GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 23, GB3011, doi:10.1029/2009GB003471, 2009

Global atmospheric As and Bi contamination preserved in 3000 year old Arctic ice

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Received 19 January 2009; revised 13 May 2009; accepted 29 May 2009; published 11 August 2009.

[1] Despite its growing environmental significance, there are no detailed historical records of atmospheric As deposition for the Northern Hemisphere. Having overcome the severe analytical challenges in measuring As in polar ice, and using an Arctic ice core representing ∼16 ka of snow accumulation, we present a complete record of atmospheric As deposition for this period which reveals significant contamination beginning 3000 years ago. While Pb enrichments unequivocally increased threefold above natural background levels during Greek/Phoenician, Roman, and Medieval periods, As is elevated by a factor of 5. Previous studies showed that these periods are not only enriched in Pb but also Sb: here we show significant contamination not only by As but also Bi, Cu, and Zn. The Pb isotope data reveal declines in the ratio $^{206}Pb/^{207}Pb$ which reflects the introduction Pb-bearing aerosols from smelting of lead ores, but the metallurgy of copper ores must also have played a role. Taken together, these findings demonstrate a deeper, broader environmental significance of sulphide ore processing in antiquity, defining the origins of global atmospheric contamination for a suite of related elements and providing a new perspective on the start of the Anthropocene. In addition, the data indicate that by far the greatest As concentrations in the ice core are recorded during the Younger Dryas cold climate event centered around 12 ka B.P., demonstrating the strong link between global climate change and the atmospheric cycling of trace elements.

Citation: Krachler, M., J. Zheng, D. Fisher, and W. Shotyk (2009), Global atmospheric As and Bi contamination preserved in 3000 year old Arctic ice, *Global Biogeochem. Cycles*, *23*, GB3011, doi:10.1029/2009GB003471.

1. Introduction

[2] Since the beginning of the Industrial Period, human activities have begun to affect the geochemical cycles of potentially toxic trace elements on a global scale [*Fyfe*, 1981], with profound implications for the health of the Biosphere [*Nriagu*, 1990]. Lead in particular has received inordinate attention, mainly because of the period of massive pollution caused by the extensive use of gasoline additives during the 20th century, but in fact atmospheric Pb contamination extends back thousands of years, and is very well preserved in ice cores from Greenland [*Boutron et al.*, 1994; *Hong et al.*, 1994; *Rosman et al.*, 1997; *McConnell et al.*, 2002] and the Canadian Arctic [*Shotyk et al.*, 2005; *Zheng et al.*, 2007]. Atmospheric Pb pollution in Antiquity was caused by the smelting of lead sulphide ores, but these deposits are rarely monomineralic, and commonly associated with a suite a chalcophile trace metals such as Cu, Zn, Ag, Cd, Sb, Tl, and Pb, as well as As [*Wedepohl*, 1969].

[3] Arsenic is one of the most toxic trace elements, and with some As species known to be carcinogenic, the distribution and fate of As in the environment is the subject of growing scientific interest [*Nriagu*, 1994]. The enrichment of As in groundwaters is causing much concern in many regions of the world, most notably in Bangladesh, but also Argentina, Germany, Mexico, Vietnam, Taiwan, and the United States where As concentrations are sometimes well above the WHO drinking water guideline value [*Nordstrom*, 2002]. Although the elevated As concentrations in these cases are entirely due to natural processes such as the weathering of As-bearing minerals, they have nevertheless highlighted the gaps which exist in our understanding of the geochemical cycle of As [*Matschullat*, 2000].

[4] The relative importance of natural versus anthropogenic emissions of As to the atmosphere are very poorly constrained. Although this past decade has seen many published reconstructions of atmospheric Pb deposition using peat cores from ombrotrophic (i.e., rain fed) bogs, for example, there are very few comparable studies of As. Arsenic was studied in an age-dated peat core from a Swiss bog in the Jura Mountains, and massive enrichments of As were seen in the peat samples dating from the Industrial Period [*Shotyk et al.*, 1996].

