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# Atmospheric Sb in the Arctic during the past 16,000 years: Responses to climate change and human impacts

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[1] Applying strict clean room procedures and sector field inductively coupled plasma mass spectrometry (ICP-MS) methods, concentrations of Sb and Sc were determined in 57 sections of a 170.6-m-long ice core drilled on Devon Island, Arctic Canada, in 1999, providing a record of atmospheric Sb extending back 15,800 years. Natural background concentrations of Sb and Sc established during the period between 1300 years BP and 10,590 years BP averaged 0.08 ± 0.03 pg/g ($N = 18$) and 0.44 ± 0.20 pg/g ($N = 17$), respectively. Scandium, a conservative reference element, was used as a surrogate for mineral dust inputs. The Sb/Sc ratio of 0.13 ± 0.07 in these ancient ice samples is comparable to the corresponding ratio of 0.09 ± 0.03 in peat samples from Switzerland from circa 6000 to 9000 years BP, indicating that this natural background ratio might have a much broader validity. The natural background flux of Sb (0.7 ± 0.5 ng/m$^2$/a) in the Arctic was approximately 500 times lower than that established in central Europe using peat cores. For comparison with background values, modern Sb fluxes calculated using 45 samples from a 5-m snow pit dug on Devon Island in 2004, reflecting 10 years of snow accumulation, yielded an average deposition rate of 340 ± 270 ng/m$^2$/a (range: 20–1240 ng/m$^2$/a) with pronounced accumulation of Sb during winter periods when air masses reaching the Arctic predominantly come from Eurasia. These data reveal that approximately 99.8% of the Sb deposited in the Arctic today originates from anthropogenic activities. Modern Sb enrichment factors averaged 25 (range: 8–121). The ice core provides evidence of Sb contamination dating from Phoenician/Greek, Roman, and medieval lead mining and smelting in Europe. Moreover, the ice core data indicate that anthropogenic sources of Sb have continuously dominated the atmospheric inputs to the Arctic for at least 700 years.

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## 1. Introduction

[2] During recent years, environmental archives such as peat bogs and ice cores have successfully been exploited to investigate changes in sources and rates of atmospheric deposition of antimony (Sb) [*Shotyk et al.*, 2002, 2004, 2005a, 2005b; *Krachler et al.*, 2005a; *Van de Velde et al.*, 1999; *Barbante et al.*, 2004; *Steinnes and Njåstad*, 1995; *Schell*, 1986; *Cloy et al.*, 2005]. In that context, analyses of peat cores from bogs revealed (1) distinct modern enrichments of Sb [*Shotyk et al.*, 2002, 2004, 2005a, 2005b; *Steinnes and Njåstad*, 1995; *Schell*, 1986; *Cloy et al.*, 2005] and (2) that the chronology and intensity of atmospheric Sb contamination in Europe since the Roman period is similar to that of Pb [*Shotyk et al.*, 2004; *Cloy et al.*, 2005]. The association between environmental contamination of Sb and Pb reflects the abundance of Sb in lead ores [*Shotyk et al.*, 2004] and the low melting point of stibnite, $Sb_2S_3$, the most common antimony sulphide [*Krachler et al.*, 2005a].

[3] Previous ice core studies from the European Alps considered Sb but examined only a few samples during the last circa 300 years and thus provided only limited insights into the changing rates of Sb atmospheric deposition [*Van de Velde et al.*, 1999; *Barbante et al.*, 2004]. Our recent ice core studies in the Canadian High Arctic, in turn, included more than 500 samples yielding a detailed chronology of atmospheric Sb deposition during the past ~160 years and revealed a 50% increase in Sb enrichment factors (Sb EF) during the last 3 decades [*Krachler et al.*, 2005a]. This distinct increase in Sb EF is very likely related to the rapidly increasing number of industrial applications of Sb [*Shotyk et al.*, 2005b, 2005c]. In the absence of natural background concentrations, however, only relative enrichments of Sb, based on the changing Sb/Sc ratio of the investigated ice and snow samples, could be calculated [*Krachler et al.*, 2005a].

[4] To date, only very limited data on the natural abundance of Sb in aerosols from preanthropogenic times are

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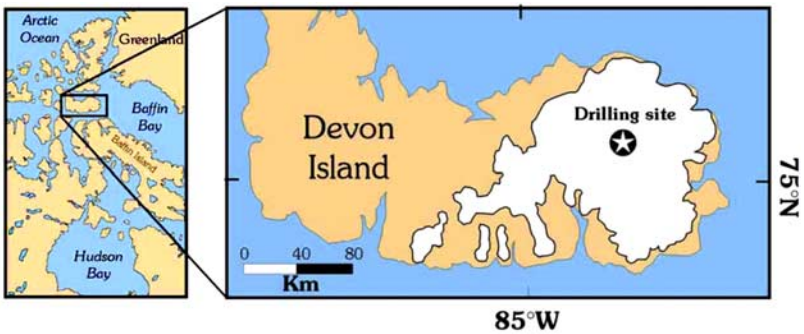

**Figure 1.** Map of a selected area of the Canadian High Arctic highlighting the Devon Island Ice Cap (1860 m above sea level) where the two ice cores and the snow pit were collected at 75°N; 82°W in the years 1999, 2000, and 2004, respectively.

available [*Shotyk et al.*, 2002]. In the absence of these data, most researchers use crustal concentration values of Sb and conservative lithogenic reference elements (such as Al or Sc) to calculate modern enrichments of Sb in atmospheric aerosols [*Van de Velde et al.*, 1999; *Barbante et al.*, 2004; *Schell*, 1986; *Cloy et al.*, 2005]. One weakness in this approach, however, is the lack of information about the relationship between elemental concentrations in the upper continental crust (UCC) and those of natural aerosols. In other words, the assumption that the Sb/Sc ratio in aerosols dating from preindustrial and preanthropogenic times is identical to the crustal ratio needs to be evaluated critically. For example, the Sb EF in recent snow and ice varies considerably, depending on whether UCC, soil, or ancient peat samples are used to determine reference levels [*Krachler et al.*, 2005a]. Studies of Sb in the peat bog at Etang de la Gruère, Switzerland [*Shotyk et al.*, 2002], suggest that natural atmospheric aerosols dating from the middle to early Holocene (circa 6000 to 9000 years BP) were already enriched by approximately 10 times compared to the average continental crust. Our hypothesis therefore is that Arctic aerosols dating from the early to mid-Holocene also were enriched in Sb, relative to crustal values, by an order of magnitude. To test this hypothesis, we have measured Sb in an Arctic ice core extending back in time approximately 16,000 years.

