrotrophic peat bog from Switzerland [Shoty et al., 1998]. Radiocarbon age dating of the peak in Pb and Sc from the Swiss bog yielded an age of 12,521 cal yr BP. In the case of the bog, the anomalous inputs of Pb and Sc were attributed to the elevated dust fluxes which characterized the cold climate of the Younger Dryas. The age-depth model for the D1999 core shown in Figure 1 agrees to within 3% of the age date for the Pb and Sc peak found in the Swiss bog. The excellent agreement between the two independent sets suggests that the age-depth model shown in Figure 1 is realistic, even with respect to the deeper, older ice layers. We assume, therefore, that the anomalous peak in Pb and Sc corresponds to the YD. Mayewski et al. [1993] concluded that the YD stands out prominently in ice record as periods of substantially elevated dust concentrations. Unfortunately, however, his report did not include Pb concentrations. Hong et al. [1996] measured Pb in an ice core from Central Greenland, covering the period from 8250 BP to 149,100 BP. Although their results showed much greater Pb concentrations during last glacial period, the resolution of their measurements is inadequate to provide data for the YD period. Boutron and Patterson [1986], however, reported elevated Pb concentrations across the Wisconsin/Holocene boundary in the Dome C ice core. In summary, the peak in Pb and Sc seen in the D1999 ice core provide a unique chronostratigraphic marker which largely substantiates the age-depth model shown in Figure 1.

3.2. Natural Background Concentrations of Pb and Sc, and Ratios of Pb/Sc and $^{206}\text{Pb}/^{207}\text{Pb}$

3.2.1. Reliability of the Data Set for Background Estimation

[14] Concentrations of Pb in the 15 samples older than 4000 years vary dramatically as shown in Table 1 and Figure 2. A number of similar retrospective studies of atmospheric Pb deposition using ice cores as well as peat bogs have shown considerable variation in the natural Pb fluxes, mainly due to climate change [Vallelonga et al., 2005; Shotyk et al., 1998; Hong et al., 1996; Boutron and Patterson, 1986]. Thus there is no reason to expect that

either Pb or Sc concentrations would be constant in the ancient ice layers from Devon Island. Our effort in this study is made to document the range in natural variation in Pb and Sc, to understand the causes to which they are due, and to determine the ratio of Pb to Sc which can be considered characteristic of natural sources of atmospheric Pb. First, however, it needs to be clearly established that the samples were not contaminated during the study. To do this, we evaluate the Pb concentrations, Pb to Sc ratios as well as Pb isotope data ($^{206}\text{Pb}/^{207}\text{Pb}$).

[15] Although Pb concentrations in the 15 samples older than 4,000 years vary dramatically, the ratios of Pb to Sc are quite constant (3.9–9.1 for Pb/Sc) except for the oldest sample (17.3) (Table 1 and Figure 2). In addition, the ratios of Pb to Al and V are also constant during this interval (Table 1). The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (1.175) of the oldest sample seems to deviate significantly from the others and the following data and arguments suggest that this oldest sample might have become contaminated. When Pb concentrations in samples are low, the risk of contamination by relatively small quantities of modern urban dusts are correspondingly greater because of their much greater Pb concentrations, Pb/Sc ratios, and less radiogenic Pb isotope signature. For example of the oldest sample, if $\sim 50\%$ of the sample Pb content (~ 2.1 out of 4.3 pg g^{-1}) came from a modern contamination source that had a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of ~ 1.16 and an average UCC Sc content, its current $^{206}\text{Pb}/^{207}\text{Pb}$ and Pb/Sc ratios could be reached simply by mixing with natural material characterized by UCC values ($^{206}\text{Pb}/^{207}\text{Pb} = \sim 1.2$ and Pb/Sc = ~ 5). The combination of an elevated Pb/Sc ratio and a correspondingly less radiogenic $^{206}\text{Pb}/^{207}\text{Pb}$ value suggests, therefore, that this sample, despite the low Pb concentration, may have been contaminated.

[16] Other than this oldest sample, two other samples with ages of 5705 BP and 10,372 BP also yielded anomalous Pb isotope ratios, of 1.342 and 1.168, respectively (Table 1 and Figure 3). However, there is no data to suggest that these anomalous Pb isotope signatures are anything other than natural variation. The main argument in favor of an exclusively natural source of Pb to these samples is the ratios of Pb to Al (2.5×10^{-3} and 1.1×10^{-3}), Sc (7.8 and 5.2) and V (1.0 and 0.9): these ratios are well within the average natural values shown in Table 1. Considering the sample of 5705 BP and assuming UCC $^{206}\text{Pb}/^{207}\text{Pb}$ ratio background was ~ 1.2 , any contamination has to be as radiogenic as $^{206}\text{Pb}/^{207}\text{Pb} = 1.5$ even if only 50% of the Pb in the sample was from contamination. A source of contamination containing such a very high $^{206}\text{Pb}/^{207}\text{Pb}$ was very unlikely to have existed during the handling and processing of the Devon Island samples. Therefore, except for the sample dating from 15,815 BP, we assume that the variations in isotopic composition of Pb in the samples are truly a reflection of the natural variation in atmospheric dusts. The sample dating from 15,815 BP, however, will not be considered further.