[5] Although As has been measured in selected ice samples from alpine regions of South America [*Hong et al.*, 2004] as well as the East Antarctic ice sheet [*Gabrielli et al.*, 2005a], and a superficial interpretation of these data has begun, a detailed reconstruction of atmospheric As

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0886-6236/09/2009GB003471

deposition in the Northern Hemisphere is altogether lacking. The main goal of this study was to fill this gap, and to reconstruct the changing rates and sources of atmospheric As deposition, in a remote region of the Canadian Arctic, for the past 16,000 years. Using Sc as a conservative, lithogenic reference element, we have determined the natural "background" As/Sc ratio in ice samples predating the onset of mining and metallurgy, to allow us to quantify the extent to which human activities have impacted the As cycle. Bismuth, also a chalcophile metal commonly enriched in metal sulphides, as well as Cu and Zn, are included for comparison. These data are compared with the corresponding data for Sb [*Krachler et al.*, 2008a] and Pb [*Zheng et al.*, 2007], as well as the isotopic composition of Pb [*Zheng et al.*, 2007], expressed as the ratio $^{206}Pb/^{207}Pb$, to help identify the source of the As enrichments.

2. Materials and Methods

2.1. Collection of Ice Core and Sample Decontamination

[6] A 170.6 m long ice core was drilled in 1999 on Devon ice cap (Devon Island; 75°N, 82°W; 1860 m asl) (Figure 1) representing precipitation from 15,876 B.P. – A.D. 1870. All samples were shipped back frozen to the Geological Survey of Canada (GSC) laboratories in Ottawa and stored at $-20°C$ before processing and analysis. The data set presented here contains 57 individual ice samples. As such, these samples do not represent a continuous record of atmospheric deposition, but correspond to specific time intervals. The ice core sections were mechanically decontaminated using clean lab protocols [*Zheng et al.*, 2006]. All samples were acidified with high-purity nitric acid while they melted and stored at $-20°C$ in precleaned high-density polyethylene (HDPE) bottles until analyses by ICP-SMS.

[7] Considering the combined inaccuracy resulting from sample lengths, electric conductivity measurements and the nonlinearity of the age-depth relationship, the total dating error of the time scale is estimated to be less than 2.5% for the first 200 years, approximately 3% for the time period between 200 B.P. and 1200 B.P., and 10% for the time period from 1200 B.P. to 8000 B.P. [*Zheng et al.*, 2007]. Details of the entire procedures including age assignment are given elsewhere [*Krachler et al.*, 2004a, 2004b, 2005; *Zheng et al.*, 2006, 2007].

2.2. Laboratories and Instrumentation

[8] The clean lab procedures applied throughout this study have been described in detail earlier [*Zheng et al.*, 2006]. Briefly, sample handling and the preparation of all standards were performed in clean rooms under laminar flow clean air benches of at least class 100 to minimize the potential risk of contamination. Decontamination of the ice and snow samples was carried out in clean air benches of class 100 at the GSC in a certified cold clean room of class 1000 (Ottawa) while melting, acidification and bottling was performed in a class 10 bench hosted in a class 100 clean room (Heidelberg). All HDPE bottles and PFA vials in contact with the samples were thoroughly cleaned using HNO_3 baths of increasing purity.

[9] All ICP-MS measurements were carried out using an Element 2 ICP-SMS (Thermo Fisher Scientific, Bremen, Germany) equipped with a guard electrode to eliminate secondary discharge in the plasma and to enhance overall sensitivity. A micro volume autosampler (ASX 100, Cetac Technologies, Omaha, Nebraska) and a sample introduction kit comprising a microflow PFA nebulizer connected to a high-efficiency sample introduction system (APEX IR, Elemental Scientific Inc., Omaha, Nebraska) and a sapphire injector tube were employed for the quantification of trace elements in the ice samples. The low flow PFA nebulizer was operated in the self-aspirating mode to exclude the risk of contamination by the peristaltic pump tubing. Further details of the entire analytical protocol can be found elsewhere [*Krachler et al.*, 2004a, 2004b, 2005, 2008a].

