GEOPHYSICAL RESEARCH LETTERS, VOL. 35, L05810, doi:10.1029/2007GL032680, 2008

Ice core record of rising lead pollution in the North Pacific atmosphere

E. Osterberg,[1,2] P. Mayewski,[1,2] K. Kreutz,[1,2] D. Fisher,[3] M. Handley,[1] S. Sneed,[1] C. Zdanowicz,[3] J. Zheng,[3] M. Demuth,[3] M. Waskiewicz,[4] and J. Bourgeois[3]

Received 16 November 2007; revised 18 January 2008; accepted 4 February 2008; published 8 March 2008.

[1] A high-resolution, 8000 year-long ice core record from the Mt. Logan summit plateau (5300 m asl) reveals the initiation of trans-Pacific lead (Pb) pollution by *ca.* 1730, and a >10-fold increase in Pb concentration (1981–1998 mean = 68.9 ng/l) above natural background (5.6 ng/l) attributed to rising anthropogenic Pb emissions from Asia. The largest rise in North Pacific Pb pollution from 1970–1998 (end of record) is contemporaneous with a decrease in Eurasian and North American Pb pollution as documented in ice core records from Greenland, Devon Island, and the European Alps. The distinct Pb pollution history in the North Pacific is interpreted to result from the later industrialization and less stringent abatement measures in Asia compared to North America and Eurasia. The Mt. Logan record shows evidence for both a rising Pb emissions signal from Asia and a trans-Pacific transport efficiency signal related to the strength of the Aleutian Low. **Citation:** Osterberg, E., et al. (2008), Ice core record of rising lead pollution in the North Pacific atmosphere, *Geophys. Res. Lett.*, *35*, L05810, doi:10.1029/2007GL032680.

1. Introduction

[2] Atmospheric lead (Pb) pollution has long been a concern because of its neurotoxic effects on children, and its capacity to be transported long distances from anthropogenic source regions [*Canfield et al.*, 2003]. Leaded gasoline combustion is the largest Pb pollution source, followed by fossil fuel burning and metal smelting [*Pacyna and Pacyna*, 2001]. Atmospheric Pb pollution in the North Atlantic and Arctic is known to have increased rapidly from ca. 1850–1970 [e.g., *Patterson*, 1965], and subsequently declined following the phase-out of leaded gasoline and the enactment of emissions abatement legislation in North America and Europe [e.g., *Boutron et al.*, 1991].

[3] Comparatively little is known, however, about anthropogenic Pb concentrations and recent trends in the North Pacific region directly downwind from rapidly developing nations in Asia. Asian Pb emissions are estimated to have increased through at least 1995 [*Pacyna and Pacyna*, 2001], but the impact of Asian, North American, and/or Eurasian Pb emissions on the North Pacific is largely unknown because the majority of long atmospheric Pb pollution records are from the North Atlantic and Arctic regions. Aerosol monitoring stations in western North America now record the episodic transport of industrial pollutants, including Pb, from Asia across the Pacific Ocean [e.g., *Jaffe et al.*, 2003], but these stations have only been in operation since the late 1970s and therefore do not have pre-anthropogenic data to quantify natural background Pb levels.

[4] Here we present the first continuous, 8000 year-long record of North Pacific atmospheric Pb concentration as recorded in an ice core collected from Prospector-Russell (PR) Col on the summit plateau of Mt. Logan (60°35′N, 140°30′W; 5300 m el.; Figure 1) in the Saint Elias Mountains, Yukon Territory, Canada. Ice cores are excellent archives of anthropogenic emissions because of their extreme matrix purity (water ice) and tight chronologic control. Mt. Logan's summit, located within the free troposphere less than 100 km from the Gulf of Alaska, is ideally situated to capture dust and industrial emissions entrained in the strong westerly flow emanating from Asia (Figure 1). Mt. Logan is also one of the few locations in the North Pacific from where a high-resolution record of climate and atmospheric pollution spanning >5000 years can be recovered.