3.2.2. Variation in Pb Concentrations Versus Time

[17] The range in Pb and Sc concentrations seen in Figure 2 reveals a number of episodes of elevated Pb and Sc inputs; these are summarized in Table 2. Toward the end

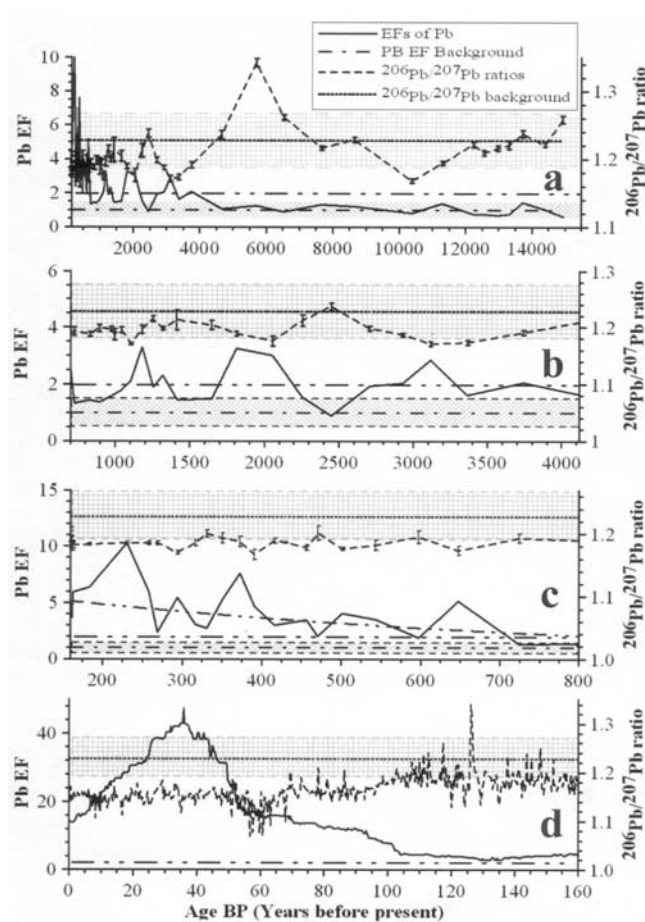


Figure 3. Chronology of atmospheric Pb deposition on the Devon Island Ice Cap since the last glaciation. Crosshatch fill is the uncertainty of natural background $^{206}\text{Pb}/^{207}\text{Pb}$ while diagonal cross fill is the uncertainty of the natural enrichment factor (EF) background; vertical bars with the $^{206}\text{Pb}/^{207}\text{Pb}$ plot are the measurement inaccuracy; The dash-dot-dotted line is at $\text{EF} = 2$. (a) A reconstructed record of Pb EFs and isotopic ratios on the Devon Island Ice Cap, Nunavut, Canada. Note that the x axis starts at 160 BP. (b) Between 700 BP and 4000 BP. (c) Between 160 BP and 700 BP. The dash-dash-dot-dotted line, showing a trend line of Pb contamination based on an exponential fit. (d) Enrichment factor plot for samples from the last 160 years recalculated on the basis of the natural background Pb/Sc from 15 samples with ages of 4000 BP or older. BP refers to calendar year 2004 AD.

of the Wisconsin glaciation, represented here by ice samples between 13 K BP to 15.8 K BP, the natural background concentrations of Pb averaged $11.8 \pm 6.0 \text{ pg g}^{-1}$ ($N = 5$). This value represents natural Pb inputs from the atmosphere during the cold period which predates the YD. As indicated earlier, elevated Pb concentrations are found in samples dating from the YD. Samples from 8 K BP to 13 K BP average $61.0 \pm 73.5 \text{ pg g}^{-1}$ ($N = 5$). These elevated concentrations of both Pb and Sc (Table 1) must reflect the severe wind conditions and availability of bare land surfaces after the gradual withdrawal of the Laurentide and

other ice sheets in the Arctic region. Both the period from 13 K BP to 15.8 K BP and that from 8 K BP to 13 K BP reveal elevated concentrations of Pb and Sc in response to the elevated dust inputs characteristic of cold climate regimes.

[18] In contrast to these cold phases, rather different circumstances characterize the mid Holocene. In the Devon Island ice core, Pb concentrations in samples dating from 4 K BP to 8 K BP average only $4.7 \pm 1.3 \text{ pg g}^{-1}$ ($N = 4$). These values represent the lowest concentrations found since the Wisconsin glaciation. These lower concentrations of natural Pb in the ice samples reflect lower rates of dust deposition. This climate phase was mild compared to earlier times, with more vegetation coverage on the land surface and a concomitant reduction in the amount of erodible soil exposed to wind [Smith, 2002; Jones et al., 2004; Kerwin et al., 2004].

3.2.3. Pb, Sc, Al, and V

[19] Because lithogenic elements deposited during the late Wisconsin and early Holocene originate from crustal sources, the ratios of elements such as Pb to conservative elements such as Sc, should show less variation than the Pb concentrations themselves. The Pb/Sc ratios shown in Figure 2 show that this is the case. In fact, the ratios of Pb to Sc are remarkably uniform ($\text{Pb}/\text{Sc} = 6.3 \pm 1.8$) until approximately 4000 years ago (Figure 2). As mentioned earlier, not only is Pb strongly correlated with Sc but also with other lithogenic elements which had been measured simultaneously, including Al and V (Table 3). Because the variations in Pb concentrations in the Devon Island ice core represent nearly 2 orders of magnitude ($2.2 - 181 \text{ pg/g}$), it is not possible to determine which natural “background” Pb concentration could be used to quantify recent Pb enrichments due to anthropogenic inputs. In contrast, the uniform ratios of Pb/Sc, Pb/Al, and Pb/V provide a legitimate, convenient and functional basis for evaluating the recent enrichments of Pb due to industrial inputs. Although climate change has certainly affected Pb concentrations, it has not significantly affected Pb to Sc ratios. Therefore we will employ the ratio of Pb to Sc in the ice samples older than 4000 BP to represent “background” values. On the basis of the “background” values of Pb to Sc, it then becomes possible to develop an accurate and realistic understanding of current Pb contamination in the Canadian High Arctic. In this study, Pb enrichments factors are calculated using Sc as a reference element for many of the same reasons given elsewhere [Shoty et al., 2001].

[20] The natural background Pb/Sc ratio reported here (6.3 ± 1.8) exceeds the corresponding ratio for the UCC of 2.4 [Wedepohl, 1995], but is only slightly greater than the Pb/Sc value for soils of 5 [Bowen, 1979] and the value for the mid-Holocene obtained for the Swiss peat bog (3.0–4.0) [Shoty et al., 2001, 2004]. Because the natural background Pb/Sc value reported here was obtained directly from ancient Canadian Arctic ice cores, it provides a basis against which recent changes in atmospheric Pb inputs to the Arctic may more reliably be compared.

