GEOPHYSICAL RESEARCH LETTERS, VOL. 32, L21814, doi:10.1029/2005GL023860, 2005

Predominance of industrial Pb in recent snow (1994–2004) and ice (1842–1996) from Devon Island, Arctic Canada

William Shotyk,[1] Jiancheng Zheng,[1,2] Michael Krachler,[1] Christian Zdanowicz,[2]
Roy Koerner,[2] and David Fisher[2]

Received 20 June 2005; revised 22 September 2005; accepted 5 October 2005; published 12 November 2005.

[1] Atmospheric Pb contamination was studied using snow and ice from the Canadian arctic. Forty-five samples representing the past ten years of snow accumulation on Devon Island contain an average of 45.2 pg/g of Pb but only 0.43 pg/g of Sc. The average ratio of Pb to Sc (105) is far greater than that of soil-derived dust particles (in the range 1 to 5) which indicates that ca. 95 to 99% of recent Pb is anthropogenic. Isotopic analyses (^{206}Pb, ^{207}Pb, ^{208}Pb) confirm that anthropogenic sources continue to dominate atmospheric Pb inputs. Unlike snow from Greenland which receives Pb predominantly from the U.S. (^{206}Pb/^{207}Pb ≈ 1.2), snow from Devon Island is less radiogenic (^{206}Pb/^{207}Pb ≈ 1.15). There are pronounced seasonal variations, and the snow samples containing the greatest Pb enrichments are from winter when the Arctic is dominated by air masses originating in Eurasia. While the elimination of gasoline lead additives in Europe, North America and Japan has helped to reduce Pb emissions during the past two to three decades, aerosols in the Arctic today are still highly contaminated by industrial Pb.
Citation: Shotyk, W., J. Zheng, M. Krachler, C. Zdanowicz, R. Koerner, and D. 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.

1. Introduction

[2] Environmental contamination by Pb has its origins in Antiquity [*Nriagu*, 1983], with significant atmospheric Pb contamination first making its appearance in Europe approximately three thousand years ago and originating from mining in the Iberian Peninsula [*Shotyk et al.*, 1998]. The periods of human history most impacted by extensive Pb contamination include the Roman and Medieval Periods, the Industrial Revolution, and the second half of the 20th century [*Shotyk and Le Roux*, 2005]. Environmental Pb contamination during the Roman and Medieval Periods was due almost exclusively to the mining, smelting, and refining of Pb ores [*Nriagu*, 1985], not only to obtain Pb, but also to recover silver which is commonly enriched in galena (PbS). During the Industrial Revolution, Pb found its way into a tremendous array of industrial products and materials [*Harn*, 1924]. The introduction of alkyllead additives to gasoline in 1923 represented an additional source of environmental Pb contamination [*Nriagu*, 1990a]. Although this most recent Pb insult occurred rather late in the history of atmospheric Pb contamination, it certainly promoted the global dispersion of this potentially toxic metal [*Patterson*, 1981]. No region of the surface of the Earth was left unaffected, with snow and ice cores providing unambiguous evidence of Pb contamination in both polar regions [*Boutron et al.*, 1994].

[3] The gradual elimination of leaded gasoline and its eventual ban in Japan, Europe, the U.S. and Canada, has had a dramatic effect on atmospheric Pb emissions and there have subsequently been rapid declines in air Pb concentrations and deposition rates [*Boutron et al.*, 1991]. While these changes are beyond question in the regions where these parameters have been measured, the reductions began to take place from concentration levels and fluxes which were extremely high (e.g. three orders of magnitude or more) relative to the "natural background" values [*Shotyk et al.*, 1998]. An evaluation of atmospheric Pb in the air today, therefore, is necessary to be able to compare recent air Pb concentrations with natural values, to document the extent of the decline. Recent snow from the Arctic, remote from all industrial emissions, provides a chemically simple matrix and can serve as a sensitive indicator of environmental change.

