



# Temporal variability of Cd, Pb, and Pb isotope deposition in central Greenland snow

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[1]0 **Abstract:** We present a decade-long (1981–1990) high-resolution (subseasonal) record of Pb and Cd concentrations and Pb isotopic composition in a series of 119 snow samples from a 6-m snow pit at Summit, Greenland. Both metals show order of magnitude seasonal variability, with maxima in spring of every year, coinciding with sulfate peaks. These short-term features complicate attempts to quantify secular decadal-scale trends associated with anthropogenic source changes (e.g., phasing out of leaded gasoline). A small (<50%) decrease during the decade is estimated for Pb, but no significant trend is observed for Cd. Mean concentrations for the snow pit (Pb = 216, Cd = 11 pmol kg<sup>-1</sup>) are indistinguishable from mean values for nearly continuous samples of the 1–6 m section of a firm core drilled 1 km away, suggesting freedom from contamination artifact. An evaluation of potential sources confirms that Pb and Cd are dominated by anthropogenic inputs. Isotopic ratios (<sup>206</sup>Pb/<sup>207</sup>Pb and <sup>208</sup>Pb/<sup>207</sup>Pb) determined on a subset of snow pit samples of varying ages within the decade indicate that springtime Pb concentration maxima are consistent with a mixture of eastern European, former Soviet Union, and western European sources, while seasonal Pb minima, especially from the early portion of the decade, plot along a different mixing line, suggesting a mixture of U.S. and European sources. The combination of Pb concentration and isotopic composition are consistent with an estimated decrease in U.S. Pb contributions of about twofold over the decade, which predicts a decadal concentration decrease in the snow of ~30%. However, the secular trends in both concentration and isotopes are barely detectable against seasonal and interannual variability. The evidence for seasonally distinct source regions may be useful for interpretation of high-resolution records of other chemical species in Greenland snow and ice. Analyses of two deep core sections dated at 1699–1700 and 1780–1788, compared to the snow pit data, indicate that both Pb and Cd deposition in central Greenland roughly doubled during the eighteenth century, then doubled again by the 1980s.

**Keywords:** Trace metals; snow; Greenland; pollution; lead; cadmium.

**Index terms:** Aerosols and particles; isotopic composition/chemistry; trace elements; global change (atmosphere).





reductions in the consumption of leaded gasoline resulted in a 6.5-fold decrease in atmospheric Pb between  $\sim 1970$  and 1992 and that the current values are below those at the beginning of the Industrial Revolution. However, the magnitude of the decrease for the more recent portion of the record is difficult to quantify precisely because of high-frequency variability of the deposition flux and its probable dependence on altitude and location of the specific sampling site. For example, *Boyle et al.* [1994] presented a detailed subseasonal resolution record for Pb at Summit, Greenland, for 1981–1990, demonstrating the difficulties of establishing a secular trend for that decade. An extreme example of site dependence is the chemical composition of snow accumulating in Antarctic versus Arctic regions; Antarctic snow, which accumulates far from most anthropogenic sources, has Pb concentrations about an order of magnitude lower than snow in Greenland [*Wolff et al.*, 1999]. These examples illustrate the need for understanding the importance of deposition location, transport path length, air mass source changes, and deposition mechanisms for inferring hemisphere-scale changes in atmospheric composition using limited sets of records from polar ice and snow.

[4] The Pb record is uniquely valuable because isotopic composition can reveal temporal changes in sources of Pb. In central Greenland, Pb isotope data have been used to argue that the decrease in Pb concentration throughout 1970–1990 was accompanied by a decrease in the fraction of North American gasoline Pb input [*Rosman et al.*, 1993, 1994]. Certainly, this seems likely for the 1970s, since the United States was the dominant consumer of leaded gasoline and was the only country that began to curtail gasoline Pb during the 1970s, partly in response to the revelations of *Murozumi et al.* [1969]. However, for the period 1980–1990, trends in Pb isotopic composition became more difficult to

interpret because industrial non-U.S. Pb sources became relatively more important and combined in an increasingly complex mixture, and average regional isotopic signatures changed over the course of the decade [*Grousset et al.*, 1994]. In addition, decreases in gasoline Pb emissions from a number of European countries, implemented mostly during the 1980s, meant that the Northern Hemisphere atmospheric Pb decrease could no longer be attributed solely to U.S. policy changes. The strong seasonality of Pb concentrations [*Boyle et al.*, 1994] suggests that Pb sources and/or atmospheric transport change seasonally and that the mean annual deposition source is strongly influenced by sources prevailing during concentration peaks. The possibilities for aliasing of the Pb isotope record suggest that there is a need for more high-resolution records before conclusions are drawn regarding the relative importance of Pb source regions to the hemispheric troposphere.

[5] The deposition history of metals other than Pb is less thoroughly documented. Existing records suggest that the metal with the most dynamic recent history of tropospheric concentration, after Pb, is Cd [*Candelone et al.*, 1995; *Hong et al.*, 1997]. *Candelone et al.* [1995] compiled Cd data from central Greenland, suggesting an eightfold increase between  $\sim 1850$  and 1970, with an approximately twofold decrease from 1970 to 1992. The increase and subsequent decrease were argued to result from the growth of the nonferrous metals industry, followed by substantial emissions abatement programs in several Northern Hemisphere countries. However, the available data show considerable scatter and are, for the most part, discontinuous. The order of magnitude seasonal and interannual variations recorded for Pb in this location [*Boyle et al.*, 1994] suggest that similar variations for Cd could generate significant aliasing in a discontinuous record.



[6] In the present study, we seek to expand our understanding of recent variations in Pb and Cd deposition in Greenland. First, we present a 10-year record showing seasonal and interannual variations in Cd deposition in the 1981–1990 time series for which seasonality in Pb concentrations was previously reported [Boyle *et al.*, 1994]. Second, we report Pb isotope ratio data for a subset of samples in this time series. Finally, we present preliminary data for two intervals of high-resolution ice core samples, showing Pb and Cd deposition at Summit during the calendar years 1699–1700 and 1780–1788, and discuss these data in relation to previous reports of metals in Greenland ice samples of similar age.

## 2. Sampling and Analysis

[7] Sampling for this study was carried out near Summit, Greenland, during the summer of 1990 as part of the Greenland Ice Sheet Project (GISP2). Details of the procedures used for snow pit and firn core sampling, sample processing, and analysis for Pb have been presented elsewhere [Boyle *et al.*, 1994]. Therefore we present here only a brief description of these methods, augmented with details of procedures used for sampling the main GISP2 ice core, analysis of Cd, and processing and analysis for stable Pb isotopes.

[8] Snow pit sampling was carried out June 21–25, 1990, at the “ATM” site (72°20′N, 38°45′W, 3190-m altitude), ~30 km southwest of the main GISP2 camp [Dibb and Jaffrezo, 1997]. Briefly, a 6-m pit was excavated and sampled using a custom-fabricated horizontal box corer to collect two parallel continuous series (A and B) of samples 5 cm thick, providing 10–15 samples per year of deposition. Stringent anticontamination procedures were followed, including the use of full clean-room garb and careful acid precleaning of all tools and storage containers. Separate samples

were collected for analysis of  $\delta^{18}\text{O}$ , sulfate, and other major ions and organic acids.

[9] Approximately 1 km from the snow pit, a 108-m, 10.2-cm-diameter firn core was drilled using a solar-powered apparatus. Samples of this core were cleaned of exterior contamination using successive plastic scraper passes while suspending the core section in a manually operated polycarbonate horizontal lathe. Subsectioning resulted in 10–25 cm pieces, which were stored in acid-cleaned polyethylene bags identical to those used for snow pit sample storage.