3.2.4. Pb Isotope Ratios and Their Variation

[21] The average natural $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of 1.230 and 2.059 (Table 2) among those samples

Table 2. Comparison of Pb and Sc Concentrations, and Pb/Sc, $^{206}\text{Pb}/^{207}\text{Pb}$, and $^{208}\text{Pb}/^{206}\text{Pb}$ Ratios Arranged by Time Periods^a

Time Period		Pb, $\mu\text{g g}^{-1}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	Sc, $\mu\text{g g}^{-1}$	Pb/Sc Ratio
Before inputs	average (N = 14)	27.3	1.230	2.059	5.37	6.3
4–15.8 K BP	standard deviation	48.6	0.040	0.075	10.4	1.8
	maximum	181	1.342	2.198	38.0	9.1
	minimum	3.0	1.168	1.862	0.54	3.9
	average (N = 5)	11.8	1.230	2.065	2.21	5.7
Late Glacial 13–15.8 K BP	standard deviation	6.0	0.017	0.009	1.5	2.1
	maximum	20	1.258	2.073	4.7	9.1
	minimum	3.2	1.216	2.055	0.83	3.9
	average (N = 5)	61.0	1.204	2.109	12.3	6.2
YD/early Holocene 8–13 K BP	standard deviation	73.5	0.024	0.066	15.9	1.8
	maximum	181	1.228	2.198	38.0	8.6
	minimum	6.7	1.168	2.042	0.88	4.8
	average (N = 4)	4.7	1.264	1.990	0.65	7.1
Mid Holocene 4–8 K BP	standard deviation	1.3	0.055	0.088	0.09	1.3
	maximum	5.9	1.342	2.050	0.75	8.4
	minimum	3.0	1.216	1.862	0.54	5.5
	average (N = 21)	4.7	1.195	2.047	0.40	12.3
700–4000 BP	standard deviation	1.6	0.016	0.031	0.15	4.2
	maximum	8.9	1.237	2.140	0.74	20.9
	minimum	2.2	1.171	1.998	0.23	5.5
	average (N = 19)	11.3	1.184	2.060	0.42	28.7
160–700 BP	standard deviation	6.4	0.009	0.024	0.19	13.6
	maximum	29.7	1.201	2.091	0.75	66.3
	minimum	3.3	1.167	1.986	0.15	12.2
	average (N = 511)	72.5	1.165	2.093	0.67	163
Recent 160 years	standard deviation	114	0.027	0.030	0.73	295
	maximum	1656	1.340	2.209	8.80	3404
	minimum	1.9	1.069	1.924	0.02	4.62

^aBP refers to calendar year 2004 AD.

older than 4000 years are very close to the ranges of eroded continental crust given by *Kramers and Tolstikhin* [1997] (1.202–1.229 and 2.022–2.089 for $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ respectively, calculated from their Table 1) and similar to those found in peat bog samples (dated ~6000 to 9000 years of age) by *Shotyk et al.* [1998, 2001] ($^{206}\text{Pb}/^{207}\text{Pb} = 1.199$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.059$). The comparability of natural Pb isotope ratios in the ancient ice of this study to those found in UCC as well as other archives of atmospheric Pb, further confirm the lithogenic origins of the dust particles preserved in the ancient ice. However, it should be pointed out that $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the ancient ice samples varied significantly (Figures 3a and 4), especially those at 5,705 BP ($^{206}\text{Pb}/^{207}\text{Pb} = 1.342$) and at 10,372 BP ($^{206}\text{Pb}/^{207}\text{Pb} = 1.168$). Although we have no convincing explanations for these shifts, we speculate that these variations could have resulted from source differences due to climate changes and shifts in atmospheric circulation systems (see auxiliary material¹).

[22] During the time period represented by this study, circulation systems changed during the transition period between Wisconsin and Holocene (corresponding to the dip of $\delta^{18}\text{O}$) [*Mayewski et al.*, 1997; *Charles et al.*, 1994]. Meanwhile, topography, land surfaces, vegetation coverage, sea ice coverage, temperature and air mass sources throughout the Arctic were gradually but dramatically changing owing to retreats of the Laurentide, Innuitian and Scandinavian/Eurasian ice sheets. These changes were accompanied by changes in sea level due to isostatic rebound which,

therefore, affected coastlines and land areas [*England et al.*, 2006; *Linden et al.*, 2006; *Steffen and Kaufmann*, 2005; *Dyke*, 2004; *Velichko et al.*, 2002]. Those changes must certainly have affected the sources of dusts in aerosols which were deposited on Devon Island. A plot of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ shows two trends, one moving toward less radiogenic values (for samples older than 9 K BP) and the other moving toward more radiogenic values (for samples with ages between 4 and 9 K BP) (Figure 4). The trend for samples older than 9 K BP (dotted arrow in Figure 4) could be related to the gradually increasing availability of dusts in newly opened areas following the withdrawals of the ice sheets while the other (dashed arrow in Figure 4) could be due to changes in vegetation coverage. However, owing to the complexity of the processes and the limited number of measurements for the time period being considered, a detailed interpretation of the variation of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the ancient ice samples with respect to climate change is beyond the scope of this paper.

[23] In the following sections, the natural Pb/Sc background ratio of 6.3 will be used for calculation of Pb enrichment factors (EFs), which, along with Pb isotope

Table 3. Correlation Between Concentrations of Pb, Al, Sc, and V in Ancient Ice Samples With Ages of 4000 BP and Older

	Pb	Sc	Al	V
Pb	1.000			
Sc	0.999	1.000		
Al	0.993	0.996	1.000	
V	0.997	0.999	0.996	1.000

¹Auxiliary materials are available in the HTML. doi:10.1029/2006GB002897.