2. Materials and Methods

[4] During the spring of 2004, a 5 m snow pit representing precipitation from 1994 to 2004 was dug by hand on Devon Island (75°22′N; 82°40′W and 1820 m asl) using appropriate clean sampling equipment, clothing, and procedures. Forty-five samples were processed in the cold clean room at the Geological Survey of Canada in Ottawa, and measured for Pb, Sc, and Pb isotope ratios using the inductively coupled plasma sector-field mass spectrometer (ICP SMS) at the Institute of Environmental Geochemistry, University of Heidelberg. Detailed descriptions of the clean lab procedures and analytical methods are presented elsewhere [*Krachler et al.*, 2004a, 2004b, 2005]. In addition, these parameters were also measured in a continuous series of 465 samples from a 65 m ice core which was drilled in 2000 and represents snow accumulation since 1842; these samples were successfully analysed earlier, but only for Pb concentrations [*Zheng et al.*, 2003]. The measurements of Sc presented here are the first reported concentrations for this element in polar snow and ice. The limits of detection for Pb and Sc were 0.06 and 0.005 pg/g, respectively. The average standard deviations of the Pb isotope measurements for the snow samples (n =

---

[1] Institute of Environmental Geochemistry, University of Heidelberg, Heidelberg, Germany.
[2] Geological Survey of Canada, Ottawa, Ontario, Canada.

0094-8276/05/2005GL023860

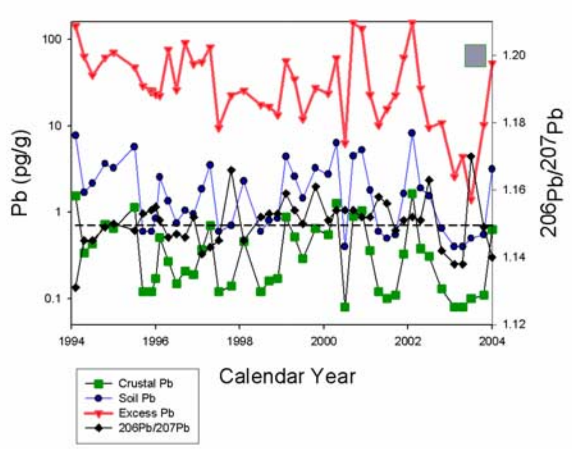

Figure 1. Lead concentrations and isotopic composition ($^{206}Pb/^{207}Pb$) of the snow pit samples. The grey square represents the $^{206}Pb/^{207}Pb$ ratio characteristic of crustal rocks and the horizontal dashed line the average isotopic composition of Pb in the snow samples ($^{206}Pb/^{207}Pb$ = 1.150 ± 0.003, n = 45). "Crustal Pb" was calculated as $[Sc]_{snow} \times ([Pb]/[Sc])_{crust}$ where $([Pb]/[Sc])_{crust} = 1$. "Soil Pb" was calculated using the same approach, but $([Pb]/[Sc])_{soil} = 5$. The concentration of "excess" Pb was calculated as the difference between the measured Pb concentrations and "soil Pb".

45) were 0.003 for $^{206}Pb/^{207}Pb$ and 0.006 for $^{208}Pb/^{206}Pb$ (RSD of 0.31 and 0.30%, respectively) with external precisions varying with Pb concentrations [*Krachler et al.*, 2004b]. Accuracy was better than 0.1% as assessed by analysis of SRM NIST 981.