[10] A 50-cm section of the dry-drilled main 13.2-cm-diameter GISP2 core (D core [Meese *et al.*, 1997]), centered at 95 m, was cleaned and subsectioned using techniques identical to those used for the firn core, with the following exceptions. An acid-cleaned commercially pure grade titanium scraper was used for the first cleaning pass, followed by two passes with acid-cleaned polycarbonate scrapers. This change was necessitated by the hardness of the ice below the firn-ice transition.

[11] Core samples were dated to  $\sim\pm 1$  year absolute age (108 m core) or  $\sim\pm 3$  months relative age (D core) by a combination of electrical conductivity measurement (ECM) identification of known volcanic eruptions [Taylor *et al.*, 1997; Zielinski *et al.*, 1997] and visual stratigraphy using annual summertime low-density bands [Alley *et al.*, 1997], respectively.

[12] Samples from all sources were melted in acid-cleaned polyethylene bags, transferred to acid-cleaned polyethylene sample bottles within a Class-100 clean bench, and acidified with 1 mL L<sup>-1</sup> of 16 N triple Vycor-distilled HNO<sub>3</sub> to prevent adsorptive loss of analyte. In the laboratory at the Massachusetts Institute of Technology (MIT), sample aliquots were concentrated  $\sim 100\times$  by subboiling evaporation in a clean air environment and



analyzed for Pb and Cd by graphite furnace atomic absorption spectroscopy using the method of standard additions. Precision for the analyses was  $\sim\pm 3\%$  for Pb and Cd, based on replicate analyses of a single concentrated solution. Overall precision was estimated conservatively at  $\sim\pm 10\%$ , based on results for replicate aliquots of a single sample carried through the procedure. Procedural blanks, generated by pouring deionized, distilled water into sample bags in the field and processing as per samples, gave  $\leq 5$  and  $\leq 0.8$  pmol kg<sup>-1</sup> for Pb and Cd, respectively, barely above the estimated detection limits of 2.5 and 0.7 pmol kg<sup>-1</sup>, contributing  $\leq 0.7$ –24% and 1.6–100% of sample concentrations for each metal ( $\leq 2.3\%$  and  $\leq 7.0\%$  of mean snow pit concentrations for Pb and Cd, respectively). Given the small relative magnitude of the blank and ambiguity as to its source, sample concentrations were not blank corrected. We believe the time series presented here are not affected significantly by procedural blanks. Snow pit data are recorded in Table 1.

### 2.1. Pb Isotope Determinations

[13] Lead isotopic composition was determined for selected samples by thermal ionization mass spectrometry (TIMS) in laboratories at Université Paul Sabatier, Toulouse, France, and University of Washington, Seattle, Washington (K.K.F.), and at MIT, Cambridge, Massachusetts (N.R.H.). Trace metal clean techniques and careful tracking of blanks were carried out throughout sample processing.

[14] In Toulouse and Seattle all manipulations involving exposure of the samples were performed in a high-efficiency particulate air (HEPA) filtered laminar flow bench within a clean laboratory. Infrared-heated closed Teflon perfluoroalkoxy (PFA) subboiling stills (Saville) were employed to concentrate 50- to 350-mL sample aliquots ( $\geq 2.0$  ng Pb). Highly

purified 22 M HF and 0.005 M H<sub>3</sub>PO<sub>4</sub> (100  $\mu$ L each) were added before evaporation to liberate any refractory detrital Pb and to ensure retention of Pb in a readily soluble form as the sample was dried to a small visible residue.

[15] Because direct loadings of these residues for TIMS analysis generated relatively unstable and weak ion beams at the Toulouse and Seattle laboratories, an anion exchange purification step based on published techniques was incorporated. Resins, reagents, and laboratory-ware were precleaned using established methods [Manhes *et al.*, 1982]. Columns were constructed from 2.3-cm lengths of 1.19-mm ID polyethylene catheter attached to 100- $\mu$ L pipette tip reservoirs. The free end of the catheter tubing was heated to produce a rounded rim which, by capillary action, enhances otherwise negligible flow through the narrow tubing (C. Gobel, personal communication, 1992). A small wad of Teflon wool was packed into the tubing that was then charged with 15  $\mu$ L (wet volume) of Dowex 1  $\times$  8 200–400 mesh strongly basic anion exchange resin (Fluka) in 50  $\mu$ L of 6 N HCl. The column was rinsed successively with 500  $\mu$ L 6 N HCl, 500  $\mu$ L 0.25 N HNO<sub>3</sub>, and 50  $\mu$ L of 0.5 N HBr, followed by sample loading and additional rinses of 50  $\mu$ L 0.5 N HBr and 100  $\mu$ L 0.4 N HCl. Lead was then eluted with 300  $\mu$ L 1.0 N HCl into a conical Teflon vial and taken to near dryness on a hot plate in the presence of 0.5  $\mu$ L of 0.05 M H<sub>3</sub>PO<sub>4</sub>. Column yields were  $92 \pm 2\%$  for up to 50 ng Pb as determined by Graphite Furnace Atomic Absorption (GFAA) analysis (Zeeman background correction) of eluants. Passage of 2.4 ng of the lead isotope standard reference material Standard Reference Material 981 from the National Institute for Standards and Technology (NIST SRM 981) through the purification procedure and TIMS determinations indicated quantitative column yields and undetectable



**Table 1.** Pb and Cd Data for 6-m Snow Pit at Summit, Greenland

Sample	Depth, cm	Pb, <sup>a</sup> pmol kg <sup>-1</sup>			Cd, <sup>a</sup> pmol kg <sup>-1</sup>		
		Series A	Series B	Mean A,B	Series A	Series B	Mean A,B
1	2.5	170.4	208.4	189.4	25.6	24.0	24.78
2	7.5	177.9	166.9	172.4	7.7	12.2	9.95
3	12.5	242.3	260.1	251.2	10.9	10.1	10.49
4	17.5	358.0	309.9	334.0	16.6	35.9	26.24
5	22.5	236.5	179.0	207.8	10.8	5.5	8.13
6	27.5	266.9	278.4	272.7	7.6		3.78
7	32.5	204.9	200.7	202.8	10.0	9.6	9.8
8	37.5	87.7	99.3	93.5	16.5	40.8	28.7
9	42.5	62.5	49.6, 99.8	70.6	3.0	3.2, 9.0	7.6
10	47.5	99.0	92.6, 81.7	91.1	4.0	9.6, 11.5	12.6
11	52.5	103.3	93.4	98.4	3.2	4.2	3.7
12	57.5	117.8	139.9	128.9	6.0	19.8	12.9
13	62.5	145.7	166.9	156.3	7.9	11.2	9.6
14	67.5	148.9	160.0	154.4	10.3	14.7	12.5
15	72.5	89.2	106.9	98.1	12.1	8.7	10.4
16	77.5	70.2	135.9	103.0	10.0	11.4	10.7
17	82.5	274.9	209.5	242.2	12.2	15.1	13.6
18	87.5	726.3	558.2	642.3	26.0	21.9	23.9
19	92.5	485.9	334.4	410.2	20.8	20.1	20.4
20	97.5	102.3	89.2	95.8	3.7	8.8	6.3
21	102.5	102.8		102.8	9.9		9.9
22	107.5	122.2		122.2	7.1		7.1
23	112.5	77.1		77.1	6.6		6.6
24	117.5	143.8		143.8	4.8		4.8
25	122.5	148.4		148.4	8.6		8.6
26	127.5	72.7		72.7	6.3		6.3
27	132.5	66.0		66.0	3.8		3.8
28	137.5	21.1		21.1	2.9		2.9
29	142.5	189.3		189.3	8.5		8.5
30	147.5	64.0		64.0	5.8		5.8
31	152.5	135.2		135.2	10.6		10.6
32	157.5	461.1		461.1	18.9		18.9
33	162.5	383.2		383.2	20.1		20.1
34	167.5	266.8		266.8	12.7		12.7
35	172.5	95.4		95.4	5.7		5.7
36	177.5	188.8		188.8	11.4		11.4
37	182.5	130.2		130.2	7.2		7.2
38	187.5	40.3		40.3	5.7		5.7
39	192.5	94.2		94.2	5.6		5.6
40	197.5	89.7		89.7	4.3		4.3
41	202.5	228.0		228.0	35.0 <sup>b</sup>		
42	207.5	157.1		157.1	11.6		11.6
43	212.5	238.7		238.7	13.4		13.4
44	217.5	161.6		161.6	10.9		10.9
45	222.5	111.7		111.7	8.7		8.7
46	227.5	229.4		229.4	13.3		13.3
47	232.5	760.2		760.2	40.3		40.3
48	237.5	763.1		763.1	38.5		38.5
49	242.5	175.8		175.8	12.0		12.0