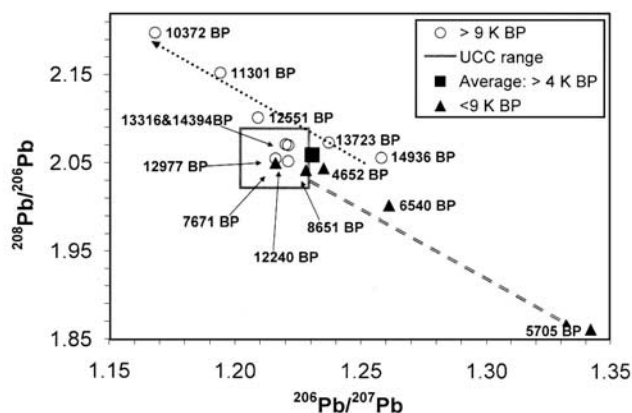


Figure 4. Plot of $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{206}\text{Pb}$ for the samples older than 4000 BP. The UCC $^{206}\text{Pb}/^{207}\text{Pb}$ range was taken from *Kramers and Tolstikhin* [1997]. BP refers to calendar year 2004 AD.

ratios (mainly $^{206}\text{Pb}/^{207}\text{Pb}$), will be used to determine the predominant sources of anthropogenic Pb.

3.3. Anthropogenic Atmospheric Pb Inputs to the Arctic

[24] With the natural background of Pb/Sc ratio of 6.3 ± 1.8 (Table 2), enrichment factors (EFs) of Pb for the samples taken from D1999 core were calculated on the basis of the following enrichment factor (EF) definition:

$$\text{EF}_{\text{Pb}} = ([\text{Pb}]/[\text{Sc}]_{\text{sample}}) / ([\text{Pb}]/[\text{Sc}]_{\text{background}})$$

where EF_{Pb} stands for enrichment factor of Pb versus Sc, $([\text{Pb}]/[\text{Sc}]_{\text{sample}})$ and $([\text{Pb}]/[\text{Sc}]_{\text{background}})$ for concentration ratios of Pb and Sc in samples and in the background values respectively. The Pb EF values, along with $^{206}\text{Pb}/^{207}\text{Pb}$ are presented in Figures 3a–3d.

3.3.1. Contamination From Phoenician and Greek Civilizations

[25] To identify the onset of atmospheric Pb contamination, a minimum 2-data point peak with $\text{EF} \geq 2$ is introduced as criterion. In other words, it is assumed that a Pb/Sc peak with at least two data points that are more than twice the “background” value is beyond the range in natural variation, and is due to anthropogenic inputs. With this criterion, the earliest evidence of atmospheric Pb contamination in the ice core dates from 3100 years ago (Figures 3a and 3b). In the D1999 core, the increase in Pb EF reveals a corresponding decrease in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios which is consistent with the lead ores which were being mined and smelted in the Mediterranean basin at the time. This significant change which was also documented in the Swiss peat bog record, corresponds to the beginning of the Pb trade in the Iberian Peninsula, reflecting the economic activities of Greek and Phoenician civilizations [Shotyk et al., 1998]. A similar chronology of the onset of atmospheric Pb contamination has been reported in other retrospective studies, and suggests a hemispheric phenomenon. *Brännvall*

et al. [2001], for example, found indications of an influx of noncatchment, airborne lead dating from 3000 to 3500 BP in Swedish lake sediments and peat bogs. *Monna et al.* [2004] examined a peat bog from Morvan, France, and found that anthropogenic lead inputs in their study area started ~ 1300 B.C.

3.3.2. Contamination From the Roman Empire

[26] The second peak in Pb EF, dating from ~ 1750 –2150 BP, represents the Roman Period. The Pb isotope data, summarized as the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio, shows a decline during the Roman Period when the Pb EF reached its zenith. Following the decline of the Roman Period, however, both the Pb EF and the Pb isotope ratios evolved back to within the range of the natural background values (Figure 3b). The beginning and end of this episode of Pb contamination reflects the rise and subsequent fall of the Western Roman Empire, reinforcing the validity of the age-depth model. Many other retrospective studies have reported Pb contamination dating from the Roman Empire, including peat bogs [Shotyk et al., 1998; Le Roux et al., 2004; Monna et al., 2004; Baron et al., 2005], lake sediments [Renberg et al., 1994; Brännvall et al., 2001] and Greenland ice cores [Hong et al., 1994; Rosman et al., 1997]. During this time period, production of Pb in Europe and Asia reached approximately 80,000 tons per year [Settle and Patterson, 1980]. It has been estimated that as much as 5% of this Pb production might have been emitted to the atmosphere [Shirahata et al., 1980]. It seems that this extensive period of atmospheric Pb contamination was registered in most natural archives, from both low and high latitudes. However, lake sediments and peat bogs from lower latitudes in Europe, with their greater proximity to the sources of Pb, are more profoundly influenced by local and regional contamination sources. In contrast, ice cores recovered from the High Arctic and Greenland are so much further removed from the emission sources that they must have recorded only those events which were truly hemispheric in proportion.

3.3.3. German Silver Mining

[27] The next occurrence of significant atmospheric Pb contamination recorded by the D1999 core is found between 1100 and 1300 BP (Figure 3b), with a corresponding decline in $^{206}\text{Pb}/^{207}\text{Pb}$. During this period of European history, it is commonly thought that atmospheric Pb contamination had gone into decline [Brännvall et al., 2001] with many of the industrial techniques having been abandoned following the fall of the Roman Empire and with the onset of the Dark Ages [Monna et al., 2004]. Recent retrospective studies of atmospheric metal contamination in the Harz Mountains, however, are beginning to call some of the earlier assumptions into question. In fact, mining in the Harz mountains started in the early Iron Age (800–400 BC), expanded during the Dark Ages (750–1000 AD) and intensified again from the High Middle Ages (1000–1250 AD) [Hettwer et al., 2003; Deicke et al., 2006; Monna et al., 2000]. To date, more than 900 smelting sites have been discovered in this region of Germany [Deicke et al., 2006]. Studies of a 13 m peat core from karstic sinkhole fen in the western Harz Mountains [Hettwer et al., 2003] found that Pb concentrations increased strongly after 400 AD, culminating

in the period 800–1300 AD when they reached values as great as $1250 \mu\text{g g}^{-1}$; these concentrations easily dwarf the values which were found in recent peat layers and reflecting contamination from industrialization and leaded gasoline use. The High Middle Ages (1000 to 1250 AD) were characterized by intensive ore smelting throughout the Harz region, the greatest devastation of forests (to obtain structural materials and fuel), and the greatest intensity of trace metal contamination [Deicke *et al.*, 2006]. The peak in Pb EF found in the D1999 core corresponding to 1100–1300 BP, may have resulted from lead mining in Germany.