2. Materials and Methods

[5] The 186 m-long Mt. Logan PR Col ice core was drilled to bedrock by the Geological Survey of Canada (GSC) during the summers of 2001 and 2002 in a relatively flat area with low ice velocities (<0.2 m a^{-1}) [*Fisher et al.*, 2004]. The mean accumulation rate at the site is 0.41 m a^{-1} (water). We continuously sampled the core at high resolution (1–5 cm/sample) in ultra-clean conditions using an ice/firn core melting system [*Osterberg et al.*, 2006]. The concentrations of major ions (e.g. Na^+, Cl^-, SO_4^{2-}) and trace elements (e.g. Pb, Al, Fe, Sr, Cs, U, REEs) were measured on a total of 6900 pristine meltwater samples by ion chromatography and inductively coupled plasma mass spectrometry [*Osterberg et al.*, 2006]. Detection limits for Pb (3σ of MilliQ (>18.2 MΩ) deionized water blanks passed through the entire melter system) were 0.9 ng/l (see auxiliary material[1]). The resulting 8000 year-long record has sub-annual resolution (4–30 samples/year) from 1700–1998 AD, and annual to multi-decadal resolution from 8000 BP to 1700 AD.

[6] The sub-annually resolved portion of the record (1700–1998 AD) was dated by annual layer counting of seasonal oscillations in $\delta^{18}O$, [Na^+], and [U], and identification of major historical volcanic eruptions (Figure S1). The entire record spans >13,000 years, but brittle sections of core create 100–300 year-long gaps between 8000–

[1]Climate Change Institute, University of Maine, Orono, Maine, USA.
[2]Department of Earth Sciences, University of Maine, Orono, Maine, USA.
[3]Geological Survey of Canada, Ottawa, Ontario, Canada.
[4]Datalogging North, Inc., Edmonton, Alberta, Canada.

0094-8276/08/2007GL032680$05.00

[1]Auxiliary materials are available in the HTML. doi:10.1029/2007GL032680.

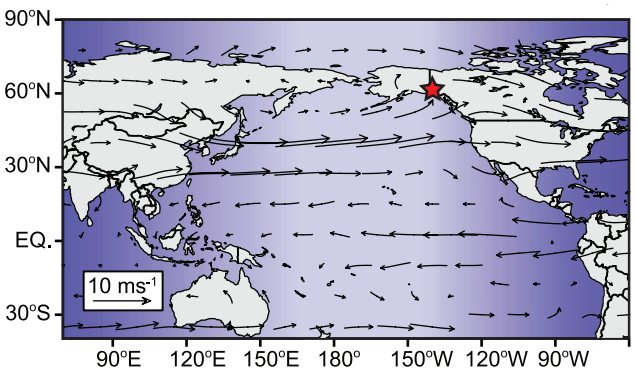

Figure 1. Mean 700 mb level wind vectors for January–May, 1968–1998, from NCEP/NCAR reanalysis data [*Kalnay et al.*, 1996], showing the winter/spring westerly flow from Asia to Mt. Logan (star) and western North America.

9000 BP. We focus here on the continuous record back to 8000 BP. The record from 13,000–300 BP was dated by an ice flow model constrained by the annually-counted top 300 years, large volcanic eruptions, and the Younger Dryas termination date of 11,640 BP from the GISP2 ice core [*Meese et al.*, 1997]. We estimate a maximum error of ±0.5 a for the 20th century, ~1–2% from 800–1998 AD, and ~5% for the remainder of the record based on repeat annual layer counts and model sensitivity studies.