[5] In our previous study, we analyzed a 63.72-m-long ice core drilled on Devon Island, Arctic Canada (Devon 2000 firn core) for Sb covering the period from 1840 to 1996 [*Krachler et al.*, 2005a]. In addition to providing the first detailed chronology of atmospheric Sb deposition for this period, the study also included 45 samples from a 5-m snow pit dug in 2004, representing the period 1994 to 2004 [*Krachler et al.*, 2005a].

[6] Applying strict clean room techniques and inductively coupled plasma (ICP) sector field mass spectrometry (MS) procedures [*Krachler*, 2007] which we developed earlier for the reliable determination of extremely low elemental concentrations in polar ice and snow [*Krachler et al.*, 2004a, 2004b, 2005a, 2005b; *Zheng et al.*, 2006], the main aims of the current study are to (1) extend the chronology of atmospheric Sb deposition to preanthropogenic times, (2) establish natural background concentrations and deposition rates of Sb and Sc, (3) establish the variability of the natural Sb/Sc ratio, and (4) investigate the dependence of atmospheric Sb deposition on climate change since the Late Glacial. Finally, using the natural "background" Sb/Sc ratio, we wish to put modern values of Sb/Sc into perspective and estimate human impacts on the global atmospheric Sb cycle.

[7] To address these issues adequately, 57 ice samples of a ~170-m-long ice core drilled in spring of 1999 on Devon Island, Canadian High Arctic, close to the previous study site and dating back to almost 16,000 years BP, were investigated. The youngest ice sample in the current core (Devon 1999 ice core) dates to 1870 which overlaps with the previously investigated core (Devon 2000 firn core) by ~30 years. The overlapping core sections match well, providing a complete record of atmospheric Sb deposition since ~16,000 years BP.

## 2. Materials and Methods

### 2.1. Laboratories and Instrumentation

[8] To minimize the potential risk of contamination, all sample handling and the preparation of all standards were performed in clean rooms under laminar flow clean air benches of at least class 100. Decontamination and further processing of the ice samples was carried out inside a class 100 clean bench in a certified cold clean room of class 1000. The ice and snow samples were melted, acidified with high-purity $HNO_3$ (68–72%) to 0.5% (v/v), and bottled in a class 10 clean air cabinet at the Geological Survey of Canada (GSC), Ottawa, Canada [*Krachler et al.*, 2005b; *Zheng et al.*, 2007].

[9] All ICP-MS measurements were carried out with an ICP sector field MS (ICP-SMS) (Element2, Thermo Fisher Scientific, Bremen, Germany) operated in a class 1000 clean laboratory. A microvolume autosampler (ASX 100, Cetac Technologies, Omaha, Nebraska, United States), a high-efficiency sample introduction system (Apex IR, Elemental Scientific Incorporated, Omaha, Nebraska, United States) including a low-flow PFA nebulizer operated in the self-aspirating mode (Elemental Scientific Incorporated) and a sapphire injector tube were employed to transport the analytes into the plasma of the ICP-SMS. The autosampler and the Apex sample introduction system were hosted in a class 100 laminar flow bench. Details of all analytical

**Table 1.** Summary of Sb and Sc Concentrations of the Two Ice Cores and Selected Samples From a 5-m Snow Pit Collected on Devon Island, Canadian High Arctic[a]

| Element | N[b] | Minimum | Maximum | Median |
|---|---|---|---|---|
| | | *Antimony* | | |
| Devon 1999 ice core (15,876 BP–AD 1870)[c] | 57 | 0.04 | 4.14 | 0.12 |
| Devon 2000 firn core (AD 1842–1996)[d] | 465 | 0.07 | 108 | 0.98 |
| Devon 2004 snow pit (AD 1994–2004)[d] | 45 | 0.13 | 3.71 | 1.03 |
| | | *Scandium* | | |
| Devon 1999 ice core (15,876 BP–AD 1870)[c] | 57 | 0.14 | 38.1 | 0.45 |
| Devon 2000 firn core (AD 1842–1996)[d] | 465 | 0.02 | 8.80 | 0.47 |
| Devon 2004 snow pit (AD 1994–2004)[d] | 45 | 0.08 | 1.64 | 0.31 |

[a] Units for Sb and Sc concentrations are pg/g.
[b] Number of samples analyzed.
[c] Results from this study.
[d] Data taken from *Krachler et al.* [2005b].

procedures including ICP-SMS operating conditions and the data acquisition parameters were reported earlier [*Krachler et al.*, 2004a, 2004b, 2005a, 2005b, *Zheng et al.*, 2006].

### 2.2. Reagents and Standards

[10] For the preparation of all solutions, high-purity water (18.2 MΩ cm) from a MilliQ-Element system (Millipore, Milford, Massachusetts, United States) designed for inorganic ultra-trace-analysis was used. Nitric acid (65%, analytical reagent grade, Merck, Darmstadt, Germany) was further purified twice by distillation, using a high-purity quartz unit for subboiling of acids (MLS GmbH, Leutkirch, Germany). Both the water purification system and the subboiling distillation unit were operated in clean rooms.