3. Results and Discussion

[5] In the snow pit samples, the Sc concentrations average 0.43 pg/g and the abundance and distribution of this element can be used as a surrogate for natural Pb. Scandium is a lithogenic trace element which can be used as an index of the concentration of soil-derived dust particles in the atmosphere [*Rahn*, 1976]. Scandium has no preference for specific mineral phases (only seven Sc minerals are known, and they are all rare), but instead is widely distributed in all of the primary and secondary minerals at the surface of the Earth. Industrial uses of Sc are negligible, with total global Sc production amounting to only 45 kg per year [*Emsley*, 2001]. The ratio of Pb to Sc in crustal rocks is approximately 1:1 [*Wedepohl*, 1995] which makes the Pb/Sc ratio a convenient parameter for quantifying the extent of Pb enrichment in atmospheric aerosols, relative to the natural abundance of Pb in crustal rocks. As a first approximation, therefore, the concentration of Sc in the snow samples can be viewed as the abundance of lithogenic Pb (Figure 1). In contrast, the measured concentrations of Pb are far greater, and range up to 165 pg/g (Figure 1). On average, the snow samples contain 45.2 pg/g Pb which exceeds the crustal ratio by two orders of magnitude.

[6] Lead in silicates is found mainly in potassium feldspar, biotite, and clay minerals where Pb^{2+} can substitute for K^+ [*Heinrichs et al.*, 1980]. During chemical weathering, there may be a residual enrichment of Pb in the profile which would give rise to a natural enrichment of Pb in the soil, relative to crustal abundance [*Shotyk et al.*, 2001]. It has been suggested that the Pb to Sc ratio in soils is typically 5:1 [*Bowen*, 1979]. In pre-anthropogenic, soil-derived atmospheric aerosols from a Swiss peat bog dating from ca. 3,000 to 14,500 years ago, the average ratio of Pb to Sc was 4:1 [*Shotyk et al.*, 1998]. Even if the soil Pb/Sc ratio suggested by *Bowen* [1979] is used for comparison, the average ratio of Pb to Sc in recent snow is still at least a factor of 20 greater than the "natural" value for Pb in soil-derived dust. Regardless of the "background" ratio of Pb/Sc which is selected as the point of reference, the recent snow samples from Devon Island are highly enriched in Pb (Figure 1) and we know of no natural, geochemical processes which can explain the enrichments. Even today, therefore, there is an overwhelming supply of industrial Pb to Arctic snow. We note further that atmospheric Pb from industrial sources has an average particle diameter of 0.5 μm [*Nriagu*, 1990b] which is far smaller than the soil-derived, lithogenic particles containing Sc and Pb from natural sources [*Rahn*, 1976]. The extent of atmospheric Pb contamination revealed by the snow pit, therefore, is a conservative estimate of the industrial enrichment of Pb being supplied to the arctic today.

[7] To put the modern values into perspective, the concentrations of Sc in ice since 1842 range from 0.02 to 8.8 pg/g which means that the concentration of "natural" Pb also falls within a factor of five of this range (Figure 2). In contrast to the concentration range of natural Pb, all of the ice samples since 1842 contain significantly higher Pb concentrations (up to 1656 pg/g). In other words, all of the samples since 1842 have been impacted with Pb emitted by human activities. In fact, the average concentration of Pb in ice (75 pg/g) from this period is two orders of magnitude greater than the average concentration of Sc (0.70 pg/g). Even the sample containing the least Pb (1.9 pg/g and dating from 1844) still contains 38 times more Pb than Sc (0.05 pg/g). Regardless of whether the crustal or the soil Pb/Sc ratio is used as the

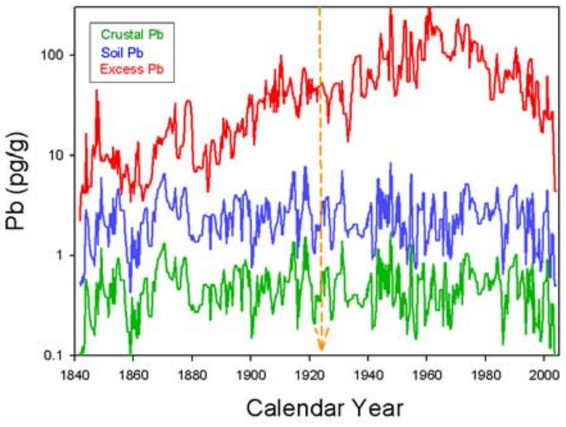

Figure 2. Concentrations of Pb in the ice core, with each data point representing the median of six consecutive samples. "Crustal Pb", "soil Pb", and "excess Pb" concentrations calculated as noted in Figure 1. The vertical arrow corresponds to the introduction of leaded gasoline in the U.S. in 1923.