3. Results

[7] The dominant natural (pre-anthropogenic) sources of Pb in the North Pacific atmosphere are crustal dust and volcanic emissions. Mt. Logan 25-year averaged [Pb] from 8000–1200 BP is highly correlated with dust element concentrations (Al, Fe, Sr, Cs, U, REEs; mean $r = 0.76$, $p < 0.001$) and $[SO_4^{2-}]$ ($r = 0.66$, $p < 0.001$) (Figure 2). Average crustal enrichment factors (EF_c) for Pb (EF_c(Pb) = average($[Pb/r]_{sample} \div [Pb/r]_{UCC}$), where r = Sr, Cs, U, Al, Fe, La, and Ce to reduce potential bias from any one upper continental crust reference element; see auxiliary material) from 8000–1200 BP range from 0.4–5.1 with a mean of 2.1, indicating an approximately equal contribution from crustal dust and volcanic emissions on average (Table 1). Several intervals with EF_c(Pb) approaching 5 (e.g. 5800 and 3100 BP) coincide with anomalously high $[SO_4^{2-}]$, and therefore most likely represent a larger relative contribution of natural Pb from volcanic emissions.

[8] The most striking feature of the Mt. Logan dataset is the abrupt, unprecedented increase in [Pb] and EF_c(Pb) from 1950 AD to the end of the record in 1998, punctuated by extremely high levels from 1981–1986 (Figures 2 and 3). The average [Pb] from 1981–1998 is an order of magnitude above the mean 8000–1200 BP level, while average 1981–1998 concentrations of crustal dust elements (Sr, Cs, U, Al, Fe, La, and Ce) and volcanic SO_4^{2-} are all lower than their 8000–1200 BP levels (Table 1). Average EF_c(Pb) reflect this contrast, ranging from 16–54 (mean = 31.2) over 1981–1998 compared to a range of 0.4–5.1 (mean = 2.1) from 8000–1200 BP. We attribute the anomalous increase

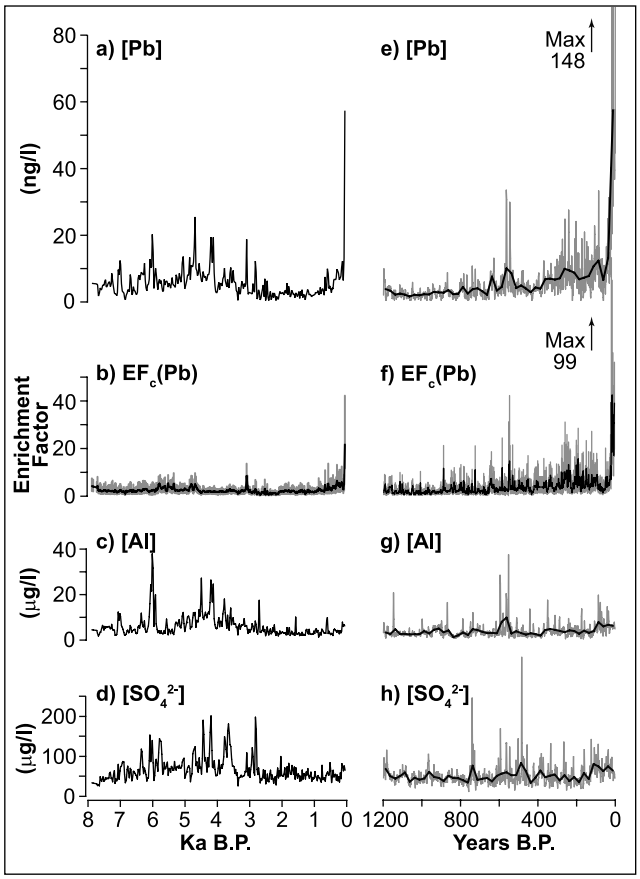

Figure 2. Mt. Logan time series of [Pb], EF_c(Pb), [Al] (dust), and $[SO_4^{2-}]$ (volcanic emissions): (a, b, c, and d) 25-year averaged data. In Figure 2b the black curve is 25-year averaged EF_c(Pb) and the gray shading represents the total range of EF_c(Pb) calculated using the seven reference elements. Also shown are (e, g, and h) 25-year averaged data in black and 2-year averaged data in gray and (f) 2-year average EF_c(Pb) (the black curve) and the total EF_c(Pb) range (gray shading). All seven crustal reference elements have similar time series ($r > 0.6$, $p < 0.001$).

in [Pb] and EF_c(Pb) since 1950 AD to a rise in anthropogenic Pb emissions in the North Pacific atmosphere. Enrichment factors indicate that >90% of the Pb deposited on Mt. Logan from 1981–1998 was anthropogenic in origin.