**Table 1.** (continued)

Sample	Depth, cm	Pb, <sup>a</sup> pmol kg <sup>-1</sup>			Cd, <sup>a</sup> pmol kg <sup>-1</sup>		
		Series A	Series B	Mean A,B	Series A	Series B	Mean A,B
50	247.5	81.3		81.3	17.6		17.6
51	252.5	39.0		39.0	7.5		7.5
52	257.5	29.3		29.3	9.9		9.9
53	262.5	88.7		88.7	23.0		23.0
54	267.5	82.0		82.0	10.7		10.7
55	272.5	130.4		130.4	4.21		4.2
56	lost						
57	282.5	77.2		77.2	5.21		5.2
58	287.5	60.9	53.5	57.2	8.63		8.7
59	292.5	138.0		137.7	8.31		8.3
60	297.5	332.5		332.5	12.95		12.9
61	302.5	217.8		217.8	6.94		6.9
62	307.5	175.2		175.2	6.13		6.1
63	312.5	216.3		216.3	11.03		11.0
64	317.5	71.0		71.0	3.99		4.0
65	322.5	133.5		133.5	1.6		1.6
66	327.5	163.6		163.6	14.6		14.6
67	lost						
68	lost						
69	342.5	229.2		229.2	6.7		6.7
70	347.5	385.7		385.7	17.2		17.2
71	352.5	304.6		304.6	25.2		25.2
72	357.5	328.3		328.3	12.8		12.8
73	362.5	476.7		476.7	10.6		10.6
74	367.5	99.6		99.6	1.8		1.8
75	372.5	165.9		165.9	4.3		4.3
76	377.5	264.2		264.2	7.3		7.3
77	382.5	229.4		229.4	7.6		7.6
78	387.5	227.2		227.2	5.5		5.5
79	392.5	275.7		275.7	8.0		8.0
80	397.5	1339.4 <sup>b</sup>			28.4 <sup>b</sup>		
81	402.5	296.9		296.9	51.8 <sup>b</sup>		
82	407.5	377.5		377.5	11.2		11.2
83	412.5	429.4		429.4	12.7		12.7
84	417.5	393.2		393.2	9.9		9.9
85	422.5	345.0		345.0	15.0		15.0
86	427.5	285.4		285.4	15.7		15.7
87	432.5	180.3		180.3	6.0		6.0
88	437.5	209.8		209.8	5.1		5.1
89	442.5	113.3		113.3	1.1		1.1
90	447.5	96.0		96.0	0.8		0.8
91	452.5	277.6		277.6	5.8		5.8
92	457.5	222.1		222.1	4.4		4.4
93	462.5	76.6		76.6	4.6		4.6
94	467.5	24.8		24.8	2.3		2.3
95	472.5	54.6		54.6	4.9		4.9
96	477.5	390.8		390.8	13.1		13.1
97	482.5	113.0		113.0	16.8		16.8
98	487.5	153.3		153.3	17.0	13.3	15.1
99	492.5	111.9	767.3	111.9	17.4	20.5	18.9
100	497.5	311.0	399.7	355.4	14.7	16.9	15.8

**Table 1.** (continued)

Sample	Depth, cm	Pb, <sup>a</sup> pmol kg <sup>-1</sup>			Cd, <sup>a</sup> pmol kg <sup>-1</sup>		
		Series A	Series B	Mean A,B	Series A	Series B	Mean A,B
101	502.5	127.0	130.9	129.0	11.6	7.6	9.6
102	507.5	70.4	76.1	73.2	6.4	3.1	4.8
103	512.5	467.2		467.2	62.2 <sup>b</sup>	17.7	17.7
104	517.5	477.4	469.6	473.5	63.8 <sup>b</sup>	15.6	15.6
105	522.5	330.2	374.7	352.4	31.8 <sup>b</sup>	22.1	22.1
106	527.5	196.2	147.2	171.7	26.0 <sup>b</sup>	11.7	11.7
107	532.5	257.6		257.6	32.4 <sup>b</sup>	19.4	19.4
108	537.5	2046.1 <sup>b</sup>	5765.3		68.9 <sup>b</sup>	50.9	50.9
109	542.5	507.4	484.7	496.1	30.2 <sup>b</sup>	12.2	12.2
110	547.5	505.4	447.0	476.2	24.6 <sup>b</sup>	8.5	8.5
111	552.5		256.2	256.2	35.4 <sup>b</sup>	7.6	7.6
112	557.5	140.6	111.3	126.0		2.7	2.7
113	562.5	135.6	122.7	129.2	5.89	5.3	5.6
114	567.5	500.9	578.2	539.6	17.0	16.0	16.5
115	572.5	40.6, 45.2	44.6	43.5	11.78	4.3	8.1
116	577.5	134.2	129.1	131.6	6.4	5.0	5.7
117	582.5		204.5	204.5		4.8	4.8
118	587.5		1063.4	531.7	23.6	24.0	23.8
119	592.5	526.6	508.2	517.4	21.2	19.4	20.3

<sup>a</sup> Paired concentrations indicate individual analyses of separate aliquots from a single sample bottle.

<sup>b</sup> Contaminated sample, not plotted or included in mean concentration for this depth.

blank contributions. However, yields may have been more variable for actual samples as discussed below.

[16] The purified sample was redissolved in 2  $\mu\text{L}$  of 2.3 g Si L<sup>-1</sup> solution (see *Manhes et al.* [1982] for Si-gel solution preparation) and deposited on a zone-refined, high-purity Re filament in small aliquots. Isotope ratios were determined on a Finnegan 261 (Université Paul Sabatier, Toulouse, France) or VG Sector (University of Washington, Seattle, Washington) multicollector mass spectrometer. Cryogenic improvement of the vacuum proved essential on both instruments to maximize signal strength and minimize molecular interferences at the low ion beam currents encountered. Although treated standards gave sufficiently strong and stable beams to allow simultaneous collection of all Pb isotope signals in multiple Faraday cups (i.e., 0.2 V on

<sup>206</sup>Pb for a 1 ng load of NIST 981), sample beam strength proved less predictable. This may have resulted from the presence of variable sample sulfate, which has a higher affinity for the resin than Br<sup>-</sup> (Bio-Rad Laboratories), and may have exceeded the ion exchange capacity of the columns (0.03  $\mu\text{mol}$ ), resulting in coelution with Pb. When possible, sample ratios were determined using multiple Faraday collectors; otherwise, the magnetic field was adjusted to position the isotopes sequentially on the electron multiplier or Daly collector of the respective instruments. The modes of operation used were calibrated for each sample suite using the lead isotope standard NIST 981. Ratios were corrected for mass fractionation based on the accepted values for NIST 981, as reported by *Hamelin et al.* [1985], with a mass fractionation factor of 0.10+/-0.03% amu<sup>-1</sup>, equivalent within error for both instruments.