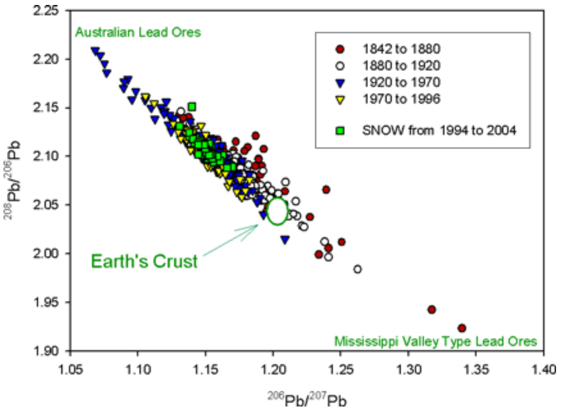

Figure 3. The isotopic evolution of atmospheric Pb recorded by the snow pit and ice core samples from Devon Island from 1842 to 2004. The values for Australian and Mississippi Valley type lead ores are taken from *Sangster et al.* [2000] and those for the Earth's Crust from *Kramers et al.* [1997].

basis for comparison, all of the ice samples are clearly impacted by industrial Pb. While the introduction of leaded gasoline in 1923 has certainly contributed to the increasing Pb concentrations seen between 1920 and 1970 (Figure 2), this is just the most recent of a series of human activities which has profoundly influenced the geochemical cycle of Pb. The abundance of excess Pb which pre-dates 1923 requires some other explanation. Other anthropogenic sources of Pb to the atmosphere, including the mining and smelting of lead and other base metal ores, emissions from various industrial applications and manufacturing, the chemicals industry, steel making, coal burning, and refuse incineration [*Nriagu*, 1990b], must be invoked to explain the extent of Pb contamination in the Arctic witnessed by the Devon Island ice core between 1842 and 1923.

[8] To help identify the predominant industrial sources, the isotopic composition of Pb has been measured in all of the snow and ice samples (Figure 3). Again, consider the isotopic composition of "natural" Pb in soil dust particles derived from rock weathering. Soil-derived atmospheric aerosols from peat samples dating from the mid-Holocene (ca. 6,000 to 9,000 years ago) have ^{206}Pb/^{207}Pb = 1.199 and ^{208}Pb/^{206}Pb = 2.059. Contemporary models of the isotopic composition of Pb in the Earth's Crust yield similar values [*Kramers and Tolstikhin*, 1997] and we assume these values are representative of atmospheric soil dust derived from the weathering of crustal rocks. In contrast to these values, the Pb in snow and ice from Devon Island records an extreme range in isotopic compositions (Figure 3). The most radiogenic samples date from the early 1840's and resemble Mississipi Valley type of lead ore deposits [*Sangster et al.*, 2000] which have ^{206}Pb/^{207}Pb in the range 1.212–1.406 and ^{208}Pb/^{206}Pb in the range 1.870–2.037; these ores were first exploited commercially in the 1820's. The least radiogenic samples date from the 1940's and 1950's and are comparable to the Broken Hill lead ores from Australia with ^{206}Pb/^{207}Pb = 1.041 and ^{208}Pb/^{206}Pb = 2.225; this lead was first imported into Europe in 1826 [*Day and Tylecote*, 1991] and was the main source of Pb used there to manufacture gasoline lead additives.