[9] Though not as dramatic as late 20th century Pb pollution, a period of elevated [Pb] and EF_c(Pb) *ca.* 1730–1910 AD represents the earliest North Pacific anthropogenic Pb emissions that we can identify with the present dataset. Lead concentrations increased ~250% from consistently low levels *ca.* 800–1200 AD, while concentrations of the

Table 1. Mean Mt. Logan Ice Core Lead, Sulfate, and Aluminum Concentrations (ng/1). Lead Crustal Enrichment Factor, and Lead Flux (micrograms m^{-2} a^{-1}) Over Four Time Intervals

	[Pb]	EF_c(Pb)	$[SO_4^{2-}]$	[Al]	Pb Flux
8000–1200 BP	5.6	2.1	68,900	6700	2.2
800–1200 AD	2.5	2	48,600	3200	1.0
1730–1910 AD	8.9	6.8	52,300	3800	3.7
1981–1998 AD	68.9	31.2	59,200	6300	25.7

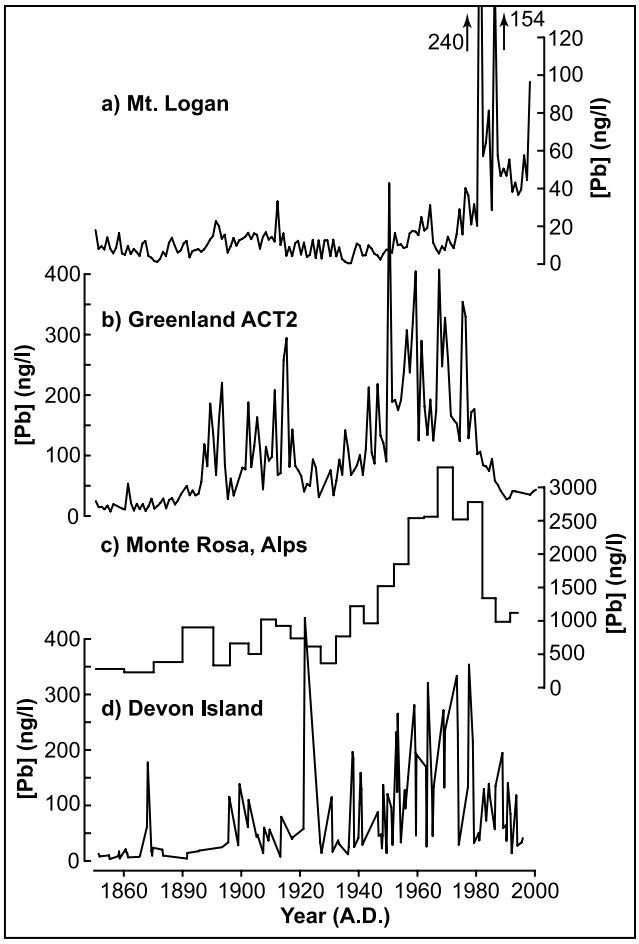

Figure 3. Comparison of ice core Pb concentration records from (a) Mt. Logan (1-year average), (b) Greenland ACT2 site (1-year average) [*McConnell et al.*, 2006], and (c) Monte Rosa in the European Alps (5-year average) [*Schwikowski et al.*, 2004], and (d) Devon Island in the Canadian Arctic (~1-year average) [*Shotyk et al.*, 2005].

seven crustal reference elements increased only 15–50% over the same interval (resulting in elevated $EF_c(Pb)$), and $[SO_4^{2-}]$ increased only 8% (Table 1). We do not find evidence of anthropogenic Pb emissions in the North Pacific during the ancient Greek or Roman eras (*ca.* 3000–1500 BP) when Pb pollution impacted Greenland [*Hong et al.*, 1994] and Europe [*Shotyk et al.*, 1998]. Lead isotope ratios are currently being analyzed on archive Mt. Logan samples, however, and may reveal evidence of earlier anthropogenic Pb emissions.