[11] Calibration solutions for Sb and Sc were prepared by appropriate dilution of 10 mg $L^{-1}$ stock standard solutions (Merck) with 0.5% (v/v) high-purity nitric acid. Quantification of trace element concentrations was performed by linear regression of the calibration curves.

### 2.3. Collection of the Ice Core and Sample Treatment

[12] Details of the ice core drilling, further processing, and decontamination of the ice samples were reported elsewhere [*Zheng et al.*, 2006, 2007]. Briefly, the 57 ice samples used in this study were taken from a core retrieved from the top of the satellite dome on the ice cap of Devon Island, Nunavut, Canada (75°N; 82°W; 1860 m above sea level), in April–May of 1999 (Devon 1999 ice core) (Figure 1). The total depth of the core was 170.6 m. The core sections were preserved at −20°C in freezers after drilling. Actual sample lengths ranged from 7 to 15 cm with the mass of the samples ranging from 32 to 71 g each, after decontamination.

[13] The age/depth relationship of the ice core was established utilizing electrical conductivity measurements on the fresh ice cores in the field, employing well-established chronostratigraphic markers and oxygen isotopes [*Zheng et al.*, 2007].

[14] For obtaining clean ice samples suitable for trace element analysis, the outside layers of the ice core were removed manually in the certified clean laboratory of the GSC inside a class 100 clean bench using high-purity titanium tools [*Krachler et al.*, 2005b; *Zheng et al.*, 2006]. The decontaminated ice samples were further processed applying ultraclean laboratory procedures as described earlier [*Krachler et al.*, 2004a, 2004b, 2005a, 2005b; *Zheng et al.*, 2006, 2007].

[15] Detailed information on the collection and further processing of the 5-m snow pit samples was given previously [*Krachler et al.*, 2005b].

### 2.4. Quality Control and Detection Limits

[16] There is no certified reference material for trace elements in polar ice currently available. However, a riverine water reference material (SLRS-4, National Research Council Canada, Ottawa, Canada) containing low Sb and Sc concentrations was used for quality control purposes. As reported previously [*Krachler et al.*, 2004a, 2005a, 2005b], good agreement between the experimentally established and certified (Sb) and reported (Sc) concentrations was established.

[17] Applying strict clean room methods and sophisticated ICP-SMS protocols [*Krachler et al.*, 2004a, 2005a, 2005b], detection limits for both elements were as low as 0.006 pg/g and thus allowed the accurate and reliable quantification of Sb and Sc in all investigated ice samples.

## 3. Results and Discussion

### 3.1. Sb, Sc, and Sb/Sc

[18] The concentrations of Sb in all 567 ice (Devon 1999 ice core, Devon 2000 firn core) and snow samples (Devon 2004 snow pit) range from 0.04 to 108 pg/g (Table 1). Despite this large variability (2700 times), the median Sb concentration is circa 1 pg/g during the last ∼160 years while the Sb concentrations in the older ice samples are approximately 1 order of magnitude lower (Table 1). A detailed description and interpretation of the Sb chronology of the recent 160 years can be found elsewhere [*Krachler et al.*, 2005a].

[19] Scandium concentrations in all investigated samples ranged from 0.02 to 38.1 pg/g (∼1900 times variability), while the median of Sc concentrations of the snow pit (0.31 pg/g) and the two ice cores (∼0.50 pg/g) varied only marginally (Table 1).

### 3.2. Background Values

[20] The lowest Sb and Sc concentrations in the Devon 1999 ice core average 0.08 ± 0.03 pg/g ($N$ = 18, median:

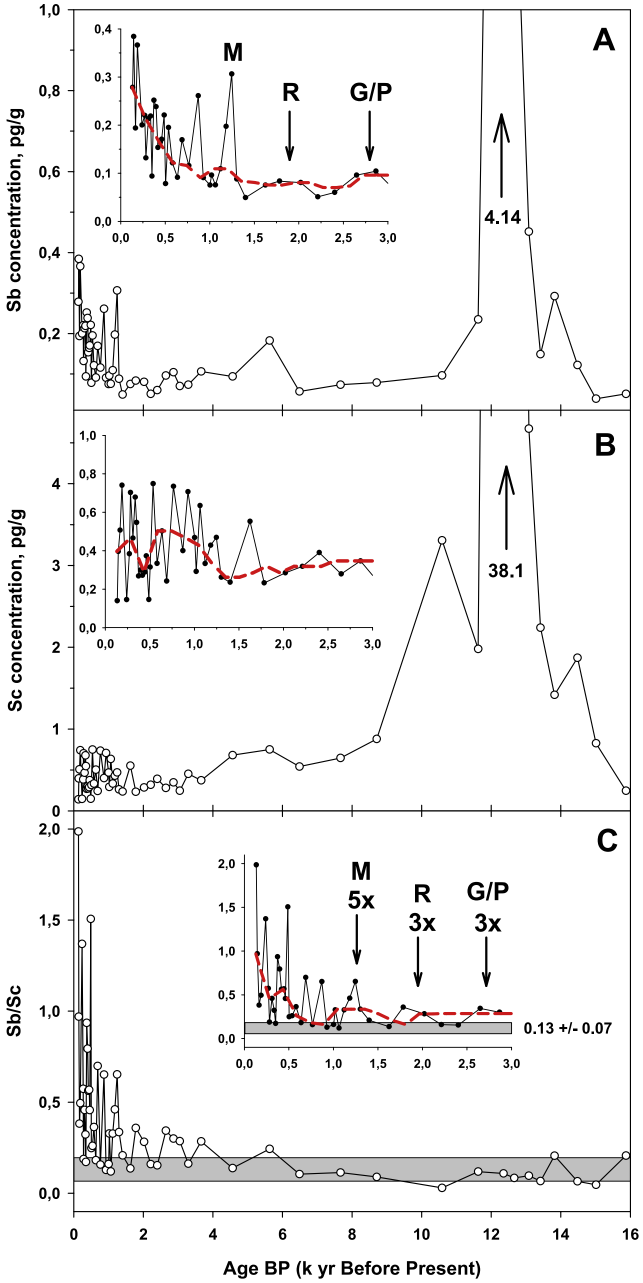

**Figure 2.** (a) Antimony concentrations in 57 ice samples of the Devon 1999 ice core covering the period AD 1870 to 15,876 ka BP. Running median in the insert (dashed line) provides the smoothed trend for the last 3000 years. M refers to the period of medieval silver mining in Germany, R refers to Roman lead smelting, and G/P refers to the Greek/Phoenician times. (b) Concentrations of Sc in the Devon 1999 ice core reflecting the increased soil dust inputs during the Younger Dryas cold climate event centered around 12,350 years BP. Running median in the insert (dashed line) provides the smoothed trend for the last 3000 years. (c) Antimony/Sc ratio of the samples. Running median in the insert (dashed line) provides the smoothed trend for the last 3000 years. Gray areas indicate the natural Sb/Sc ratio of 0.13 ± 0.07.

0.08 pg/g, range: 0.05–0.18 pg/g) and 0.44 ± 0.20 pg/g ($N$ = 17, median: 0.37 pg/g, range: 0.23–0.88 pg/g) during the period between 1302 years BP and 10,588 years BP (Figure 2). As the Sb and Sc concentrations of this extended period, lasting ~9300 years, provide the lowest concentrations found in the entire ice core, these data might be considered as natural background levels of both elements on Devon Island. The low Sb concentrations established in this study are the lowest concentrations ever reported for ice and snow. In addition, this is the first report of Sc concentrations in ancient polar ice.

[21] Previous ice core studies considering Sb focused on samples that were only a few hundred years old [*Van de Velde et al.*, 1999; *Barbante et al.*, 2004; *Krachler et al.*, 2005a]. Clearly, these modern and recent ice layers which are contaminated with antimony from industrial sources cannot be used to determine natural "background" values.

### 3.3. Variation in Response to Climate Change Since the Last Glacial

[22] Prior to the past millennium, the greatest Sb concentrations (up to 4.14 pg/g) are found during the Younger Dryas (YD) cold climate event centered around 12,350 years BP (Figure 2a). This period is characterized by sparse vegetation cover and high wind strengths favoring the transport and deposition of more and larger dust particles into the Arctic. A closer look at the Sc concentration profile of the Devon 1999 ice core clearly reveals that starting from 3 ka BP and extending back to ~15 ka BP, the dust inputs to the Devon ice cap were far greater than they are today, peaking in a maximum Sc concentration of 38.1 pg/g around 12,350 years BP (Figure 2b) and corresponding to the zenith of the YD event.

[23] Scandium, a conservative lithogenic reference element, is commonly used as a surrogate for atmospheric soil dust [*Shotyk et al.*, 2001; *Krachler et al.*, 2005b]. Scandium is a useful reference element because it is uniformly distributed within the UCC and has effectively no industrial uses [*Wedepohl*, 1995; *Emsley*, 2001]. Only 50 kg Sc are consumed annually worldwide, thus anthropogenic emissions of the element to the atmosphere are negligible. Even intensified coal burning during the Industrial Revolution and thereafter did not elevate measurably Sc concentrations in Arctic ice and snow [*Krachler et al.*, 2005b]. In addition, Sc behaves conservatively during chemical weathering and, relative to Al, is neither significantly enriched nor depleted in atmospheric mineral dusts and soils, relative to crustal rocks. A detailed geochemical discussion on the preference of using Sc over other lithogenic reference elements in environmental studies can be found elsewhere [*Shotyk et al.*, 2001].

[24] The distinct dust inputs corresponding to the YD around 12–14 ka BP (Figures 2a and 2b) hamper the establishment of a single, site-specific natural background level of either Sb or Sc. However, rather than considering the "natural background" concentrations of individual elements, the Sb/Sc ratio should be a more sensitive and robust indicator for background characterization. As a first step, we consider samples older than 3200 years which are known from other studies to predate the onset of global atmospheric Pb contamination [*Shotyk et al.*, 1998]. Averaging the Sb/

Sc ratios of the oldest 17 ice samples (3291–15,876 years BP) yields a value of 0.13 ± 0.07 (median: 0.11; range: 0.03 to 0.28) (Figure 2c). Even though large variations are seen in the ice core during this period (Figures 2a and 2b), the Sb/Sc ratio exhibited only very small variations during the period of enhanced dust deposition during the YD event (Figure 2b) indicating that Sb deposited during this period by far originates primarily from lithogenic sources. Having established a relatively constant and low Sb/Sc ratio using the 17 oldest ice samples covering a period of more than 12,500 years, the mean ratio of 0.13 is now used as the natural Sb/Sc background ratio to calculate absolute values of modern Sb enrichments in the most recent ice samples.

[25] Plotting the Sb/Sc ratio allows the Sb concentrations to be corrected for variations in soil dust inputs (Figure 2c). Even though the greatest concentrations of both elements are found in ancient ice samples dating back several thousand years and reaching their maxima during the YD, the Sb/Sc ratio is remarkably constant (0.13 ± 0.07) until approximately 1000 years ago (Figure 2c).