[17] The procedure used for Pb isotope determinations at MIT differed somewhat from that used at Toulouse/Seattle. Samples were evaporated in 120-mL Teflon beakers (50 mm × 66 mm diameter) with threaded tops. Following cleaning steps in hot HCl, HNO<sub>3</sub>, and HF, beakers were stored in HCl until use. Using Pb concentrations previously determined as described above, snow samples were weighed out to obtain at least 1 ng of total Pb. Samples were then spiked with <sup>205</sup>Pb and dried down with a drop of phosphoric acid, loaded on single rhenium filaments with silica gel and phosphoric acid, and analyzed on a VG Sector-54 thermal ionization mass spectrometer. On the basis of preliminary attempts to analyze the isotopic composition of samples prepared in this manner, it was decided that sample purification was necessary before loading because major ion constituents inhibited ionization. Samples were therefore dried down, and 2 to 3 drops of 3N HCl were immediately added prior to loading onto ion exchange columns. The column chemistry used was developed for zircons [after Krogh, 1973] but is suitable for separating Pb from the snow samples. The procedure uses very little acid and therefore introduces negligible Pb blank (<1 pg). After collecting the Pb eluant, samples were dried down, loaded onto filaments, and analyzed as above. Some samples were large enough to be analyzed in multicollector mode using the Faraday collectors. Smaller samples had to be run using the Daly collector. Mass fractionation corrections determined by analysis of NIST 981 were  $0.12 \pm 0.03$  ‰ amu<sup>-1</sup> for the Faraday and  $0.15 \pm 0.03$  amu<sup>-1</sup> for the Daly collectors.

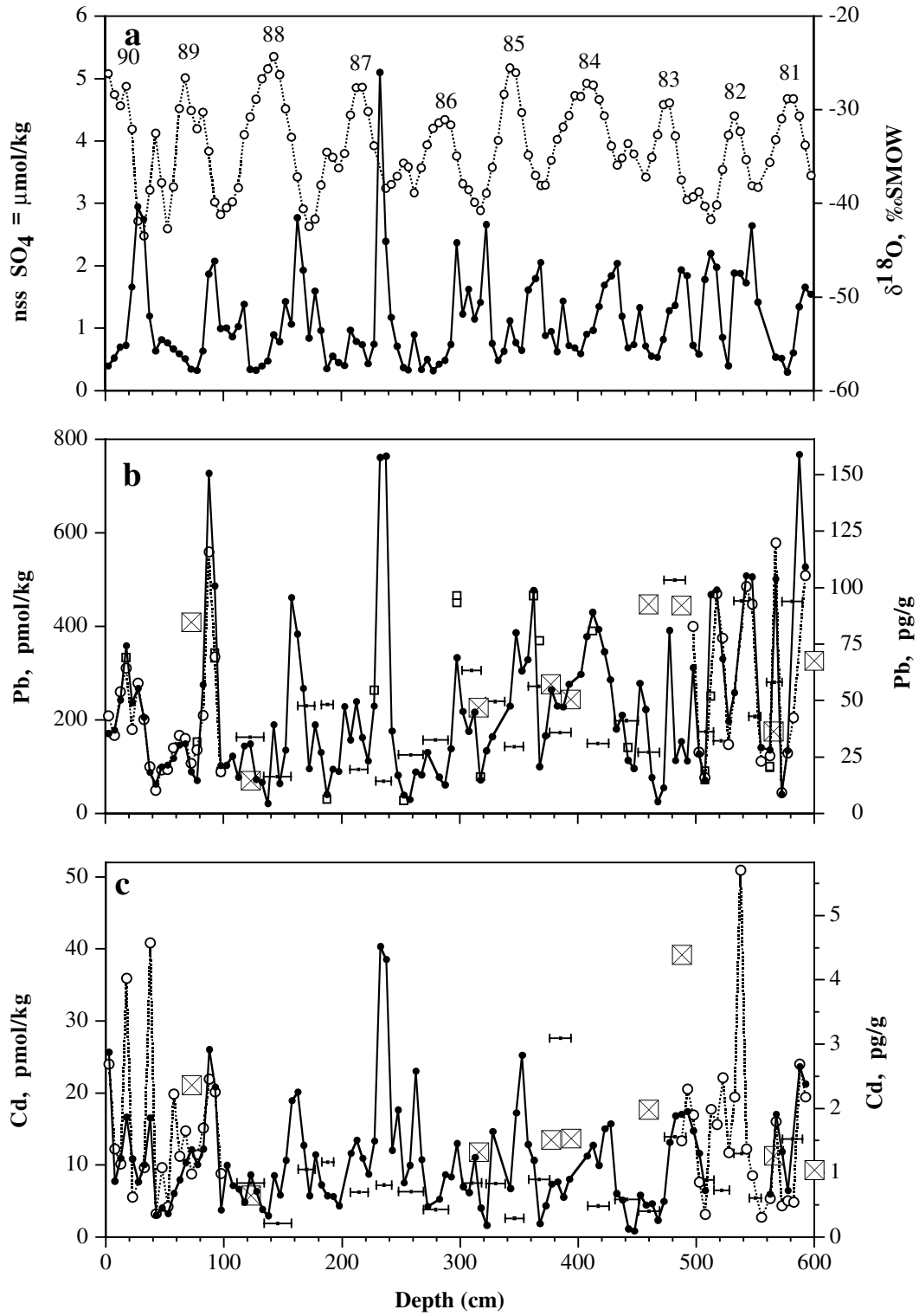
[18] Blanks associated with the evaporation procedure were determined by weighing out 20–50 mL of ultra pure water (blank estimated at 0.5–0.9 pg Pb mL<sup>-1</sup>), spiking with <sup>205</sup>Pb and drying down with a drop of phosphoric acid on a hot plate under a laminar flow hood. Pb was loaded on rhenium filaments as above

and isotopic composition was determined using a Daly detector in ion-counting mode. Blanks were very consistent on all beakers and ranged from 0.4 to 0.9 pg mL<sup>-1</sup> of water. These measured blanks are lower than or comparable to the MIT laboratory's previous blank measurements. Therefore it was concluded that the Pb blank associated with evaporation in the beakers was negligible.

[19] The atomic absorption analyses of blanks associated with the original bags in which the samples were melted suggest that these procedural blanks are larger than any contributed during laboratory manipulations. Still, the maximum 5 pmol kg<sup>-1</sup> blank, if assumed composed of typical N. American Pb (<sup>206</sup>Pb/<sup>207</sup>Pb = 1.21), would cause an error of only 0.003 in the determined <sup>206</sup>Pb/<sup>207</sup>Pb value for a typical European-dominated sample (1.15) with Pb concentration of 100 pmol kg<sup>-1</sup>. Thus we estimate that blank contributions are insignificant to the determined isotopic ratios at typical measurement precision.

### 3. Seasonal Variability in Pb and Cd Deposition

[20] Lead and cadmium concentrations in the snow pit samples varied widely, from 21 to 770 pmol kg<sup>-1</sup> and 0.8 to 51 pmol kg<sup>-1</sup>, respectively (Figures 1b and 1c). These concentrations are within the range of other reliable Pb and Cd measurements in individual fresh snow samples or short (1–2 year) sequences of recent snow deposits at nearby Summit locations [Boutron *et al.*, 1991; Candelone *et al.*, 1996; Gorlach and Boutron, 1990; Savarino *et al.*, 1994]. This similarity and, more importantly, the agreement of metal concentrations determined for the dual parallel series of samples in our pit (Figures 1b and 1c) lend confidence to our assertion that no significant contamination occurred during sampling. For Pb the uppermost 20 samples of each series agree within an