4. Discussion and Conclusions

[10] A comparison of ice core Pb records from Greenland [*Candelone et al.*, 1995; *McConnell et al.*, 2006], Devon Island [*Shotyk et al.*, 2005], Monte Rosa in the European Alps [*Schwikowski et al.*, 2004], and Mt. Logan (this study) reveals that the North Pacific history of Pb pollution differs significantly from the well-established and consistent history of Pb pollution and recovery in the North Atlantic and Arctic regions. The Greenland, Devon Island, and Alpine records all document a similar rise in Pb concentrations beginning in earnest in the late 19th century, peaking in the early 1970s, and declining to present after the phasing out of leaded gasoline and the enactment of emission abatement legislation [e.g., *Boutron et al.*, 1991] (Figure 3). The Mt. Logan record, however, shows that the most dramatic increase in North Pacific Pb contamination occurred after 1970 when North Atlantic and Arctic records show a rapid decline in Pb levels (Figure 3). The unique signature of the Mt. Logan core suggests that it has a different primary Pb source region from the other records.

[11] Stable Pb isotope studies indicate that North America, Eurasia (includes Eastern and Western Europe and former U.S.S.R.), and Western Europe are the dominant anthropogenic Pb sources for Greenland, Devon Island, and the European Alps, respectively [*Rosman et al.*, 1994, 2000; *Shotyk et al.*, 2005]. While we cannot conclusively exclude minor Pb contributions from these source regions in the North Pacific, we conclude that Asia is the primary source for anthropogenic Pb on Mt. Logan, with the post-1950 increase in trans-Pacific Pb pollution reflecting the region's accelerated industrialization. Several lines of evidence support this conclusion.

[12] The trans-Pacific transport of Asian dust and pollution is now well established based on satellite observations and North American air monitoring station data. Strong winter and spring mid-latitude cyclones regularly advect Asian dust and pollution into the free troposphere where they are transported to western North America by prevailing westerly winds [e.g., *Jaffe et al.*, 2003] (Figure 1). Subannual trace element data from the Mt. Logan core indicate that anthropogenic Pb is deposited with dust-borne elements (e.g., Al, Fe, Sr, REEs) in the winter and spring, indicating that Pb pollution and dust are transported to Mt. Logan in the same air mass and have a similar source region (Figure S2). Previous mineral and isotopic analyses identified Asia as the most likely source region for dust deposited at >3000 m elevation on Mt. Logan [*Zdanowicz et al.*, 2006]. Furthermore, Asia is the only Northern Hemisphere region where industrial Pb emissions increased from 1983–1995 [*Pacyna and Pacyna*, 2001].

[13] Although the regional sources of Pb pollution differ at the Northern Hemisphere ice core sites discussed here, the maximum (1981–1998 average) Pb flux (concentration times annual accumulation rate) on Mt. Logan of ~26 $\mu g\ m^{-2}\ a^{-1}$ is similar to the maximum (1950–1975 average) Pb flux at Summit, Greenland [*Candelone et al.*, 1995; *McConnell et al.*, 2006] and Devon Island [*Shotyk et al.*, 2005] of ~19 and ~39 $\mu g\ m^{-2}\ a^{-1}$, respectively. Interestingly, the Greenland PARCA Act2 site [*McConnell et al.*, 2006], located ~775 km south of Summit, Greenland, has a maximum Pb flux 4–5 times higher (91 $\mu g\ m^{-2}\ a^{-1}$) than at Summit. This is most likely due to the higher accumulation rate and closer proximity of the ACT2 site to industrial sources. The importance of proximity is also reflected in the high Pb flux at Monte Rosa in the European Alps (~800 $\mu g\ m^{-2}\ a^{-1}$), despite the high elevation (4450 m) of that core site [*Schwikowski et al.*, 2004].