2.3. Quality Control

[10] A certified reference material for the determination of trace element concentrations in ice is currently not available. Therefore, the riverine water reference material SLRS-4 from the National Research Council Canada, Ottawa, Canada was analyzed at regular intervals during sample analysis to help assess the accuracy of the trace metal determinations. The experimental values were always in good agreement with either the certified value (As, Cr, Cu, V, Zn) or concentrations (Bi, Sc) established in previous studies [*Krachler et al.*, 2004a, 2005, 2008a].

3. Results and Discussion

3.1. As, Bi, and Sc Concentrations

[11] The lowest concentrations of As and Bi found in the ice core are comparable to the lowest concentrations ever reported for these elements in polar ice [*Tao et al.*, 2001; *Vallelonga et al.*, 2004; *Gabrielli et al.*, 2005b]. The extremely low concentrations encountered in the majority of the samples underscore the importance of exceptional precautions to guard against possible contamination.

[12] The greatest concentrations of both As (90.3 pg/g) and Bi (2.92 pg/g) found in the Devon Island ice core correspond to the Younger Dryas (YD), a well known cold climate event centered around 12,350 years B.P. Both As and Bi concentrations in the ice samples increased approximately 45-fold during this period (Figures 1a and 1c) which is comparable to the increase seen for Sc [*Krachler et al.*, 2008a]. The YD was a thousand year period of lower global temperatures, characterized by reduced vegetation cover, increased exposure of soil surfaces, and elevated concentrations of atmospheric soil dust [*Mayewski et al.*, 1993]. The elevated As and Bi concentrations during the YD, therefore, illustrates the importance of soil dust particles to the atmospheric geochemical cycle of both elements.

[13] The first step involved in understanding the variation in As and Bi concentrations in the ice core, therefore, is to quantify the variation in abundance of soil dust particles derived from the weathering of crustal rocks and supplied to the Arctic by long-range atmospheric transport. Because Sc behaves conservatively during chemical weathering and has no preference for specific mineral phases, it can be conveniently employed as lithogenic reference element, acting as a surrogate for the abundance of atmospheric soil dust