[9] The isotopic composition of Pb in the snow pit samples is well removed from both of these extremes, and fall in the range ^{206}Pb/^{207}Pb = 1.131–1.170 and ^{208}Pb/^{206}Pb = 2.088–2.151 (Figure 3). This range of values is less radiogenic than soil dust which reinforces the view that Pb derived from natural sources can account for very little of the modern Pb flux. The snow pit data from 1994 to 2004 overlaps to a great extent with the ice core data from 1970 to 1996 (Figure 3). Of particular environmental relevance is the fact that there has been a rapid decline in consumption of leaded gasoline in North America from more than 200,000 tonnes per year in 1970 to almost nothing today [*Wu and Boyle*, 1997]. This drastic reduction, however, has had effectively no impact on the isotopic composition of Pb over the same time interval (Figure 3). Consumption of leaded gasoline additives in Europe also has gone into a strong decline, but again, there is no detectable impact of this change in the Pb isotope ratios.

[10] For comparison with the Devon Island data presented here, the pioneering work on the isotopic composition of Pb in Greenland ice by Rosman and colleagues [*Rosman et al.*, 1994, 1998] is of particular relevance. Analyses of the isotopic composition of Pb in Greenland snow dating from 1960 to 1988 showed that industrial Pb was dominated by two components: radiogenic Pb (^{206}Pb/^{207}Pb $\approx$ 1.2) from North America, and less radiogenic Pb (^{206}Pb/^{207}Pb $\approx$ 1.15) from Eurasia [*Rosman et al.*, 1994]. In a snow sample dating from 1976, when the consumption of leaded gasoline in North America had reached its zenith, snow in Greenland yielded ^{206}Pb/^{207}Pb = 1.2015 ± 00017. Radiogenic values such as these argued strongly in favour of Greenland snow being impacted predominantly by North American Pb [*Rosman et al.*, 1994]. Snow samples collected in Greenland during 1988 to 1989 recorded considerable seasonal variation [*Rosman et al.*, 1998]: the values in summer contained lower Pb concentrations which were less radiogenic (^{206}Pb/^{207}Pb $\approx$ 1.15) and reflect inputs from Eurasia; in contrast, winter samples contained greater Pb concentrations, and the Pb was more radiogenic (^{206}Pb/^{207}Pb $\approx$ 1.2), reflecting inputs from North America.

[11] Comparing the data from Devon Island with that of Greenland, three remarkable differences emerge. First, the snow pit samples from Devon (^{206}Pb/^{207}Pb = 1.150 ± 0.003, n = 45) are less radiogenic than the values reported for Greenland snow. Second, the Devon Island samples show little, if any, seasonal variation in their isotopic composition (Figure 1). Third, whereas Greenland snow is most impacted by North American Pb during the winter, and Eurasian Pb during summer; at Devon, the opposite is true.

[12] The isotopic composition of arctic aerosols dominated by Eurasian Pb [*Sturges and Barrie*, 1989] is virtually indistinguishable from aerosols collected in southern Canada [*Sturges and Barrie*, 1987]. As a consequence, it is not possible to distinguish Eurasian from Canadian inputs to Devon Island based on the isotopic composition of Pb alone [*Sturges and Barrie*, 1989]. However meteorological and chemical studies have consistently shown that in winter, the Canadian arctic is mainly influenced by a haze originating in Eurasia [*Barrie*, 1986]. As a result, haze particles in the arctic exhibit strong seasonal variations, with acidity,

sulphur and Pb concentrations typically 20 to 40 times more abundant in winter than during summer [*Barrie*, 1986]. The stratigraphy of the snow pit on Devon Island shows that the elevated Pb concentrations and enrichments correspond to winter samples, and these must have originated in Eurasia [*Sturges and Barrie*, 1989; *Barrie*, 1986].