[14] It has been hypothesized previously by *Yalcin and Wake* [2001] that the Eclipse Icefield (3000 m el.) and Mt. Logan summit (5300 m el.; located 45 km apart) have different anthropogenic source regions. Eclipse ice cores predominantly record Eurasian pollution [*Yalcin and Wake*, 2001], while we have demonstrated a dominantly Asian

pollution source for Mt. Logan. We attribute this to a vertical source gradient in the St. Elias Mountains associated with the structure of cyclonic systems in the Gulf of Alaska that deliver the majority of precipitation in this region [*Holdsworth et al.*, 1991; *Fisher et al.*, 2004]. Sites above ~4500 m in the St. Elias record dominantly Pacific air masses and moisture (e.g. Asian sources), while lower elevations receive larger contributions from local sources [*Holdsworth et al.*, 1991; *Fisher et al.*, 2004], including southward-penetrating Arctic air masses laden with Eurasian pollution [e.g., *Barrie*, 1986]. Continuing investigations using Pb isotope ratios will help to refine our interpretation.

[15] Mt. Logan annually averaged [Pb] is correlated ($r = -0.40$, $p < 0.001$) with wintertime (Nov.–Mar.) sea-level pressure in the Aleutian Low (ALOW) region of the North Pacific from 1900–1998, emphasizing the importance of atmospheric circulation patterns for delivering Asian Pb to Mt. Logan. Stronger and more frequent wintertime storms (lower ALOW pressure) deliver more anthropogenic Pb to Mt. Logan via stronger central Pacific westerlies, consistent with the findings of *Liang et al.* [2005]. Thus, while the dramatic increase in [Pb] since 1950 is attributed to an increase in anthropogenic Pb emissions primarily from Asia (source strength), the year-to-year variability around the rising trend is influenced by the strength of the ALOW (transport efficiency).

[16] The distinct Pb pollution records in the North Atlantic and North Pacific regions are a reflection of the different Pb emission and abatement histories of countries in the two regions. Whereas most North American and Western European nations phased out leaded gasoline in the 1970s and 1980s, Asian nations with the exception of Japan (1980) outlawed leaded gasoline in the 1990s or later. Furthermore, Pb emission restrictions on metal smelting and electricity generation are not as strict in many Asian nations as they are in North America and Europe despite the rapid recent growth of these industries in Asia [*Pacyna and Pacyna*, 2001]. China, for example, is the world's largest consumer of coal and the world's largest producer of non-ferrous metal (Pb, Zn, Cu, Cd, Ni), with increases of 44–46% from 2000–2004 [*U.S. Geological Survey*, 1933–2006]. Given the scale and rapid growth of these Pb-emitting industries in Asia, more efficient emission controls would be required before a North Atlantic-type reduction in atmospheric Pb pollution could be expected in the North Pacific.

[17] **Acknowledgments.** This research was supported by the U.S. National Science Foundation Office of Polar Programs, the International Arctic Research Center (Alaska), Natural Resources Canada, and the U.S. National Oceanic and Atmospheric Administration. Logistical support was provided by the Arctic Institute of North America, Parks Canada, Trans-North Helicopters, Aklak Air, and Icefield Ranges Expeditions.

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.

Candelone, J. P., S. M. 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.

Canfield, R. L., C. R. Henderson, D. A. Cory-Slechta, C. Cox, T. A. Jusko, and B. P. Lanphear (2003), Intellectual impairment in children with blood lead concentrations below 10 μg per deciliter, *N. Engl. J. Med.*, *348*, 1517–1526.

Fisher, D., et al. (2004), Stable isotope records from Mt. Logan, Eclipse ice cores and nearby Jellybean Lake. Water cycle of the North Pacific over 2000 years and over five vertical kilometers: Sudden shifts and tropical connections, *Geogr. Phys. Quat.*, *58*, 337–352.