[28] In summary, during the period 700 BP to 4000 BP, there were three notable periods of atmospheric Pb contamination in the arctic: \sim 3100 BP, the Roman Period, and the Medieval Period. During each of these intervals, the Pb/Sc ratio was at least double the natural value. To explain these enrichments, therefore, it is necessary to invoke an additional source of Pb, in addition to soil dust. Given the correspondence between these periods of Pb contamination and the history of mining and metallurgy in Europe, the smelting of these lead ores is the most likely source of atmospheric Arctic Pb contamination in antiquity. The declines in $^{206}\text{Pb}/^{207}\text{Pb}$ during these periods are consistent with this interpretation.

3.4. Increasing Pb EF During Recent Centuries

[29] From 700 BP to 160 BP, industrial inputs of Pb to Devon Island increased further, such that Pb deposition became dominated by anthropogenic sources (Figure 3c). During this period, EFs increased continuously and natural background values have not been seen since. Correspondingly, $^{206}\text{Pb}/^{207}\text{Pb}$ ratios gradually, though slowly, decreased and remained outside their natural background range for almost the whole period. On the basis of the trend line plotted in Figure 3c, anthropogenic Pb had already comprised approximately 50% of the total Pb deposition (i.e., twice the natural background) by 700 BP. During the same period, the average $^{206}\text{Pb}/^{207}\text{Pb}$ ratio further decreased from 1.195 ($N = 21$, between 700 BP and 4000 BP) to 1.184 ($N = 19$, between 160 BP and 700 BP), taking it still further away from the background value of 1.230 (Table 2). However, the average $^{208}\text{Pb}/^{206}\text{Pb}$ ratio (2.060) during the same period did not change significantly compared with its corresponding natural value (2.059).

[30] Since 700 BP, therefore, anthropogenic Pb has continually dominated Pb deposition to Devon Island. In fact, even prior to the Industrial Revolution, \sim 80% of the total atmospheric Pb fallout was anthropogenic (Figure 3c). Significant Pb contamination predating the Industrial Revolution has been reported earlier in studies employing peat bogs and sediments from various locations in Europe [Renberg *et al.*, 1994; Shotyk *et al.*, 1998; Brännvall *et al.*, 2001; Le Roux *et al.*, 2004; Monna *et al.*, 2004; Baron *et al.*, 2005] as well ice cores from Greenland [Hong *et al.*, 1994; Rosman *et al.*, 1997].

3.5. Pb Enrichment Factors for Ice and Snow Samples Since 1842

[31] Enrichment factors calculated for ice and snow samples from the past 160 years were based on the Pb/Sc

ratio of the UCC [Shotyk *et al.*, 2005]. On this basis, it was estimated that 95 to 99% of Pb currently being deposited on Devon Island was from anthropogenic sources. With the natural Pb/Sc ratio found in preanthropogenic ice determined from the same ice cap in this study (6.3 ± 1.8), EFs for those samples were recalculated and plotted in Figure 3d, along with the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios. These new EF values as well as the Pb isotope ratios are also summarized in Table 2. Although the extent of enrichment certainly does depend on the reference value selected (UCC: 2.4, soil: 5 and Devon ancient ice: 6.3), the chronology of the changes in EF does not. The value of Pb/Sc obtained for the ancient layers of ice presented here provides the most accurate assessment to date of the chemical composition of natural, Pb-bearing aerosols to this region of the arctic, and provides a reasonable reference level against which values obtained in future may be compared.

[32] The Pb EF and isotope data (Figure 3d and Table 2) clearly show that human activities have left a legacy of Pb contamination on the ice cap, with the intensity of contamination especially pronounced during the period between 1940s and 1980s when leaded gasoline additives were used on a massive scale. However, although the majority of the large, broad Pb peak resulted from the use of gasoline additives from approximately 20 to 60 years ago, the results show clearly that Pb contamination predates the use of gasoline Pb by a considerable margin. The snow pit samples representing accumulation from 1994 to 2004 suggest that even today, over 90% of Pb deposition on Devon Island is still from anthropogenic sources. Although it is not clear to what extent contemporary Pb contamination could be explained in terms of resuspension of anthropogenic, Pb-bearing particles which had already been deposited on plants and soils [Harris and Davidson, 2005; Sun *et al.*, 2006], results predating \sim 1850 AD suggest that Pb contamination problem existed far before use of leaded gasoline additives. In fact, already in the early 20th century, more than 90% of the Pb deposition was from anthropogenic sources. The direct consequence of this finding is that the global problem of atmospheric Pb contamination will not disappear with the phase-out of leaded gasoline. The Pb/Sc ratio of the aerosols being supplied to the arctic will not return to their natural background levels because the other anthropogenic sources which contributed so significantly to the Pb burden prior to the use of leaded gasoline still exist.

4. Summary and Conclusions

[33] The D1999 ice core from Devon Island has been recording atmospheric Pb deposition for 15,800 years. Although there are large variations in Pb concentrations and isotope ratios throughout the core, only those changes prior to approximately 4000 BP can be attributed to natural processes. Elevated Pb concentrations are found during the Wisconsin glaciation and throughout the Younger Dryas, and lower Pb concentrations during the mid-Holocene Climate Optimum. However, throughout these periods the Pb/Sc ratio was remarkably uniform (6.3 ± 1.8) and the Pb isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$) consistent with soil dust particles derived from crustal weathering. Atmo-

spheric deposition of soil dust alone, therefore, is sufficient to explain the supply to Pb to the High Arctic from approximately 15,800 until ~4000 years ago.