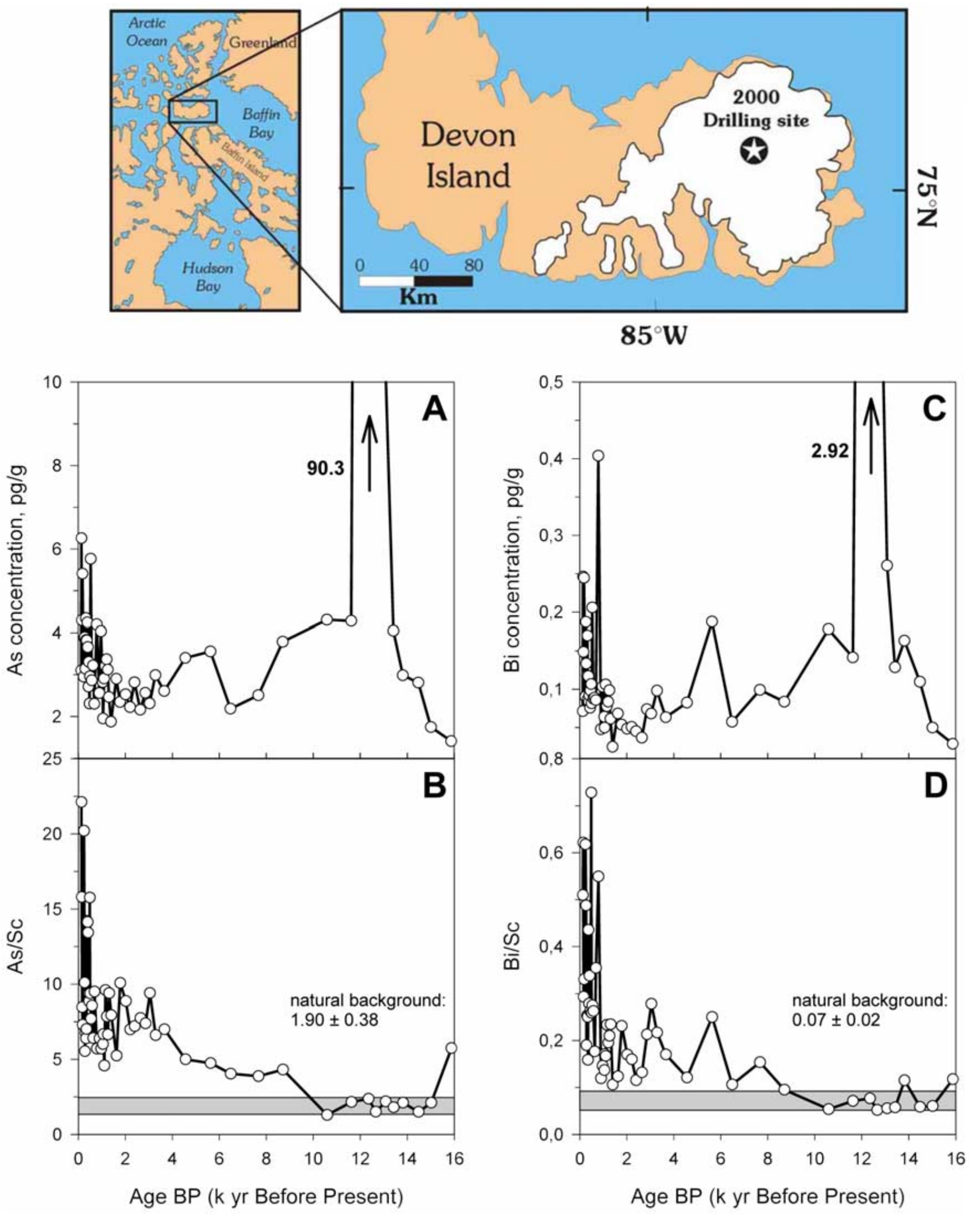

Figure 1. Map of a selected area of the Canadian High Arctic highlighting the Devon Island ice cap (1860 m asl) where the ice core was drilled at 75°N, 82°W in 1999. Chronologies of (a) As and (c) Bi concentrations as well as (b) As/Sc and (d) Bi/Sc ratios during the last 16,000 years as determined in the ice core from Devon Island. The huge peaks seen in Figures 1a and 1c refer to the Younger Dryas (YD) cold climate event centered around 12,350 years B.P., while the peaks dated ~4 ka to 6 ka B.P. refer to the Holocene Climate Optimum. Grey bars in Figures 1b and 1d indicate site-specific natural background ratios.

particles [*Mayewski et al.*, 1993; *Krachler et al.*, 2008a]. In addition, the industrial and commercial uses of this element are so low (global Sc production amounts to 45 kg per year) that the possible importance of anthropogenic contributions of this element can reasonably be ignored. Scandium (Sc) concentrations in all samples ranged from 0.14 to 38.5 pg/g, with a median concentration of 0.45 pg/g [*Krachler et al.*, 2008a].

3.2. As/Sc and Bi/Sc

[14] When the As and Bi concentrations are normalized to those of Sc, the peak corresponding to the YD disappears, indicating that the elevated concentrations of As and Bi during that time were due exclusively to the increased abundance of soil dust particles in the atmosphere (Figures 1b and 1d). This finding illustrates the overwhelming significance of climate-driven changes in the fluxes of soil-derived dusts, not only for the geochemical cycles of these trace elements, but also for Pb [*Zheng et al.*, 2007] and Sb [*Krachler et al.*, 2008a].