**Table 2.** Pb Isotopic Composition for Selected Snow Pit Samples (Series B), Analyzed at Independent Laboratories

Sample	Pb, <sup>a</sup> pmol kg <sup>-1</sup>	Analyses at MIT (N.R.H.)				Analyses at Toulouse/Seattle (K.K.F.)			
		206/207	2-σ	208/207	2-σ	206/207	2-σ	208/207	2-σ
2						1.153	0.004	2.432	0.008
4	333.3	1.183	0.005	2.441	0.012				
16	153.3	1.153	0.004	2.429	0.012	1.151	0.005	2.424	0.008
17						1.148	0.004	2.429	0.003
19	343.1	1.154	0.003	2.436	0.008		0.007		0.016
19	332.7	1.154	0.004	2.435	0.010	1.154	0.002	2.433	0.003
20	90.0	1.163	0.003	2.443	0.008	1.170	0.009	2.450	0.022
32						1.145	0.005	2.420	0.012
38	30.6	1.163	0.008	2.436	0.018				
47						1.157	0.006	2.436	0.007
46	264.0	1.159	0.015	2.441	0.034				
51	27.8	1.162	0.004	2.434	0.009				
60	451.1	1.141	0.006	2.420	0.015				
60	465.8	1.141	0.004	2.421	0.011				
64	78.7	1.167	0.003	2.433	0.008				
73	466.1	1.179	0.008	2.459	0.017				
73	465.3	1.179	0.003	2.460	0.005				
74	369.2	1.171	0.007	2.451	0.016				
83	390.2	1.153	0.004	2.422	0.011				
89	141.3	1.180	0.005	2.439	0.012				
102	90.7	1.183	0.006	2.441	0.014				
102	72.4	1.185	0.007	2.441	0.017				
103	251.3	1.172	0.012	2.438	0.028				
113	98.4	1.180	0.005	2.435	0.010				
113	100.8	1.181	0.010	2.436	0.022				
118						1.156	0.0003	2.430	0.001

<sup>a</sup> Determined at MIT by isotope dilution mass spectrometry.

average of 9% difference about the mean, about the same as overall measurement precision. Anomalously high Pb values for five samples and Cd values for six samples were discarded as contaminated; these usually were for samples taken from a “shelf” in the pit wall that was exposed during overnight breaks in the sampling sequence. Freedom from contamination during subsequent sample processing and

analysis is demonstrated by reproducibility, within stated precision, of analyses of replicate sample aliquots. Analyses of separate aliquots of the same samples by GFAA and ID-TIMS showed that the two methods gave the same Pb concentration, within measurement precision (Tables 1 and 2). This data set (including Pb data reported previously by *Boyle et al.* [1994]) constitutes the first continuous >2-year record

**Figure 1.** Chemical data, 0–6 m depth near Summit: (a)  $\delta^{18}\text{O}$  (open circles, dotted line, with years indicated at summer maxima; data of P. Grootes) and non-sea-salt sulfate (nss  $\text{SO}_4$ ,  $\mu\text{mol kg}^{-1}$  is correction of  $\mu\text{e}\mu\text{g kg}^{-1}$  in Figure 5 of *Boyle et al.* [1994]; data of S. Whitlow and P. Mayewski); (b) Pb data: snow pit sample series A (closed circles, solid line) and series B (open circles, dotted line); firn core 1–6 m interval (bars showing length of each sample interval); core data of *Boutron et al.* [1991], converted to present depth scale from timescale assuming linear accumulation between  $\delta^{18}\text{O}$  peaks (boxed crosses); (c) Cd data (symbols as in Figure 1b).



of subseasonal deposition variability for trace metals in glacial snow.

[21] The principal feature evident in the 10-year record is a regular pattern of coherent Pb and Cd concentration maxima superimposed on background levels roughly an order of magnitude lower (Figure 1). Comparison of these peaks to the parallel record of temperature-dependent  $\delta^{18}\text{O}$  cycles in the snow shows the Pb and Cd peaks to be annual features occurring without exception during the increase of  $\delta^{18}\text{O}$  from winter minima to summer maxima. Trace metal and sulfate peak shapes are quite sharp in the upper 3 m of the pit, the maxima extending over an interval of 10–15 cm and possibly corresponding to a single precipitation event. Before 1986, the peaks are wider and shorter. Peak height attenuation is an expected result of decreased temporal resolution caused by sampling a compacted snow column at a constant depth interval, but the increased peak width appears to be a real effect, with 1983–1985 sulfate maxima extending over 20–30 cm.

[22] The Pb and Cd peaks are strongly coherent with non-sea-salt sulfate, which is believed to be largely anthropogenic [Mayewski *et al.*, 1990; Neftel *et al.*, 1985]. This is especially evident in the upper 290 cm of the pit, where trace metal and sulfate samples were collected in contiguous series [Boyle *et al.*, 1994] (Figure 1). The coherence is weaker at greater depths, where trace metal and sulfate samples were separated laterally by 25–85 cm; lateral heterogeneity in snow accumulation and postdepositional ablation or drifting can produce discontinuous and nonhorizontal layering [Dibb, 1989; Wolff *et al.*, 1998; R. Alley, personal communication, 1991], which complicates comparison of fine-scale features in records collected even centimeters apart. The similarity of the trace metal input timing with that of sulfate is not surprising, because all three species are derived principally from anthropo-

genic sources at lower latitudes and altitudes and because submicron sulfate particles constitute a major fraction of the total aerosol over the Greenland ice sheet in spring [Dibb and Jaffrezo, 1997]. However, this record of trace metals in Arctic snow is of sufficient length and sampling resolution to quantify the amplitude, constrain the precise timing, and investigate interannual variability of the seasonal deposition spikes.

[23] It is clear that the trace metal and sulfate peaks occur in spring (i.e., after the  $\delta^{18}\text{O}$  minimum) of every year sampled, but it is not possible to specify the month of maximum deposition flux because (1) the timing of the  $\delta^{18}\text{O}$  rise is not precisely known, (2) seasonal variations in snow accumulation, while thought to favor spring and summer by a modest margin, are not well understood [Arsenault *et al.*, 1998], (3) drifting and ablation can result in seasonal loss of accumulated snow and significant postdepositional mixing, decoupling precipitation timing from accumulation timing in firn records [Hawley and Albert, 1998]. It should also be noted that temporal peaks in aerosol metal concentrations over the sampling site may not be recorded if precipitation does not co-occur. More precise input timing would help to constrain source regions of anthropogenic element inputs. A better understanding of aerosol concentrations and their relationship to year-round accumulated snow composition should result from recent and planned over-winter occupations of Summit [Dibb *et al.*, 1998].

[24] Other snow pit and shallow core trace metal records from the Summit region have suggested a late-spring peak in Pb and Cd (as well as Cu and Zn) but also indicated a secondary summer peak, which we do not observe. These published records are only 1–2 years long, however, and show the summer peaks in 1990 [Savarino *et al.*, 1994] and 1991 [Candelone *et al.*, 1996] after our occupation. We

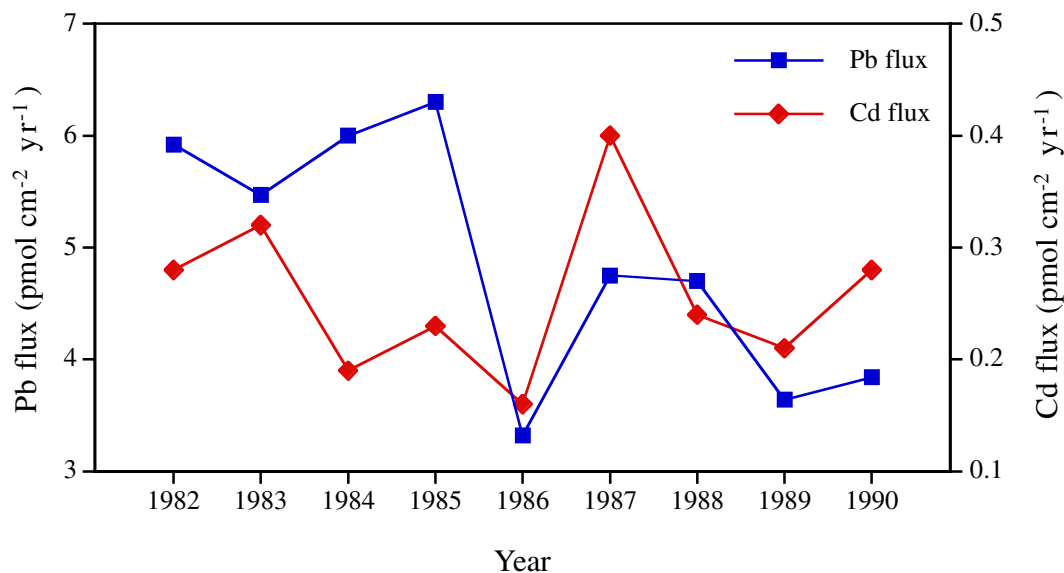
therefore focus our attention on likely sources for the spring concentration peak and whether these sources are different from those supplying the lower concentration accumulation during the rest of the year.