[34] In contrast to the variations in natural supply of atmospheric Pb, 3100 years ago the ratio of Pb to Sc doubled for the first time; this, coupled to a significant decline in $^{206}\text{Pb}/^{207}\text{Pb}$, is attributed to the onset of atmospheric Pb contamination, with lead mining and smelting in the Iberian Peninsula the most likely source. Unambiguous evidence of atmospheric Pb contamination dating from the Roman Period as well as the Middle Ages are also preserved in the ice core. Between these anthropogenic phases, however, the Pb/Sc ratio and the $^{206}\text{Pb}/^{207}\text{Pb}$ values returned to within their natural range.

[35] Starting 700 years ago, the Pb/Sc ratio exceeded the background value by a factor of five for the first time. The natural “background” Pb/Sc ratio has never been seen again since. In the 1840s, long before Pb additives were used in gasoline, approximately 80% of the Pb deposition on the Devon Ice Cap was already from anthropogenic sources. Even in the 1920s, still predating the use of leaded gasoline additives, ~90% of Pb deposition was anthropogenic. Clearly, the use of leaded gasoline is only a small, and the most recent chapter, in a very long history of atmospheric Pb contamination.

[36] Lead enrichments in snow and firn from Devon Island have gone into decline during the most recent decades [Shotyk et al., 2005] in response to the gradual elimination of leaded gasoline. However, using the natural, background Pb/Sc ratio and Pb isotope data of ancient ice samples to provide a reference level of the pre-industrial condition, even today, at least 90% of the Pb in the High Arctic is from anthropogenic sources. The elemental and isotopic data presented here, the first ever long-term Pb record from Canadian High Arctic ice cores, therefore, provides a reference level against which further changes in future may be compared.

[37] **Acknowledgments.** This work was funded and sponsored by the following institutions and organizations: Geological Survey Canada (GSC) of Natural Resources of Canada, European Commission, Northern Contaminants Program Canada and The University of Heidelberg, Heidelberg, Germany. Thanks go to Bernd Kober for his helpful comments about the Pb isotope data and Roy Koerner for his valuable suggestions during preparation of this manuscript. Two anonymous reviewers provided valuable comments.