3.3. Natural Background As/Sc and Bi/Sc

[15] The lowest As/Sc (1.90 ± 0.38, median: 2.11) and Bi/Sc (0.07 ± 0.02, median: 0.06) ratios were found in the nine ice samples dating between 10,590 and 15,010 years B.P. (gray rectangles in Figures 1b and 1d). These low and relatively constant element/Sc ratios established for this extended period of ~4500 years are assumed to represent the atmospheric dusts which were deposited in the Arctic between the end of the Last Glacial Maximum and the start of the Holocene (10,000 years B.P.). These element ratios provide a baseline against which subsequent enrichments of As and Bi on Devon Island may be compared. According to Wedepohl [*Wedepohl*, 1995], the ratios of As/Sc and Bi/Sc in the Upper Continental Crust (UCC) are 0.286 and 0.0176, respectively. Thus, the natural "background" As/Sc and Bi/Sc ratios determined in the old ice samples from Devon Island exceed the corresponding values for the UCC by approximately 7 and 4 times, respectively. The danger in using element ratios of the UCC to represent aerosols, however, is the lack of consideration of natural trace element enrichments in the fine fraction of soils due to chemical weathering [*Bear*, 1964]. For this reason, it is desirable, and in fact preferable, to use a site-specific natural background metal/Sc ratio as reference level for the calculation of elemental enrichment factors [*Shotyk et al.*, 2002]. Here, the As/Sc and Bi/Sc ratios obtained from the ice core predating the start of the Holocene, are used throughout this study.

3.4. Natural As and Bi Enrichments During the Holocene

[16] In contrast to the "background" As/Sc and Bi/Sc ratios prior to 10,000 B.P., much greater values were found during the Holocene, and especially during recent centuries (Figures 1b and 1d). Elevated M/Sc ratios during the mid-Holocene (~4 to 8 ka B.P.) are also seen for Ag [*Shotyk et al.*, 2002; *Krachler et al.*, 2008b] and Cd [*Shotyk et al.*, 2002; *Zheng*, 2008], and correspond to the Holocene climate optimum: extensive vegetation cover during that time would have diminished the supply of soil dust from some of the dominant source areas, relative to the pre-Holocene period; in addition, the development of increasingly weathered soil profiles, and the enrichment of trace elements in the clay fraction (i.e., < 2 microns), may also have contributed to the elevated M/Sc ratios.

[17] An enrichment of As and Bi during warm periods compared to glacial times was also observed in Antarctica [*Gabrielli et al.*, 2005b] with volcanic quiescent emissions as a likely source. This source had already been discussed in detail by [*Hinkley et al.*, 1999], especially for elements with high vapor pressure of halides (among others As and Bi). While the ratios of Pb:As:Bi in Hawaiian volcanic gases [*Hinkley et al.*, 1999] are approximately 1:1:4, these ratios amount to 1:0.5:0.01 in Devon ice samples from the mid-Holocene. These divergent ratios (especially for Bi) may be related to the complex reactivity and different chemical behavior of these elements influencing their fate along the pathway of emission, long-range transport and deposition.

[18] The natural "background" ratio of As to Sc reported here provides a valuable basis for calculating modern as well as ancient As enrichment factors, whether they are due to natural or anthropogenic processes. Regardless of the cause of the natural enrichment during the mid-Holocene, of particular interest in the present study are the elevated As/Sc and Bi/Sc ratios corresponding to periods of known mining and metallurgical activities.

3.5. Enrichments Due to Anthropogenic Activities

[19] To emphasize these changes, the As/Sc and Bi/Sc ratios for the period corresponding to 4000 to 1000 years ago are shown in Figure 2, along with the corresponding values for Sb/Sc [*Krachler et al.*, 2008a], Pb/Sc [*Zheng et al.*, 2007], and the isotopic composition of Pb [*Zheng et al.*, 2007]. There are three well documented periods of atmospheric Pb contamination dating from this time, namely the Medieval period (M), Roman period (R), and Greek/Phoenician (G/P) times (Figures 2d and 2e). From historical records and archeological investigations [*Patterson*, 1972], as well as retrospective studies using peat cores from ombrotrophic bogs [*Shotyk et al.*, 1998] and arctic ice [*Zheng et al.*, 2007], we know that these episodes are times of extensive lead mining and smelting: this is seen in the elevated Pb/Sc ratios (Figure 2e) as well as the declines in ^{206}Pb/^{207}Pb ratios (Figure 2d) toward less radiogenic values characteristic of lead ores. Enrichments of Sb in ice samples from the Canadian Arctic dating from the Roman Period and Medieval Periods (Figure 2c) is also a consequence of lead mining, as Sb is one of the trace elements most commonly enriched in lead ores [*Nriagu*, 1983]. The data in Figure 2a, however, show that the enrichment of As during these periods, relative to backgrounds values, exceeds those of either Pb or Sb. Mining and smelting of lead sulphide ores by Medieval and ancient civilizations not only began to contaminate the Arctic atmosphere with Pb, therefore, but also released substantial amounts of As and Bi, raising As/Sc and Bi/Sc ratios up to values as much as 5 times above natural background levels. The impact of these mining and smelting activities is also seen in the Cu/Sc and Zn/Sc data (Figures 3a and 3b) as well as the Ag/Sc and Tl/Sc ratios [*Krachler et al.*, 2008b]. Clearly, the environmental impacts of metallurgical activities undertaken by past societies and civilizations have been more