### 3.4. Comparison With Peat Bog Archives

[26] Ombrotrophic peat bogs have been successfully exploited as archives of environmental change and have helped to elucidate the fate of Sb in the environment [*Shotyk et al.*, 2002, 2004, 2005a, 2005b; *Steinnes and Njåstad*, 1995; *Schell*, 1986; *Cloy et al.*, 2005]. The well-studied bog at Etang de la Gruère (EGR), Jura Mountains, Switzerland, for example, yielded the lowest Sb and Sc concentrations in peats dating from circa 6000 to 9000 calendar years BP [*Shotyk et al.*, 2004]. Antimony and Sc concentrations averaged 8 ± 3 ng/g and 76 ± 16 ng/g, respectively, during this period when the vegetation cover was at its greatest extent and the fluxes of atmospheric soil dust were at their lowest [*Shotyk et al.*, 2004]. Despite the fact that natural background concentrations of both Sb and Sc in the peat samples from EGR are roughly 5 orders of magnitudes higher than in ancient Arctic ice, the natural Sb/Sc background ratio of 0.13 ± 0.07 established in the Canadian Arctic is remarkably similar to the natural background ratio of Sb/Sc (0.09 ± 0.03, $n = 8$) obtained in peats in Switzerland dating from the Holocene climate optimum [*Shotyk et al.*, 2004].

### 3.5. Elevated Sb/Sc During Greek, Roman, and Medieval Times

[27] Significant pollution of the Arctic, reflected by increasing Sb concentrations in the deposited snow layers, started about 800–1000 years ago as can be depicted from the running median in the insert of Figure 2a. Because of the relatively large variability of Sb concentrations of even neighbored samples and the coarse subsampling of the ice core, a more precise estimate of the rise of anthropogenic Sb cannot be assessed from the current data set. Anthropogenic activities, however, such as medieval silver mining in Germany and the impact of Roman lead smelting, both releasing substantial amounts of Sb to the atmosphere, are clearly reflected by the current Sb chronology (Figure 2a). Despite the fact that mining in the Harz Mountains of Germany started as early as the early Iron Age (800–400 years BC), mining activities peaked during the High Middle Ages (1000–1250 AD): Evidence of these impacts are found not only in European peat bog archives [*Monna et al.*, 2000; *Hettwer et al.*, 2003; *Deicke et al.*, 2006], but also in the Arctic ice core from Devon Island (Figure 2c).

[28] As calcophile elements, Sb and Pb frequently occur together in sulphidic minerals and thus are largely emitted simultaneously during smelting and mining activities. The peaks in the Sb and Sb/Sc profiles indicated by vertical arrows in Figures 2a and 2c and labeled M, R, and G/P correspond to periods of significant Pb enrichments and decreasing $^{206}$Pb/$^{207}$Pb ratios [*Zheng et al.*, 2007]: These are periods of intensive lead mining in Europe, namely dating from medieval, Roman, and Greek/Phoenician times. It should be noticed, however, that these events are documented by only a few data points in the present chronology. Even though striking evidence of anthropogenic activities is provided with the relatively small set of samples currently available, one should keep in mind that the main goal of the analysis of these old ice samples was the establishment of natural background levels and their variation with time. To undertake a more detailed study of the impacts of mining and smelting in antiquity, a more detailed subsampling of the ice core would be necessary.

[29] The Sb EF during Roman and Greek/Phoenician times documented by our ice core is supported through previous ice [*Hong et al.*, 1994] and peat [*Shotyk et al.*, 1998] core studies revealing substantial Pb contamination during these periods. Additional evidence of Sb contamination during the Roman and medieval period is provided through analyses of peat samples from bogs from EGR [*Shotyk et al.*, 2004], Scotland [*Shotyk et al.*, 2004; *Cloy et al.*, 2005], and the Faroe Islands [*Shotyk et al.*, 2005a].

### 3.6. Elevated Sb/Sc During Recent Decades

[30] The trend of increasing Sb/Sc ratios depicted in Figure 2c starting about one millennium ago peaks in the 1960s reflecting the growing importance of anthropogenic activities such as coal burning, mining, and smelting of lead and copper ores during the first half of the last century [*Krachler et al.*, 2005b]. The use of dedicated filter technologies in coal-fired power plants helped to cut the Sb/Sc ratio into half during the late 1960s, before increasing again by 50% during the last 3 decades. It appears to be the increasing modern uses of Sb in a large variety of industrial applications [*Krachler et al.*, 2005b] that continue to promote the increasing extent of Sb contamination in Arctic aerosols during recent decades.

### 3.7. Natural Enrichments of Sb in Aerosols, Relative to Upper Continental Crust

[31] Given the fact that the natural Sb/Sc ratio reported for soil of ~0.14 [*Bowen*, 1979] is comparable to that established in peat samples in central Europe dating from circa 6000 to 9000 calendar years BP as well as to corresponding values found in ancient ice samples from the Canadian Arctic dating from 3291–15,876 years BP (Figure 3), our findings imply that the natural background ratio of Sb/Sc (circa 1:10) has a broader validity. Corresponding values for the upper continental crust (~0.04) and the lower continen-

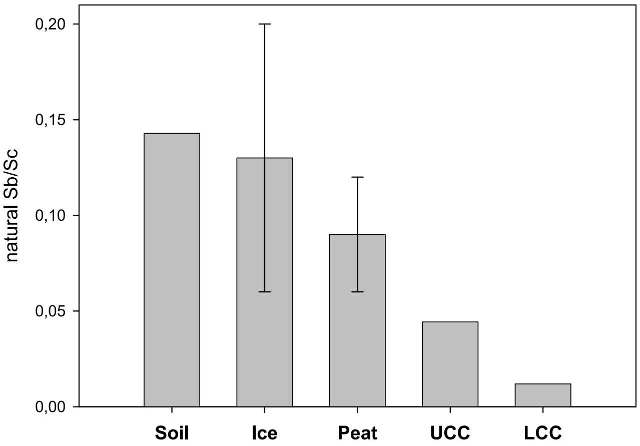

**Figure 3.** Natural Sb/Sc ratios of different environmental compartments. Values are taken from *Bowen* [1979] for soil, *Shotyk et al.* [2004] for ancient peat, and *Wedepohl* [1995] for the upper and lower continental crust, respectively. Error bars of the Sb/sc ratio in ancient ice and peat reflect the natural variation of Sb/Sc background values. No variability is reported for the Sb/Sc ratio in soil [*Bowen*, 1979] and the continental crust [*Wedepohl*, 1995].