References

- Baron, S., M. Lavoie, A. Ploquin, J. Carignan, M. Pulido, and J.-L. De Beaulieu (2005), Record of metal workshops in peat deposits: History and environmental impact on the Mont Lozere Massif, France, *Environ. Sci. Technol.*, *39*, 5131–5140.
- Boutron, C. F., and C. C. Patterson (1983), The occurrence of lead in Antarctic recent snow, firn deposited over the last two centuries and prehistoric ice, *Geochim. Cosmochim. Acta*, *47*, 1355–1368.
- Boutron, C. F., and C. C. Patterson (1986), Lead concentration changes in Antarctic ice during the Wisconsin/Holocene transition, *Nature*, *323*, 222–225.
- Boutron, C. F., J.-P. Candelone, and S. Hong (1994), Past and recent changes in the large-scale tropospheric cycles of lead and other heavy metals as documented in Antarctic and Greenland snow and ice, *Geochim. Cosmochim. Acta*, *58*, 3217–3225.
- Boutron, C. F., J.-P. Candelone, and S. Hong (1995), Greenland snow and ice cores: unique archives of large-scale pollution of the troposphere of the Northern Hemisphere by lead and other heavy metals, *Sci. Total Environ.*, *160/161*, 233–241.
- Bowen, H. J. M. (1979), *Environmental Chemistry of the Elements*, 333 pp., Academic, New York.
- Brännvall, M.-L., R. Bindler, O. Emteryd, and I. Renberg (2001), Four thousand years of atmospheric lead pollution in northern Europe: a summary from Swedish lake sediments, *J. Paleolimnol.*, *25*, 421–435.
- Candelone, J.-P., S. Hong, C. Pellone, and C. F. Boutron (1995), Post-industrial revolution changes in large-scale atmospheric pollution of the Northern Hemisphere by heavy metals as documented in central Greenland snow and ice, *J. Geophys. Res.*, *100*, 16,605–16,616.
- Charles, C. D., D. Rind, J. Jouzel, R. D. Koster, and R. G. Fairbanks (1994), Glacial-interglacial changes in moisture sources for Greenland: influences on the ice core record of climate, *Science*, *263*, 508–511.
- Deicke, M., H. Ruppert, and J. Schneider (2006), Mining and smelting in the Harz Mountains (Germany): A never-ending environment story, in *Sediment 2006. Abstract and Field Trips*, edited by H. van Eynatten et al., pp. 237–256, Dtsch. Geol. Ges., Leipzig, Germany.
- Dyke, A. (2004), An outline of north America deglaciation with emphasis on central and northern Canada, in *Quaternary Glaciations—Extent and Chronology: Part II. Developments in Quaternary Science*, vol. 2b, edited by J. Ehlers and P. L. Gibbard, pp. 373–424, Elsevier, Amsterdam.
- England, J., N. Atkinson, J. Bednarski, A. S. Dyke, D. A. Hodgson, and C. O. Cofaigh (2006), The Innuitian Ice Sheet: configuration, dynamics and chronology, *Quat. Sci. Rev.*, *25*(7–8), 689–703.
- Fisher, D. A. (1979), Comparison of 10^7 years of oxygen isotope and insoluble impurity profiles from the Devon Island and Camp Century ice cores, *Quat. Res.*, *11*, 299–305.
- Fisher, D. A., and R. M. Koerner (2003), Holocene ice-core climate history—A multi-variable approach, in *Global Change in the Holocene*, edited by A. Mackay et al., pp. 281–293, Arnold, London.
- Fisher, D. A., R. M. Koerner, and N. Reeh (1995), Holocene climatic records from Agassiz Ice Core, Ellesmere Island, NWT, Canada, *Holocene*, *5*, 19–24.
- Harris, A. R., and C. I. Davidson (2005), The role of resuspended soil in lead flows in the California South coast air basin, *Environ. Sci. Technol.*, *39*, 7410–7415.
- Hettwer, K., M. Deicke, and H. Ruppert (2003), Fens in karst sinkholes—Archives for long lasting ‘immission’ chronologies, *Water Air Soil Pollut.*, *149*, 363–384.
- Hong, S., J.-P. Candelone, C. C. Patterson, and C. F. Boutron (1994), Greenland ice evidence of hemispheric lead pollution two millennia ago by Greek and Roman civilizations, *Science*, *265*, 1841–1843.
- Hong, S., J.-P. Candelone, C. Turetta, and C. F. Boutron (1996), Changes in natural lead, copper, zinc and cadmium concentrations in central Greenland ice from 8250 to 149,100 years ago: Their association with climatic changes and resultant variations of dominant source contributions, *Earth Planet. Sci. Lett.*, *143*, 233–244.
- Hong, S., C. F. Boutron, R. Edwards, and V. I. Morgan (1998), Heavy metals in Antarctic ice from Law Dome: Initial results, *Environ. Res.*, *78*(2), 94–103.
- Jones, V. J., M. J. Leng, N. Solovieva, H. J. Sloane, and P. Tarasov (2004), Holocene climate of the Kola Peninsula: Evidence from the oxygen isotope record of diatom silica, *Quat. Sci. Rev.*, *23*(7–8), 833–839.
- Kerwin, M. W., J. T. Overpeck, R. S. Webb, and K. H. Anderson (2004), Pollen-based summer temperature reconstructions for the eastern Canadian boreal forest, subarctic, and Arctic, *Quat. Sci. Rev.*, *23*(18–19), 1901–1924.
- Krachler, M., J. Zheng, D. A. Fisher, and W. Shotyk (2004a), Direct determination of lead isotopes (^{206}Pb , ^{207}Pb , ^{208}Pb) in Arctic ice samples at picogram per gram levels using inductively coupled plasma-sector field MS coupled with a high-efficiency sample introduction system, *Anal. Chem.*, *76*, 5510–5517.
- Krachler, M., J. Zheng, D. A. Fisher, and W. Shotyk (2004b), Novel calibration procedure for improving trace element determinations in ice and water samples using ICP-SMS, *J. Anal. Atmos. Spectrom.*, *19*(8), 1017–1019.
- Krachler, M., J. Zheng, D. A. Fisher, and W. Shotyk (2005), Analytical procedures for improved trace element detection limits in polar ice from Arctic Canada using ICP-SMS, *Anal. Chim. Acta.*, *530*, 291–298.
- Kramers, J., and I. N. Tolstikhin (1997), Two terrestrial lead isotope paradoxes, forward transport modeling, core formation and the history of the continental crust, *Chem. Geol.*, *139*, 75–110.
- Le Roux, G., D. Weiss, J. Grattan, N. Givélet, M. Krachler, A. Cheburkin, N. Rausch, B. Kober, and W. Shotyk (2004), Identifying the sources and timing of ancient and medieval atmospheric lead pollution in England using a peat profile from Lindow bog, Manchester, *J. Environ. Monit.*, *6*, 502–510.
- Linden, M., P. Moller, S. Bjorck, and P. Sandgren (2006), Holocene shore displacement and deglaciation chronology in Norrbotten, Sweden, *Boreas*, *35*, 1–22.