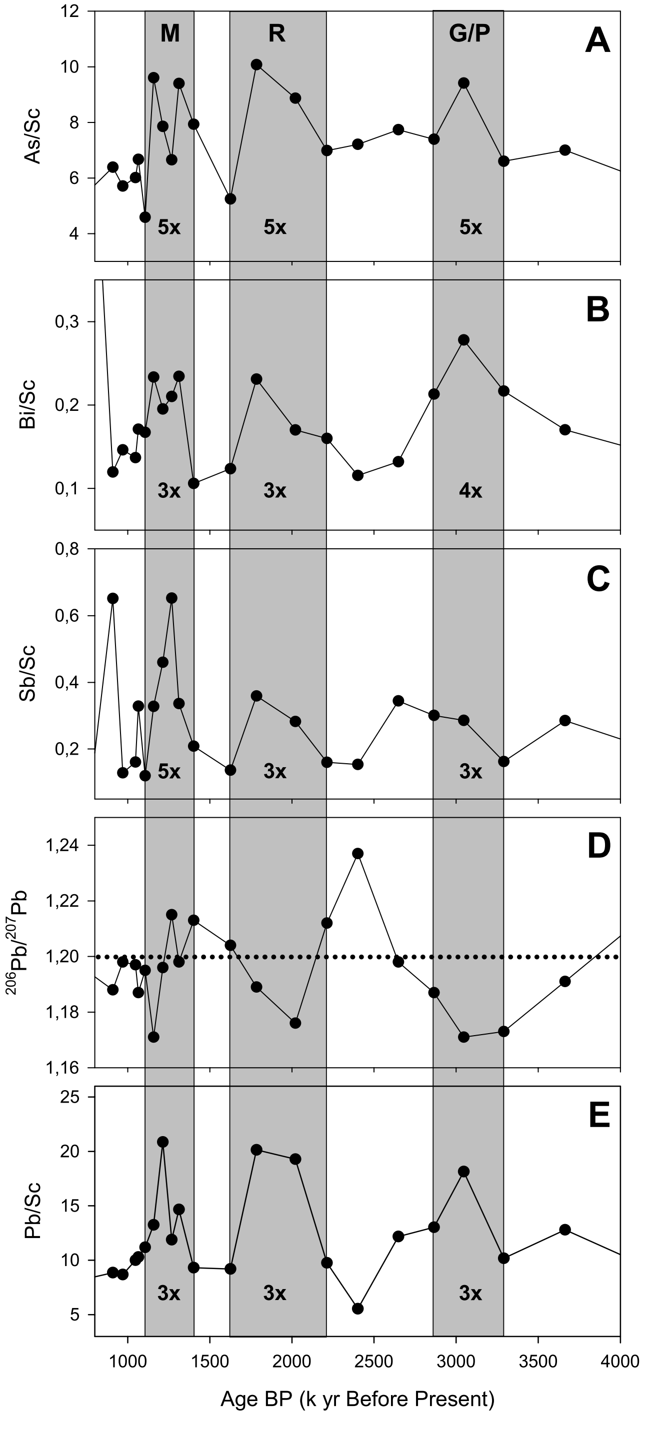

Figure 2. Chronologies of (A) As/Sc, (B) Bi/Sc, (C) Sb/Sc, (D) $^{206}Pb/^{207}Pb$, and (E) Pb/Sc ratios between 800 years B.P. and 4000 years B.P. as determined in ice from Devon Island, Arctic Canada. Grey bars highlight periods of increased atmospheric contamination with As, Bi, Pb, and Sb during Medieval (M), Roman (R), and Greek/Phoenicians (G/P) times. Corresponding numbers indicate the extent of the enrichment of As, Bi, Pb, and Sb above site-specific natural background levels. The dotted horizontal line in Figure 2d marks the $^{206}Pb/^{207}Pb$ ratio of natural aerosols [*Shotyk et al.*, 1998; *Zheng et al.*, 2007].

extensive and had more profound impacts and greater implications than previously believed. In contrast, the chronologies of lithophile elements such as Cr and V, for example, remain largely unaffected by these anthropogenic activities (Figures 3c and 3d).

[20] The chief ores of As are arsenopyrite (AsFeS), realgar (As_4S_4), and orpiment (As_2S_3), but very little As is mined today simply because global demand (~50,000 t/a) is exceeded by As generated as a by-product of other sulphide ores [*Emsley*, 2001].

[21] The association of As with lead sulphides means that lead mining in Antiquity is the obvious source of atmospheric As contamination simply because there was so much of it: during the zenith of the Roman Period, for example, approximately 100,000 tons of lead were produced annually [*Settle and Patterson*, 1980]. But As is also associated with copper sulphides, and copper mining was also very important in ancient times, with 500,000 tons of Cu produced between 2000 and 700 BC, along with 1,000,000 tons of Pb [*Patterson*, 1972]. Copper sulphide ores not only may be rich in As, but