[13] Taken together, the elevated concentrations of excess Pb found in winter samples (Figure 1) indicate that the High Arctic of Canada is receiving most of its anthropogenic Pb from Eurasia. This finding is consistent with recent measurements of the isotopic composition of Pb in snow from Alert (http://www.ainc-inac.gc.ca/ncp/pub/phy/occtre11_e.html). The comparatively low and apparently declining concentrations of excess Pb during the summer months suggests that North American sources are becoming relatively unimportant, at least in the arctic, a finding which is consistent with sediment cores from Canadian lakes [*Outridge et al.*, 2002]. The fundamental differences in isotopic composition between Greenland and Devon Island indicates that further studies of the geographic and temporal variations in contaminant deposition within the Arctic are warranted.

[14] The decline in gasoline lead consumption in North America since 1970, and in Europe since 1980, have clearly contributed to the decline in Pb concentrations seen in the ice core (Figure 2). However, the Pb concentrations and isotope ratios obtained from the snow pit (Figure 1) show that other sources of anthropogenic Pb are still supplying significant amounts of Pb to the Arctic and that this remote region continues to be subjected to a massive Pb burden, relative to the natural Pb flux. Taken together, the Pb and Pb isotope data from Devon Island snow indicates that

[15] 1. even today, inputs of Pb to the Arctic are overwhelmingly dominated by anthropogenic sources,

[16] 2. modern anthropogenic Pb inputs to the Arctic can no longer be attributed to the consumption of gasoline additives in North America or Europe, and

[17] 3. other sources of industrial Pb need to be invoked to explain the current intensity of Arctic Pb contamination.

[18] While the gradual elimination of leaded gasoline has been an important step toward reducing atmospheric Pb emissions, other steps must be taken to further reduce the fluxes of anthropogenic Pb to the arctic. Unlike gasoline lead, the dominant industrial sources of atmospheric Pb today can contribute a broad range of trace elements, in addition to Pb. The enrichments of Pb in aerosols originating in Eurasia and their seasonal variation may have broader implications for the dispersion of other potentially toxic trace metals in the arctic.

References

Barrie, L. A. (1986), Arctic air pollution: An overview of current knowledge, *Atmos. Environ.*, *20*, 643–663.

Boutron, C. F., U. Görlach, J.-P. Candelone, M. A. Bolshov, and R. J. Delmas (1991), Decrease in anthropogenic lead, cadmium and zinc in Greenland snows since the late 1960s, *Nature*, *353*, 153–156.

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: A review, *Geochim. Cosmochim. Acta*, *58*, 3217–3225.

Bowen, H. J. M. (1979), *Environmental Chemistry of the Elements*, Elsevier, New York.

Day, J., and R. F. Tylecote (1991), *The Industrial Revolution in Metals*, The Inst. of Metals, London.

Emsley, J. (2001), *Nature's Building Blocks. An A–Z Guide to the Elements*, 539 pp., Oxford Univ. Press, New York.

Harn, O. C. (1924), *Lead The Precious Metal*, 323 pp., Jonathan Cape, London.

Heinrichs, H., B. Schulz-Dobrick, and K. H. Wedepohl (1980), Terrestrial geochemistry of Cd, Bi, Tl, Pb, Zn and Rb, *Geochim. Cosmochim. Acta*, *44*, 1519–1533.

Krachler, M., J. Zheng, D. A. Fisher, and W. Shotyk (2004a), Novel calibration procedure for improving trace element determinations in ice and water samples using ICP-SMS, *J. Anal. At. Spectrom.*, *19*, 1017–1019.

Krachler, M., J. Zheng, D. A. Fisher, and W. Shotyk (2004b), Direct determination lead isotopes (^{206}Pb, ^{207}Pb, ^{208}Pb) in Arctic ice samples at pg/g levels using ICP-SMS coupled to a high efficiency sample introduction system, *Anal. Chem.*, *76*, 5510–5517.

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. D., and I. D. Tolstikhin (1997), Two terrestrial lead isotope paradoxes, forward transport modelling, core formation, and the history of the continental crust, *Chem. Geol.*, *139*, 75–110.

Nriagu, J. O. (1983), *Lead and Lead Poisoning in Antiquity*, John Wiley, Hoboken, N. J.