- Mayewski, P. A., L. D. Meeker, S. Whitlow, M. S. Twickler, M. C. Morrison, R. B. Alley, P. Bloomfield, and K. Taylor (1993), The atmosphere during the Younger Dryas, *Science*, *261*, 195–197.
- Mayewski, P. A., L. D. Meeker, M. S. Twickler, S. Whitlow, Q. Yang, W. B. Lyons, and M. Prentice (1997), Major features and forcing of high-latitude Northern Hemisphere atmospheric circulation using a 110,000-year-long glaciochemical series, *J. Geophys. Res.*, *102*, 26,345–26,366.
- McConnell, J. R., G. W. Lamorey, and M. A. Hutterli (2002), A 250-year high-resolution record of Pb flux and crustal enrichment in central Greenland, *Geophys. Res. Lett.*, *29*(23), 2130, doi:10.1029/2002GL016016.
- Monna, F., K. Hamer, J. L  v  que, and M. Sauer (2000), Pb isotopes as a reliable marker of early mining and smelting in the Northern Harz province (Lower Saxony, Germany), *J. Geochem. Explor.*, *68*, 201–210.
- Monna, F., C. Petit, J.-P. Guillaumet, I. Jouffroy-Bapicot, C. Blanchot, J. Dominik, R. Losno, H. Richard, J. L  v  que, and C. Chateau (2004), History and environmental impact of mining activity in Celtic Aeduan territory recorded in a peat bog (Morvan, France), *Environ. Sci. Technol.*, *38*, 665–673.
- Ng, A., and C. Patterson (1981), Natural concentrations of lead in ancient Arctic and Antarctic ice, *Geochim. Cosmochim. Acta*, *45*, 2109–2121.
- Othman, D. B., W. M. White, and J. Patchett (1989), The geochemistry of marine sediments, island arc magma genesis, and crust-mantle recycling, *Earth Planet. Sci. Lett.*, *94*, 1–21.
- Planchon, F. A. M., C. F. Boutron, C. Barbante, G. Cozzi, V. Gaspari, E. W. Wolff, C. P. Ferrari, and P. Cescon (2002), Changes in heavy metals in Antarctic snow from Coats Land since the mid-19th to the late-20th century, *Earth Planet. Sci. Lett.*, *200*, 207–222.
- Planchon, F. A. M., K. Van De Velde, K. J. R. Rosman, E. W. Wolff, C. P. Ferrari, and C. F. Boutron (2003), One hundred fifty-year record of lead isotopes in Antarctic snow from Coats Land, *Geochim. Cosmochim. Acta*, *67*, 693–708.
- Rahn, K. A. (1976), Silicon and aluminum in atmospheric aerosols: Crust-air fractionation?, *Atmos. Environ.*, *10*(8), 597–601.
- Renberg, I., M. W. Persson, and O. Emteryd (1994), Pre-industrial atmospheric lead contamination detected in Swedish lake sediments, *Nature*, *368*, 323–326.
- Rosman, K. J. R., W. Chisholm, S. Hong, J.-P. Candelone, and C. F. Boutron (1997), Lead from Carthaginian and Roman Spanish mines isotopically identified in Greenland ice dated from 600 B.C. to 300 A.D., *Environ. Sci. Technol.*, *31*, 3413–3416.
- Settle, D. M., and C. C. Patterson (1980), Lead in albacore: Guide to lead pollution in Americans, *Science*, *207*, 1167–1176.
- Shirahata, H., R. W. Elias, C. C. Patterson, and M. Koide (1980), Chronological variations in concentrations and isotopic compositions of anthropogenic atmospheric lead in sediments of a remote subalpine pond, *Geochim. Cosmochim. Acta*, *44*, 149–162.
- Shotyk, W., D. Weiss, P. G. Appleby, A. K. Cheburkin, R. Frei, M. Gloor, J. D. Kramers, S. Reese, and W. O. Van Der Knaap (1998), History of atmospheric lead deposition since 12,370 ¹⁴C yr BP recorded in a peat bog profile, Jura Mountains, Switzerland, *Science*, *281*, 1635–1640.
- Shotyk, W., D. Weiss, J. D. Kramers, R. Frei, A. K. Cheburkin, M. Gloor, and S. Reese (2001), Geochemistry of the peat bog at Etang de la Gru  re, Jura Mountains, Switzerland, and its record of atmospheric Pb and lithogenic trace metals (Sc, Ti, Y, Zr, and REE) since 12,370 ¹⁴C yr BP, *Geochim. Cosmochim. Acta*, *65*, 2337–2360.
- Shotyk, W., M. Krachler, and B. Chen (2004), Antimony in recent, ombrotrophic peat from Switzerland and Scotland: Comparison with natural background values (5320 to 8020 ¹⁴C yr BP) and implications for the global atmospheric Sb cycle, *Global Biogeochem. Cycles*, *18*, GB1016, doi:10.1029/2003GB002113.
- Shotyk, W., J. Zheng, M. Krachler, C. M. Zdanowicz, R. M. Koerner, and D. A. Fisher (2005), Predominance of industrial Pb in recent snow (1994–2004) and ice (1842–1996) from Devon Island, Arctic Canada, *Geophys. Res. Lett.*, *32*, L21814, doi:10.1029/2005GL023860.
- Smith, I. R. (2002), Diatom-based Holocene paleoenvironmental records from continental sites on northeastern Ellesmere Island, high Arctic, Canada, *J. Paleolimnol.*, *27*, 9–28.
- Stacey, J. S., and J. D. Kramers (1975), Approximation of terrestrial lead isotope evolution by a two-stage model, *Earth Planet. Sci. Lett.*, *26*, 207–221.
- Steffen, H., and G. Kaufmann (2005), Glacial isostatic adjustment of Scandinavia and northwestern Europe and the radial viscosity structure of the Earth's mantle, *Geophys. J. Int.*, *163*, 801–812.
- Sun, Y., G. Zhuang, W. Zhang, Y. Wang, and Y. Zhuang (2006), Characteristics and sources of lead pollution after phasing out leaded gasoline in Beijing, *Atmos. Environ.*, *40*(16), 2973–2985.
- Vallelonga, P., P. Gabrielli, K. J. R. Rosman, C. Barbante, and C. F. Boutron (2005), A 220 kyr record of Pb isotopes at Dome C Antarctica from analyses of the EPICA ice core, *Geophys. Res. Lett.*, *32*, L01706, doi:10.1029/2004GL021449.
- Van de Velde, K., P. Vallelonga, J.-P. Candelone, K. J. R. Rosman, V. Gaspari, G. Cozzi, C. Barbante, R. Udisti, P. Cescon, and C. F. Boutron (2005), Pb isotope record over one century in snow from Victoria Land, Antarctica, *Earth Planet. Sci. Lett.*, *232*, 95–108.
- Velichko, A. A., N. Catto, A. N. Drenova, V. A. Klimanov, K. V. Kremenski, and V. P. Nechaev (2002), Climate changes in East Europe and Siberia at the Late glacial–Holocene transition, *Quat. Int.*, *91*, 75–99.
- Wedepohl, K. H. (1995), The composition of the continental crust, *Geochim. Cosmochim. Acta*, *59*, 1217–1232.
- Zheng, J., A. Kudo, D. A. Fisher, E. W. Blake, and M. Gerasimoff (1998), Solid electrical conductivity (ECM) from four Agassiz ice cores, Ellesmere island NWT, Canada: High-resolution signal and noise over the last millennium and low resolution over the Holocene, *Holocene*, *8*(4), 413–421.
- Zheng, J., D. A. Fisher, E. W. Blake, G. Hall, J. Vaive, M. Krachler, C. M. Zdanowicz, J. Lam, G. Lawson, and W. Shotyk (2006), An ultra-clean firn core from Devon Ice Cap, Nunavut, Canada retrieved using a titanium drill specially designed for trace element studies, *J. Environ. Monit.*, *8*, 406–413.

D. A. Fisher and J. Zheng, Geological Survey of Canada, Natural Resources Canada, 601 Booth Street, Ottawa, Ontario, Canada K1A 0E8. (jzheng@nrcan.gc.ca)

M. Krachler and W. Shotyk, Institute of Environmental Geochemistry, University of Heidelberg, D-69117 Heidelberg, Germany.