[25] Air mass trajectories can provide insight into likely source regions during different seasons, although the data employed are generally not sufficient for adequately resolving vertical air movements. For Summit, climatological 10-day backward air mass trajectories show significant fractions from North American, North Pacific, and East Asian regions for all seasons at the 500-hPa pressure altitude but suggest that vigorous wintertime circulation brings air masses from Asia or Europe 67% of the time [Kahl *et al.*, 1997]. For the 700-hPa altitude, also thought to influence transport to Summit, North American sources appear to dominate (70–85%) trajectories in all seasons. European sources for 10-day-old air masses are rare (<10%) at either altitude. The transport dynamics were found to be roughly comparable to those determined from 5-day trajectories to Dye 3 in southern Greenland [Davidson *et al.*, 1993]. Hence it is useful to compare our snow record to data collected at Dye 3.

[26] As in the Summit deposition record, boundary layer aerosol sulfate concentrations during 1988–1989 at Dye 3 also show a maximum in spring, with the highest concentration events occurring in April [Davidson, 1993]. Secondary sulfate maxima were observed in fall 1988 at Dye 3 and were attributed primarily to transport from North America. Our Summit record shows hints of fall peaks for sulfate in most years, although these are restricted to single points with the exception of peaks occurring just before the  $\delta^{18}\text{O}$  minima in 1982, 1985, and 1988. No fall peaks are clearly defined in the Summit trace metal data. Pb concentrations in fresh snow collected over the same period also peaked during April pre-

cipitation events, confirming earlier evidence for a spring metals peak at Dye 3 [Wolff and Peel, 1988], although high levels were also seen in June snow. Similar maxima were seen for Cd, although the June snow events were more concentrated in this element [Boutron *et al.*, 1993]. Thus a limited data set indicates approximate coincidence of the input timing to the two sites.

[27] In comparing chemical records to modeled air mass trajectories it is important to realize that the relative importance of sources contributing to snow pit–recorded deposition fluxes depends on both favorable transport dynamics and on chemical concentrations in the source regions. For example, North American trajectories may carry relatively little signature of elevated U.S. anthropogenic sources if source regions are limited to northern Canada. Conversely, trajectories passing over the Arctic Basin may carry substantial pollutant aerosol loads if springtime mixing of air masses from lower altitudes carries Arctic haze aerosols to Summit. The Arctic haze associated anthropogenic aerosols are most concentrated in the Arctic Basin between January and April at <2.5-km altitude [Raatz, 1985] owing to wintertime accumulation [Barrie and Barrie, 1990; Nriagu *et al.*, 1991]. The coincidence of vertical transport and scavenging by spring snowfall [Bergin *et al.*, 1995] could constitute an important springtime source of metals and sulfate to Summit snow. If so, then a significant portion of the Pb and Cd is derived from the sources that contribute most to the Arctic haze, thought to be largely Eurasian inputs [Barrie and Barrie, 1990; Nriagu *et al.*, 1991]. Distinguishing Arctic Basin sources from other long-range metals sources, with seasonal resolution, will help determine whether snow accumulation at Summit faithfully records changes in the composition of the average hemispheric free troposphere [Boutron *et al.*, 1995; Candelone *et al.*,



**Figure 2.** Annually averaged Pb and Cd flux variations for year ending in summer ( $\delta^{18}\text{O}$  maxima) of year indicated. Note interannual variability and lack of Pb-Cd coherence in first half of decade.

1995] or whether it constitutes an essentially regional record of inputs from a more geographically constrained high-latitude continental source. As explained further below, the present data do not fully resolve this question.

#### 4. Sources of Trace Metals in Central Greenland

##### 4.1. Dominance of Anthropogenic Pb and Cd

[28] The covariation between Pb, Cd, and  $\text{SO}_4^-$  concentrations implies that anthropogenic sources dominate for all three constituents. Estimates of the magnitude of natural Pb and Cd sources confirms that an overwhelming fraction of both metals is derived from human activities at lower latitudes. Allowing for the largest estimates of Pb/Na enrichment in bubble-produced aerosols from a pollutant Pb-enriched sea surface [Boyle *et al.*, 1986; Ng and Patterson, 1981], Na concentrations in our snow pit (M. J. Spencer and P. Mayewski,

personal communication, 1992) and other nearby sites [Whitlow *et al.*, 1992] imply that sea-salt aerosols cannot contribute significantly to even the lowest Pb concentration measured in the snow; similar considerations for Cd lead to upper limit estimates of mean sea-salt derived Cd [Patterson and Duce, 1991] equal to 0.2% of mean Cd in the snow pit. A gravimetric measurement of dust concentration (made by filtration at 0.4- $\mu\text{m}$  pore size) gave  $60 \pm 2 \mu\text{g kg}^{-1}$  for a 10 kg snow pit sample which integrated accumulation for calendar year 1982. More recent measurements of Al concentrations for a subset of our samples support this estimate, giving a mean calculated crustal dust concentration of  $73 \mu\text{g kg}^{-1}$  for the depth interval 125–310 cm, with strongly seasonal spring peaks nearly coincident with those of Pb and Cd (R. Sherrell, unpublished data, 1992), in agreement with previous seasonal studies [Candelone *et al.*, 1996]. Using average crustal concentrations of Pb, Cd, and Al [Wedepohl, 1995], these results suggest a mean crustal contribution to Pb of 3% (range 0.4–10%)



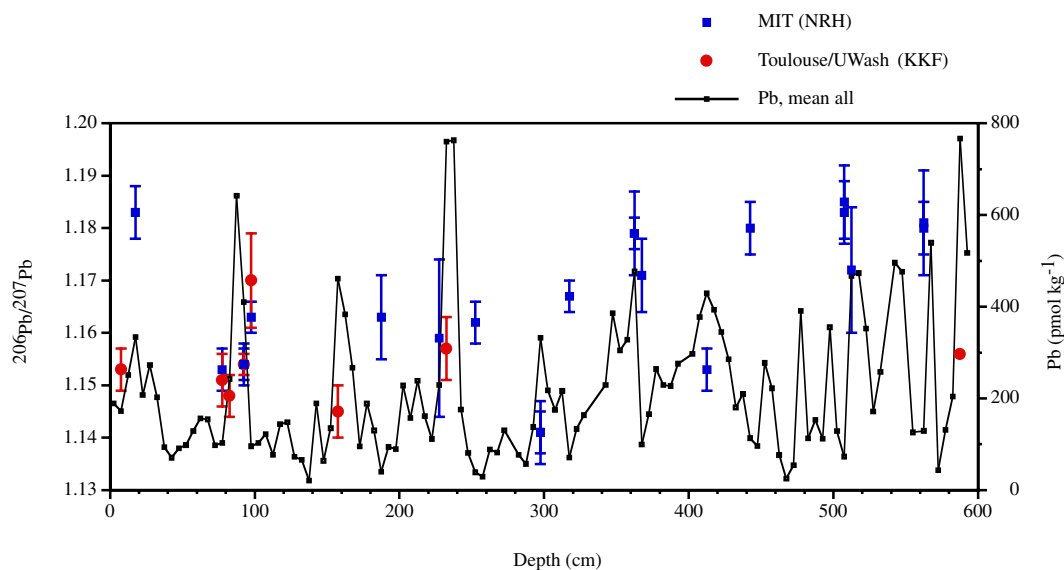
and to Cd of 0.7% (range 0.04–2.2%). These conclusions are consistent with previous estimates for Greenland snow [Boutron *et al.*, 1991; Candelone *et al.*, 1996; Murozumi *et al.*, 1969; Ng and Patterson, 1981; Savarino *et al.*, 1994]. Volcanic, forest fire, and biogenic Pb contributions are also probably minor [Candelone *et al.*, 1996; Nriagu, 1989a; Hinkley *et al.*, 1999]. Volcanic Cd emissions may be the largest single natural source to the atmosphere [Nriagu, 1989a; Hinkley *et al.*, 1999], but the time-averaged flux to this remote site is likely to be less than a few percent of the anthropogenic flux. Similar conclusions were reached for estimating sources to tropospheric aerosols over the remote North Pacific Ocean, where 93% of Cd was estimated to be of anthropogenic origin [Patterson and Duce, 1991]. Our determinations of Pb/Cd ratios ( $23.7 \pm 18.9 \text{ mol mol}^{-1}$  (1-sigma)) are similar to those observed in precipitation and aerosols collected at sea level in the North Atlantic and North Pacific [Church *et al.*, 1990; Jickells *et al.*, 1984; Patterson and Duce, 1991] despite our much lower absolute fluxes and indeed agree well with the global emissions ratio of  $\sim 24 \text{ mol mol}^{-1}$  in 1983 [Nriagu and Pacyna, 1988]. Thus, although the mean annual flux of Pb and Cd to Summit (Figure 2) in the 1980s is small compared to low-altitude, low-latitude sites (e.g.,  $<1\%$  of the flux derived from North American and European sources recorded at Bermuda in 1982 [Jickells *et al.*, 1984]), anthropogenic sources are overwhelmingly dominant and the observed deposition variations can be understood in terms of source strength and transport of mid-latitude anthropogenic inputs.