Holdsworth, G., S. Fogarasi, and H. R. Krouse (1991), Variation of the stable isotopes of water with altitude in the Saint Elias Mountains of Canada, *J. Geophys. Res.*, *96*, 7483–7494.

Hong, S. M., 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.

Jaffe, D., I. McKendry, T. Anderson, and H. Price (2003), Six "new" episodes of trans-Pacific transport of air pollutants, *Atmos. Environ.*, *37*, 391–404.

Kalnay, E., et al. (1996), The NCEP/NCAR 40-year reanalysis project, *Bull. Am. Meteorol. Soc.*, *77*, 437–471.

Liang, Q., L. Jaeglé, and J. M. Wallace (2005), Meteorological indices for Asian outflow and transpacific transport on daily to interannual timescales, *J. Geophys. Res.*, *110*, D18308, doi:10.1029/2005JD005788.

McConnell, J. R., S. Kipfstuhl, and H. Fischer (2006), The NGT and PARCA shallow ice core arrays in Greenland: A brief overview, *PAGES Newsl.*, *14*, 13–14.

Meese, D. A., A. J. Gow, R. B. Alley, G. A. Zielinski, P. M. Grootes, M. Ram, K. C. Taylor, P. A. Mayewski, and J. F. Bolzan (1997), The Greenland Ice Sheet Project 2 depth-age scale: Methods and results, *J. Geophys. Res.*, *102*, 26,411–26,423.

Osterberg, E. C., M. J. Handley, S. B. Sneed, P. A. Mayewski, and K. J. Kreutz (2006), Continuous ice core melter system with discrete sampling for major ion, trace element, and stable isotope analyses, *Environ. Sci. Technol.*, *40*, 3355–3361.

Pacyna, J. M., and E. G. Pacyna (2001), An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide, *Environ. Rev.*, *9*, 269–298.

Patterson, C. C. (1965), Contaminated and natural lead environments of man, *Arch. Environ. Health*, *11*, 344–360.

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., C. Ly, K. van de Velde, and C. F. Boutron (2000), A two century record of lead isotopes in high altitude alpine snow and ice, *Earth Planet. Sci. Lett.*, *176*, 413–424.

Schwikowski, M., et al. (2004), Post-17th-century changes of European lead emissions recorded in high-altitude alpine snow and ice, *Environ. Sci. Technol.*, *38*, 957–964.

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 C-14 yr BP from a peat bog, Jura Mountains, Switzerland, *Science*, *281*, 1635–1640.

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.

U.S. Geological Survey (1933–2006), *U.S. Geological Survey Minerals Yearbook*, vol. 1, *Metals and Minerals*, U.S. Dep. of the Inter., Washington, D.C.

Yalcin, K., and C. P. Wake (2001), Anthropogenic signals recorded in an ice core from Eclipse Icefield, Yukon Territory, Canada, *Geophys. Res. Lett.*, *28*, 4487–4490.

Zdanowicz, C., G. Hall, J. Vaive, Y. Amelin, J. B. Percival, I. Girard, P. E. Biscaye, and A. Bory (2006), Asian dustfall in the St. Elias Mountains, Yukon, Canada, *Geochim. Cosmochim. Acta*, *70*, 3493–3507.

J. Bourgeois, M. Demuth, D. Fisher, C. Zdanowicz, and J. Zheng, Geological Survey of Canada, Ottawa, ON, Canada K1A 0E8.

M. Handley and S. Sneed, Climate Change Institute, University of Maine, Orono, ME 04469, USA.

K. Kreutz and P. Mayewski, Climate Change Institute and Department of Earth Sciences, University of Maine, Orono, ME 04469, USA.

E. Osterberg, Department of Earth Sciences, Dartmouth College, Hanover, NH 03755, USA. (erich.c.osterberg@dartmouth.edu)

M. Waskiewicz, Datalogging North, Inc., Edmonton, AB, Canada T6C 0M3.