tal crust (~0.01) are approximately 2.5 to 10 times lower than our natural Sb/Sc background ratios established using ancient ice and peat and clearly show the limitations of employing crustal values for calculating elemental enrichment factors (Figure 3). In other words, using the continental crust as reference level would underestimate the natural Sb/Sc ratio by up to 1 order of magnitude, thereby overestimating Sb EF by a corresponding amount. The relatively constant "natural background" Sb/Sc ratio found in the ice core from Devon Island (Figure 2c) suggests that Sb inputs were dominated by atmospheric soil dust. The similar values for Sb/Sc obtained from the ice core and by *Bowen* [1979] for soils is a further argument that dust particles derived from soils dominated the natural flows of Sb to the atmosphere.

### 3.8. Estimating the Anthropogenic Sb Component in the Ice Core

[32] Natural Sb immissions ($Sb_{natural}$) recorded in the ice core have been calculated as

$$[Sb]_{natural} = [Sc]_{sample} \times (Sb/Sc)_{background} \tag{1}$$

where $[Sc]_{sample}$ refers to the Sc concentration in the ice samples and $(Sb/Sc)_{background}$ to the natural background ratio of 0.13. "Anthropogenic" or "excess" Sb was calculated as the difference between total Sb and natural Sb (Figure 4). Using this approach, excess Sb appeared during Greek/Phoenician, Roman, and medieval times. Additionally, this figure emphasizes the predominance of natural Sb in ice samples older than approximately 3000 years, confirming our previous statement (Figure 2c). The insert in Figure 4, highlighting the smoothed trend of excess Sb for the last 3000 years, clearly shows the start of the distinct rise of excess Sb about 900 years ago, when atmospheric Sb contamination began a progressive increase. Thus this graph indicates that excess Sb dominates the ice core record for nearly 1000 years. Thus Sb is not only a modern, global environmental contaminant [*Shotyk et al.*, 2005c], but one with a very long history indeed.

### 3.9. Natural Rates of Atmospheric Sb Deposition

[33] The snow accumulation rate, density, and the Sb concentration of the individual snow samples of the snow pit allow the rates of Sb deposited at the snow surface to be calculated as

$$\begin{aligned} &\text{Sb accumulation rate } (\text{ng m}^{-2}\ \text{a}^{-1}) \\ &\quad = \text{density } (\text{g cm}^{-3}) \times \text{Sb concentration}(\text{pg g}^{-1}) \\ &\qquad \times \text{snow accumulation rate } (\text{cm a}^{-1}) \times 10 \end{aligned} \tag{2}$$

[34] Considering the 17 ice samples (1302–10,588 years BP) that have been used to establish natural background levels of Sb, a flux of 0.7 ± 0.5 (median: 0.5) $ng/m^2/a$ Sb has been calculated. During the Holocene climate optimum (5320–8020 $^{14}C$ years BP) the natural Sb flux recorded in the Swiss peat bog at EGR amounted to 350 $ng/m^2/a$ [*Shotyk et al.*, 2004]. This record provided the first natural background rate of atmospheric Sb deposition not only for this part of Europe, but worldwide. The background Sb flux on Devon Island therefore is as much as 500 times lower than that established in central Europe [*Shotyk et al.*, 2004]. This observation is reasonable and in good agreement with the general observation that atmospheric trace metal deposition rates decrease with increasing latitude.

### 3.10. Modern Rates of Atmospheric Sb Deposition

[35] For the period 1994–2004 the Sb accumulation rate averages 340 ± 270 $ng/m^2/a$, ranging from 20 to 1240 $ng/m^2/a$

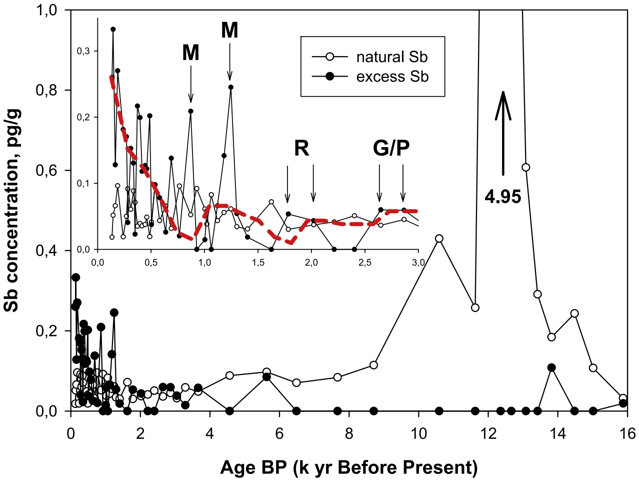

**Figure 4.** Natural and excess Sb in the Devon 1999 ice core indicating the predominance of natural Sb over extended periods and the distinct rise of excess Sb starting approximately 900 years ago. Dashed line in the insert provides the smoothed trend of excess Sb using the running median for the last 3000 years.