[29] A priority in this effort is to understand the source of the spring peak that accounts for  $\sim 50$  and 40% of the annual flux of Pb and Cd, respectively. Relationships between temporal chemical records in snow and source regions identified from modeled air mass trajectories are not generally straightforward [Davidson *et*

*al.*, 1993; Kahl *et al.*, 1997]. As well, the accuracy of backward trajectories beyond 2 days in the Arctic has been questioned (J. Merrill, personal communication, 1992), although multiyear mean seasonal climatology may be more reliable. In any case, synoptic meteorological modeling suggests that upper level Arctic haze found above the stable Arctic boundary layer (2.5 km) may be influenced by sources that are further south and have input timing that is distinct from sources that contribute to most of the lower-altitude haze [Iversen and Joranger, 1985; Raatz, 1991; Raatz *et al.*, 1985]. Given these considerations, it may be an oversimplification, for example, to consider the Pb record from near Camp Century, collected  $\sim 1000$  km north of Summit at 1890-m altitude, as an extension of the Summit record to earlier times [Boutron *et al.*, 1991]. Recent comparison of Pb concentrations at Summit and at Camp Century [Candelone *et al.*, 1995] show the Summit Pb concentrations to be substantially lower during the important period of increasing anthropogenic input from 1770 to 1970. In general, the utility of meteorological models for discerning source regions for spring Pb peaks from sources for low-Pb deposition during other seasons may be best evaluated with source-specific chemical signatures.

#### 4.2. Pb Isotope Ratios

[30] To investigate the variability of source regions for Pb deposition in central Greenland on seasonal to decadal timescales, we measured stable Pb isotope ratios in a subset of the snow pit samples (Table 2). Samples were selected from low and high Pb concentration samples representing the full decade of deposition. Significant temporal changes were observed in  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{207}\text{Pb}$ , with the  $^{206}\text{Pb}/^{207}\text{Pb}$  signatures showing larger variations relative to measurement error. Replication of analyses is good; three samples measured in Toulouse/Univer-



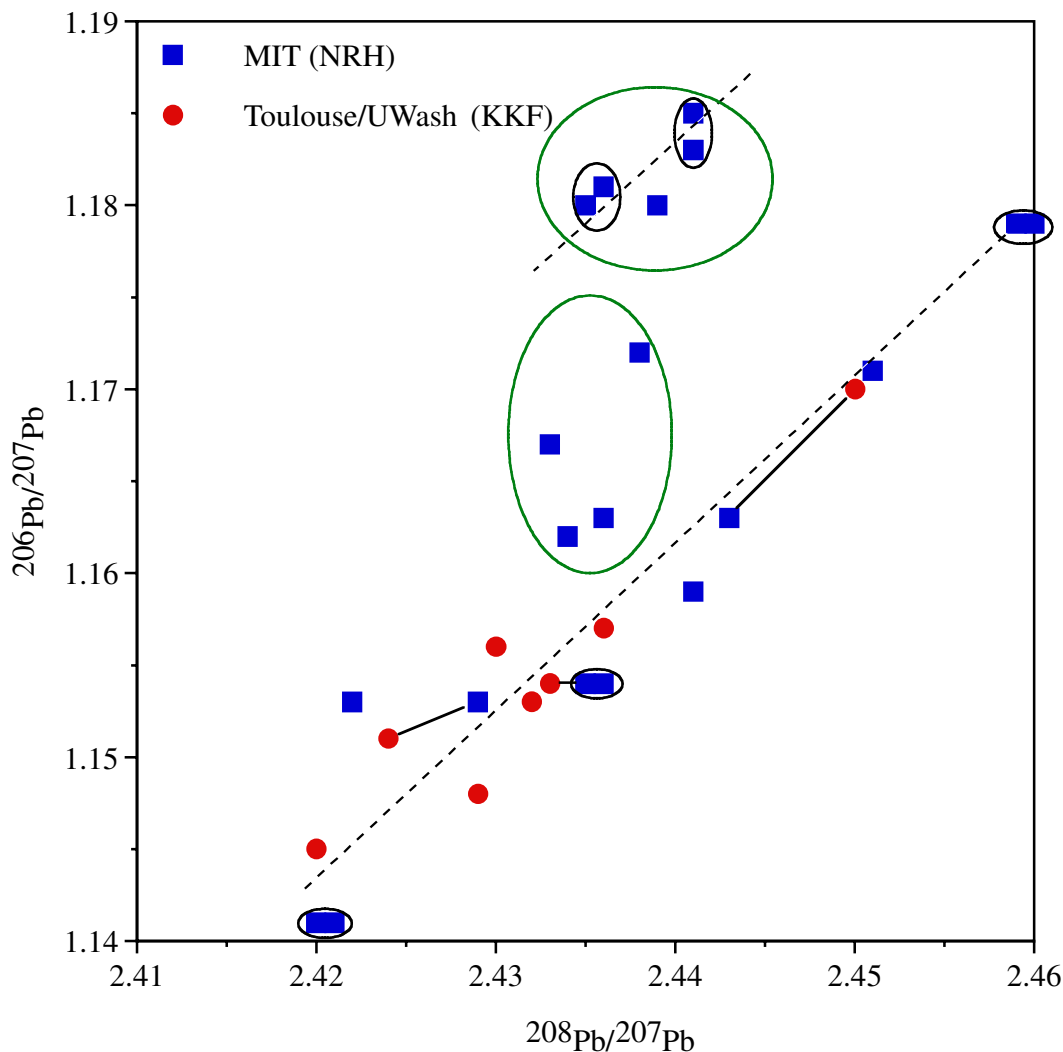
**Figure 3.** Isotopic composition ( $^{206}\text{Pb}/^{207}\text{Pb}$ ) and Pb concentration (mean of series A and B in Figure 1) versus depth in snow pit. Symbols indicate laboratories in which Pb isotope determinations were made, and paired symbols at a single depth denote independent processing and analysis of replicate aliquots of a single sample. Error bars are  $2\sigma$ , based on statistics for individual mass spectrometric analyses.

sity of Washington and later at MIT showed agreement within 2-sigma error (Table 2). Five samples were measured in duplicate at MIT, with a 2-year gap between analysis of duplicate pairs. These generally agreed to within 0.001 in each isotope ratio, several times better than the determined 2-sigma error.