also Sb and Bi. Tetrahedrite, $(Cu, Fe)_{12}Sb_4S_{13}$, for example, is mainly a copper ore, but Sb is an important by-product [*Emsley*, 2001]. The main ore minerals of Sb and Bi are stibnite, Sb_2S_3 and bismuthinite, Bi_2S_3, respectively. However, a considerable contribution to Sb production today is from Cu refining, and Bi from both Cu and Pb refining [*Emsley*, 2001]. Smelting of lead and copper ores in Antiquity, therefore, would not only have released Pb (and Cu) to the atmosphere, but also As, Bi, Sb, and other chalcophile elements.

[22] Chalcophile elements received their appellation from Goldschmidt [*Goldschmidt*, 1954] because they are depleted from the silicate crust, but enriched in sulphide minerals, relative to their abundance in the bulk Earth. Thus, their abundance in the UCC is low and, with the exception of Zn (52 ppm), Pb (17 ppm), and Cu (14 ppm), below 1 ppm: Ag, 0.06, Bi, 0.12, Cd, 0.10, Sb, 0.31, Tl, 0.75 [*Wedepohl*, 1995]. Atmospheric soil dust particles derived from the weathering of crustal rocks, therefore, are expected to contain low concentrations of all of these elements. In contrast, the abundance of these elements in sulphide ores is many orders of magnitude greater. Consider the case of Ag which has always been derived almost exclusively from smelting lead ores [*Nriagu*, 1985]. Silver occurs as microcrystals of silver sulphide disseminated within macrocrystals of lead sulphide [*Patterson*, 1972], and the concentration of Ag in lead sulphide ores can easily exceed its abundance in crustal rocks by 10^5 to 10^6 times. Smelting of metal sulphide ores, therefore, can have a dramatic effect on the concentration of chalcophile elements in atmospheric aerosols, relative to their abundance in soil-derived particles.