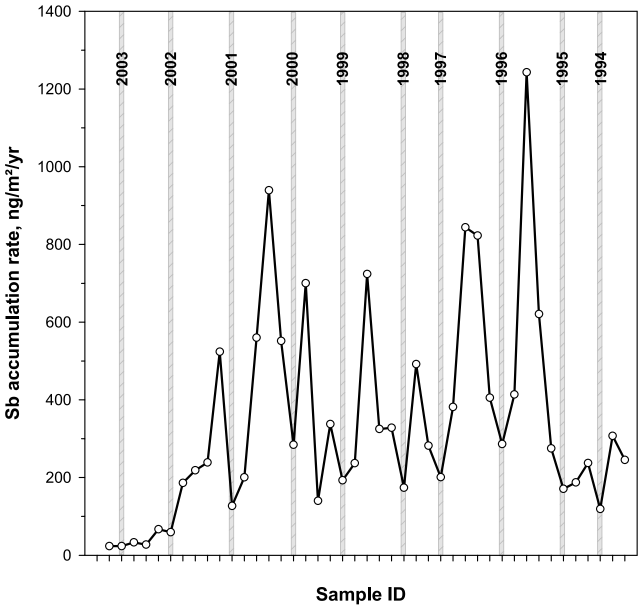

**Figure 5.** Antimony accumulation rates on Devon Island during 1994–2003 reveal increased deposition rates during winter periods when air masses reaching the Arctic predominantly originate from Eurasia. Gray bars indicate the summer of the respective year.

(Figure 5). Because of the seasonal resolution of the snow pit data, summer and winter deposition can be clearly separated. Similar to the trend already observed for Sb concentrations [*Krachler et al.*, 2005b], distinctly more Sb is deposited during the winter when the air masses reaching the Canadian Arctic predominantly originate from Eurasia. In that context it is worth mentioning that China satisfies 88% of the current annual world Sb production. Although the flux calculations suggest a tremendous decrease in the Sb fluxes since 2002, this should be viewed critically because of the difficulty in reliably establishing the density of the snow surface. The apparent decrease in atmospheric Sb deposition rates during the past few years therefore requires independent evaluation and assessment.

[36] Considering the natural background flux at Devon Island of 0.7 ng/m$^2$/a and the current average flux of 340 ng/m$^2$/a (1994–2004) reveals that more than 99.8% of the Sb deposited in the Arctic currently originates from anthropogenic sources.

[37] Among the natural emission sources of Sb to the Arctic, accounting for ~0.2% of total Sb depositions, quiescent degassing of volcanoes might contribute significantly to the Sb inventory. Calculated Sb emissions of the Stromboli volcano, Italy, for example, are ~0.5 tons/year [*Allard et al.*, 2000]. Considering that ~1600 tons Sb are emitted through anthropogenic activities each year worldwide [*Pacyna and Pacyna*, 2001], however, the "natural" Sb emissions from Stromboli account for ~0.03% of current annual anthropogenic Sb emissions.

## 3.11. Reassessment of Published Data for Sb EF in Modern Aerosols

[38] A recent Japanese study reported Sb EF as high as ~21,000 in aerosols with diameters <2 $\mu$m collected between 1994 and 2004 [*Furuta et al.*, 2005]. This Sb EF was calculated using Al as reference element and the UCC as reference level and thus might be too high by a factor of ~2.5 (i.e., the difference between natural background concentrations of ice/peat/soil and UCC; see above). However, the "corrected" Sb EF of ~8400 is still extremely high and points to the fact that because of the extended use of $Sb_2S_3$ as a lubricant for brake linings for automobiles, Sb is the single most highly enriched element in urban environments today [*Gómez et al.*, 2005; *Weckwerth*, 2001]. The size-classified Sb EF of the recent Japanese study [*Furuta et al.*,

**Table 2.** Concentrations of Sb and Sc, Sb/Sc Ratios, Sb Enrichment Factors of Atmospheric Aerosols Collected at Different Regions of the Globe During the Last Decades[a]

| Location | Remarks | Sb | Sc | Sb/Sc | Sb EF Original | Sb EF Recalculated[b] | Year | Reference |
|---|---|---|---|---|---|---|---|---|
| Wraymires, United Kingdom | 1 year | 1.6 | 0.059$^{c}$ | 27.1$^{c}$ | -$^{d}$ | 205 | 1973 | *Peirson et al.* [1973] |
| Heidelberg, Germany | urban | 5100 | 500 | 10.2 | 3300$^{e}$ | 79 | 1973 | *Bogen* [1973] |
| South Pole | | 1700 | 125 | 13.6 | 1300$^{f}$ | 105 | 1974 | *Zoller et al.* [1974] |
| Heimaey (volcano), Iceland | site A | 470 | 470 | 1.0 | 97$^{f}$ | 8 | 1975 | *Mroz and Zoller* [1975] |
| | site B | 530 | 410 | 1.3 | 115$^{f}$ | 10 | 1975 | |
| North Atlantic atmosphere | | 110 | 35 | 3.1 | 250$^{f}$ | 24 | 1979 | *Buat-Menard and Chesselet* [1979] |
| Antarctica | winter | 2.1 | 0.037 | 56.7 | -$^{d}$ | 436 | 1981 | *Cunningham and Zoller* [1981] |
| | summer | 0.45 | 0.18 | 2.5 | -$^{d}$ | 19 | 1981 | |
| Ny Ålesund, Spitsbergen | winter | 92 | 4.3 | 21.4 | -$^{d}$ | 165 | 1989 | *Maenhaut et al.* [1989] |
| | summer | 2.4 | 1.2 | 2.0 | -$^{d}$ | 15 | 1989 | |
| Vardø, Norway | winter | 120 | 3.0 | 40 | -$^{d}$ | 308 | 1989 | *Maenhaut et al.* [1989] |
| | summer | 12.6 | 0.34 | 37.1 | -$^{d}$ | 285 | 1989 | |
| Tokyo, Japan | <2 $\mu$m | 4930 | -$^{c}$ | - | 20,900$^{f}$ | | 2005 | *Furuta et al.* [2005] |
| | 2–11 $\mu$m | 2290 | -$^{c}$ | - | 4330$^{f}$ | | | |
| | >11 $\mu$m | 227 | -$^{c}$ | - | 634$^{f}$ | | | |

[a] Units for Sb and Sc are pg/m$^3$. EF: enrichment factors.