Nriagu, J. O. (1985), Cupellation: The oldest quantitative chemical process, *J. Chem. Educ.*, *62*, 668–674.

Nriagu, J. O. (1990a), The rise and fall of leaded gasoline, *Sci. Total Environ.*, *92*, 13–28.

Nriagu, J. O. (1990b), Heavy metal pollution poisoning the biosphere?, *Environment*, *32*(7–11), 28–33.

Outridge, P. M., M. H. Hermanson, and W. L. Lockhart (2002), Regional variations in atmospheric deposition and sources of anthropogenic lead in lake sediments across the Canadian Arctic, *Geochim. Cosmochim. Acta*, *66*, 3521–3531.

Patterson, C. C. (1981), An alternative perspective—Lead pollution in the human environment: Origin, extent, and significance, Comm. on Lead in the Human Environ., U.S. Natl. Acad. of Sci., Washington, D. C.

Rahn, K. A. (1976), The chemical composition of the atmospheric aerosol, technical report, 265 pp., Grad. Sch. of Oceanogr., Univ. of R. I., Kingston.

Rosman, K. J. R., W. Chisholm, C. F. Boutron, J. P. Candelone, and S. Hong (1994), Isotopic evidence to account for changes in the concentration of lead in Greenland snow between 1960 and 1988, *Geochim. Cosmochim. Acta*, *58*, 3265–3269.

Rosman, K. J. R., W. Chisholm, C. F. Boutron, J. P. Candelone, J.-L. Jaffrezo, and C. I. Davidson (1998), Seasonal variations in the origin of lead in snow at Dye 3, Greenland, *Earth Planet. Sci. Lett.*, *160*, 383–389.

Sangster, D. F., P. M. Outridge, and W. J. Davis (2000), Stable lead isotope characteristics of lead ore deposits of environmental significance, *Environ. Rev.*, *8*, 115–147.

Shotyk, W., and G. Le Roux (2005), Biogeochemistry and cycling of lead, in *Biogeochemical Cycles of the Elements*, edited by A. Sigel, H. Sigel, and R. K. O. Sigel, *Metal Ions Biol. Syst.*, *43*, 240–275.

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 ^{14}C 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 Gruère, Jura Mountains, Switzerland, and its record of atmospheric Pb and lithogenic trace elements (Sc, Ti, Y, Zr, Hf and REE) since 12,370 ^{14}C yr BP, *Geochim. Cosmochim. Acta*, *65*, 2337–2360.

Sturges, W. T., and L. A. Barrie (1987), Lead 206/207 isotope ratios in the atmosphere of North America as tracers of U.S. and Canadian emissions, *Nature*, *392*, 144–146.

Sturges, W. T., and L. A. Barrie (1989), Stable lead isotope ratios in Arctic aerosols: Evidence for the origin of Arctic air pollution, *Atmos. Environ.*, *23*, 2513–2520.

Wedepohl, K. H. (1995), The composition of the continental crust, *Geochim. Cosmochim. Acta*, *59*, 1217–1232.

Wu, J. F., and E. A. Boyle (1997), Lead in the western North Atlantic Ocean: Completed response to leaded gasoline phaseout, *Geochim. Cosmochim. Acta*, *61*, 3279–3283.

Zheng, J., C. M. Zdanowicz, D. Fisher, G. Hall, and J. Vaive (2003), A new 155-yr record of Pb pollution from Devon ice cap, Canada, *J. Phys. IV*, *107*, 1405–1408.

D. Fisher, R. Koerner, and C. Zdanowicz, Geological Survey of Canada, Ottawa, ON, Canada K1A 0E8.

M. Krachler, W. Shotyk, and J. Zheng, Institute of Environmental Geochemistry, University of Heidelberg, INF 236, D-69120 Heidelberg, Germany. (shotyk@ugc.uni-heidelberg.de)