[23] The high combustion temperatures required to smelt ores generate fine aerosols, with all of the chalcophile elements forming aerosols with median diameters below 1 micron [*Nriagu*, 1990]; aerosols of this size typically have an atmospheric residence time of several days to one week [*Nriagu*, 1990], and are therefore capable of long-range atmospheric transport. Smelting of sulphide ores by ancient European civilizations, therefore, created the onset of

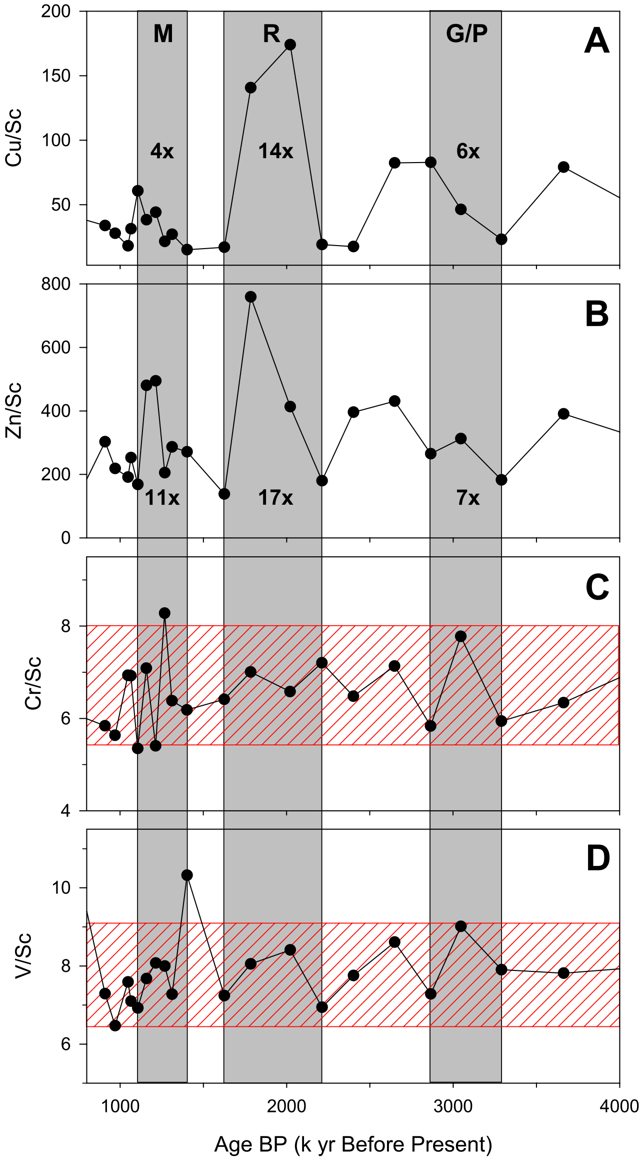

Figure 3. Chronologies of (A) Cu/Sc, (B) Zn/Sc, (C) Cr/Sc, (D) V/Sc ratios between 800 years B.P. and 4000 years B.P. as determined in ice from Devon Island, Arctic Canada. Grey bars highlight periods of increased atmospheric contamination with chalcophile elements due to metallurgical activities during Medieval (M), Roman (R), and Greek/Phoenicians (G/P) times. Corresponding numbers in Figures 3a and 3b indicate the extent of the enrichment of Cu and Zn above site-specific natural background levels. The hatched areas in Figures 3c and 3d highlight the site-specific natural background levels of Cr and V, respectively. In contrast to Cu and Zn, Cr and V are not enriched at all during periods of metal sulphide ore processing.

atmospheric contamination throughout the Northern Hemisphere, even reaching the most remote areas of the Canadian Arctic more than 5000 kilometers away. Differences in the abundance and fate of the chalcophile elements during combustion, atmospheric transport, and deposition, may give rise to differences in the extent of enrichment in Arctic snow and ice, relative to background values. However, all of the chalcophile elements measured in the ice core from Devon Island (Ag, As, Bi, Cd, Cu, Pb, Sb, Tl, and Zn) reveal significant responses to human activities. This fact needs to be considered not only when modern enrichments of trace metals in aerosols are being interpreted, but also in any discussions of the dawn of the Anthropocene [*Zalasiewicz et al.*, 2008].

[24] **Acknowledgments.** This work was funded by the European Commission, the University of Heidelberg, and the Enhancing Resilience in a Changing Climate (ERCC) Program of Earth Science Sector, Natural Resources Canada.

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