[b] This study.

[c] Concentrations are given as ng/kg.

[d] No numerical values available.

[e] Sb EF were calculated using Na as reference element and the Earth crust as reference level.

[f] Sb EF were calculated using Al as reference element and the Earth crust as reference level.

2005], yielding the highest values for the smallest particle size fraction, also highlights the substantial dependence of Sb EF on particle size (Table 2).

[39] Aerosols from remote as well as urban areas from all over the globe have been investigated for Sb and partially for Sb EF during the last decades (Table 2). Similar constraints on the validity of the Sb EF need to be considered for other previous studies (Table 2) including the extensive compilation of Sb EF in aerosols from 64 studies collected around the world [*Rahn*, 1979].

[40] It is worth noting here that reported Sb/Sc ratios range from circa 1 in atmospheric particulate matter after a volcanic eruption [*Mroz and Zoller*, 1975] to ∼60 in aerosols collected during the winter in Antarctica [*Cunningham and Zoller*, 1981]. These Sb/Sc ratios should be reevaluated using the background Sb/Sc ratio (0.13) reported here.

### 3.12. Sb EF in Arctic Snow and Ice

[41] In the past, the absence of site-specific natural background values meant that Sb EF for snow and ice had to be calculated using the continental crust, soil, or ancient peat samples as reference level [*Krachler et al.*, 2005b]. Even though a rough estimate of the Sb EF could be thus obtained, actual values varied by ∼7.5 times between the highest and lowest Sb EF depending on the reference level employed [*Krachler et al.*, 2005b].

[42] Considering the natural background ratio of Sb/Sc ($([\mathrm{Sb}]/[\mathrm{Sc}])_{\mathrm{background}}$) of 0.13, enrichment factors (EF) of Sb for the most recent ice samples can be recalculated as

$$\mathrm{Sb\ EF} = ([\mathrm{Sb}]/[\mathrm{Sc}])_{\mathrm{sample}}/([\mathrm{Sb}]/[\mathrm{Sc}])_{\mathrm{background}} \quad (3)$$

where [Sb] and [Sc] refer to the corresponding elemental concentrations in the ice samples. For the period 1994–2004 the median value of Sb EF of 45 snow samples from a 5-m snow pit collected in 2004 on Devon Island close to the site where the ice cores were drilled [*Krachler et al.*, 2005b] amounts to 25 with a range of 8 to 121. Even using the background value of Sb/Sc ratio of 0.13, the Sb EF data for the recent snow samples from Devon Island indicate that modern aerosols reaching the Arctic are highly contaminated with Sb.

[43] Using the Sb/Sc ratios published earlier (Table 2) and the background Sb/Sc of 0.13 from the Devon 1999 ice core, we calculated the following Sb EF for Antarctica: ∼440 and ∼20 for winter and summer, respectively [*Cunningham and Zoller*, 1981]. Similarly, for the aerosol samples collected at Ny Ålesund, Spitsbergen, we calculate Sb EF of 165 and 15, respectively [*Maenhaut et al.*, 1989]. Both of these studies [*Cunningham and Zoller*, 1981; *Maenhaut et al.*, 1989], as well as the data shown in Figure 5, highlight the importance of seasonal variations in air mass transport and consequently Sb deposition rates.

### 3.13. Antimony: Global Atmospheric Contaminant

[44] To date, as much as 142,000 tons of Sb are produced annually worldwide [*Shotyk et al.*, 2005b]. Modern uses of Sb include the manufacture of flame retardants (2/3 of worldwide production) for plastics and textiles and the production of polyester [*Thiede*, 2004] including PET bottles and fleece garments. Incineration of these materials yields aerosols with particle diameters below 1 $\mu$m which can easily make their way from industrialized countries to the most remote regions of the globe such as the Arctic, for example [*Nriagu*, 1990; *Krachler et al.*, 2005b].

[45] The extensive compilation of Sb EF in aerosols from 64 studies worldwide by *Rahn* [1979] reported a median Sb EF of ∼2000 (range: 3.8–24,000) indicating widespread contamination with Sb. Even if this Sb EF is corrected using the background Sb/Sc of 0.13 instead of the crustal value, this is still a tremendous Sb enrichment. Moreover, global annual Sb production has doubled during the last 3 decades, with the Sb EF in Arctic snow and ice having increased 50% during this period [*Krachler et al.*, 2005b]. Antimony found in recent snow and ice layers in the Arctic are derived from long-range atmospheric transport.

[46] Despite the increasing Sb enrichment during recent times, there is no consensus on the relative importance of anthropogenic versus natural sources of Sb to the global atmosphere. *Pacyna and Pacyna* [2001] have suggested that the ratio of anthropogenic/natural to the global atmosphere is circa 1:1. In contrast, *Lantzy and Mackenzie* [1979] had suggested a ratio of 40:1. Here the snow pit from Devon Island shows Sb accumulation rates of ∼340 ng/m$^2$/a from 1994 to 2004. In contrast, the natural background flux amounts to 0.7 ng/m$^2$/a. On the basis of these data the natural inputs to the atmosphere in the Northern Hemisphere are dwarfed by the anthropogenic ones.

[47] In summary, like Pb, Sb should be considered a global atmospheric contaminant. The consequences of increasing Sb emissions and Sb EF for human and ecosystem health are unclear. Therefore further studies are warranted to elucidate the fate of Sb in the environment as well as the impact of anthropogenic activities on the geochemical cycle of this emerging element [*Shotyk et al.*, 2005c].

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