[31] A quick perusal of the measured isotope ratios against time (or depth) suggests that a shift in Pb source occurred between the early and late portions of the decade. This is particularly evident in the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio trend (Figure 3). Plotting the ratios as an isotope-isotope plot shows that the isotope signatures do not all fall on a single mixing line but fall into two distinct mixing groups, suggesting a more complex combination of Pb sources (Figure 4). While the majority of data points, weighted somewhat

toward the latter portion of the decade, appear to fall on one mixing line, a separate cluster of points is clearly distinct and more radiogenic (higher  $^{206}\text{Pb}/^{207}\text{Pb}$ ) relative to this line, while a third “bridge” group connects this cluster to the middle of the main mixing line.

[32] The isotope signatures suggest influences of both secular changes in mean Pb source through the decade as well as seasonal changes correlated to Pb concentration. For example, the high- $^{206}\text{Pb}/^{207}\text{Pb}$  cluster corresponds to relatively low-Pb samples ( $\leq 141$   $\text{pmol kg}^{-1}$ ) deposited during 1981–1982. The main mixing line is defined by samples deposited after 1982, with five of eight samples corresponding to Pb concentration peaks of  $>300$   $\text{pmol kg}^{-1}$ . The bridge group of four points joining the more radiogenic cluster with the main mixing line corresponds to generally

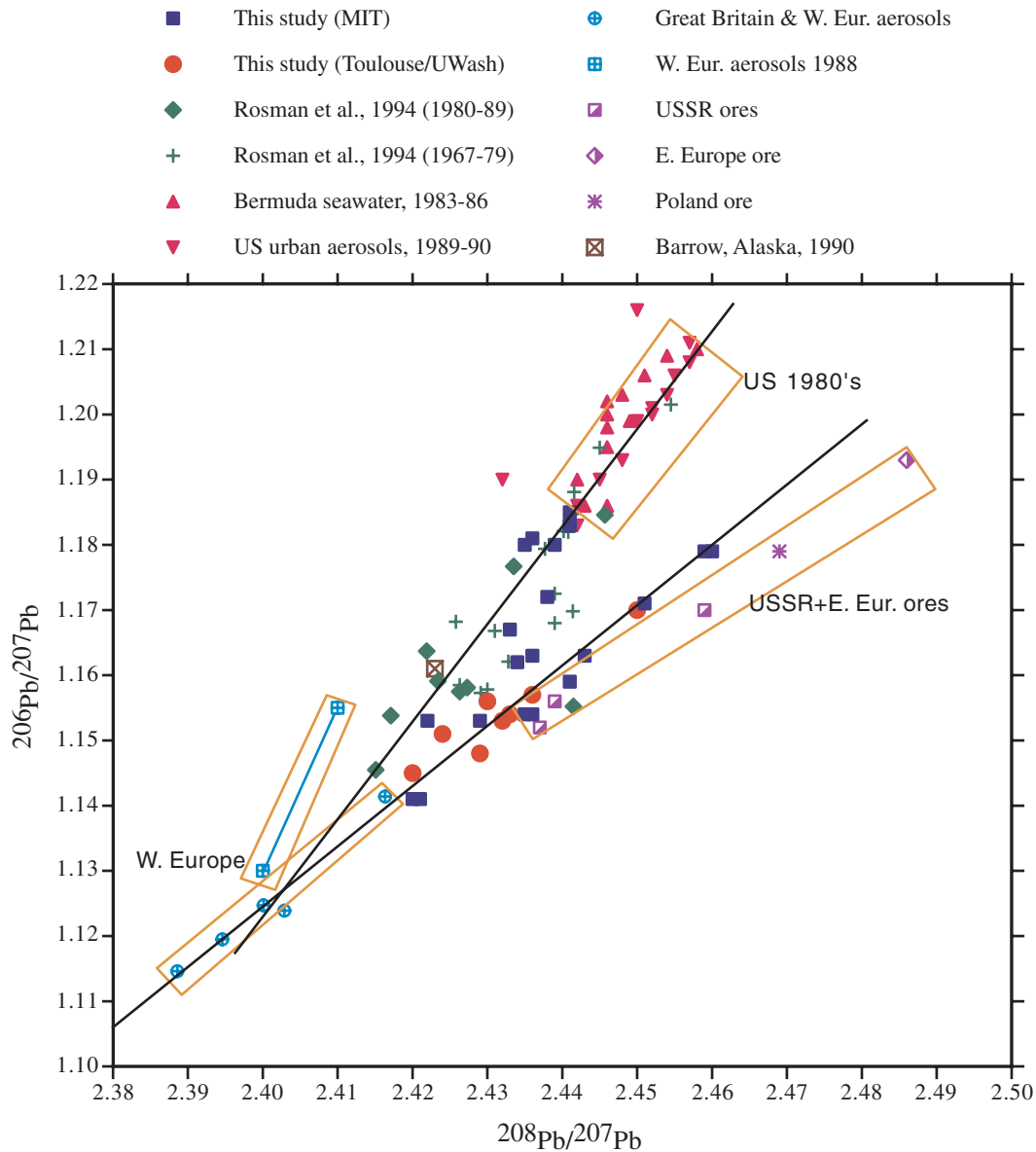


**Figure 4.** Pb isotopic composition for 6-m snow pit samples. Symbols as in Figure 3. Large ovals show anomalous high-206/207 group (top) and “bridge” group (bottom; see text). Small ovals surround replicate pairs of analyses of individual samples. Solid lines connect points for individual samples analyzed in separate laboratories. Dashed lines denote hypothetical Pb source mixing lines.

low Pb concentration samples deposited between 1982 and 1987. All samples from the high cluster and the bridge group correspond to Pb concentration minima, with the single exception of sample 103. In sum, signatures from low-Pb samples seem distinct from those at Pb peaks, but there is a suggestion as well that Pb sources in 1981–1982 are generally

distinct from those influencing deposition later in the decade. In the following, these results are interpreted with the goal of identifying pollutant Pb sources contributing to deposition at Summit over this period.

[33] The relative influence of U.S. versus various Eurasian sources can be estimated by



**Figure 5.** Snow pit Pb isotopic data (symbols as in Figure 3) on expanded isotope-isotope plot, compared with published shallow core data [Rosman et al., 1994] for the 1980s and for 1967–1980. Also plotted are values for Bermuda seawater [Shen and Boyle, 1988], for U.S. urban aerosols (R. Flegal, personal communication, 1993), for aerosols derived from sources in Great Britain and western Europe in 1992 [Véron and Church, 1997], for western European aerosols and ores from the former Soviet Union and eastern Europe [Hopper et al., 1991], and for mean Arctic haze aerosol sampled in 1990 in Barrow, Alaska [Sturges et al., 1993].



comparing the snow pit data to Pb isotope signatures of various pollutant and ore sources. (Figure 5). This isotope-isotope plot shows that the main mixing line, defined largely by Pb concentration peaks after 1982, is consistent with sources from the former Soviet Union and eastern Europe mixing with contributions from western Europe. The cluster of three samples from 1981 to 1982 fall on a separate mixing line defined by U.S. sources of the 1970s and 1980s, as recorded in late 1980s urban aerosols, in mid-1980s Bermuda surface seawater, and in pre-1980s snow from Summit [Rosman *et al.*, 1994]. Interestingly, this cluster is very similar to the isotopic signature of deep seawater off eastern Greenland, sampled in 1993 and estimated to have formed from surface waters roughly a decade earlier [Alleman *et al.*, 1999]. The bridge group appears to span these two distinct mixing lines. Thus the Pb peaks, especially after 1982, appear dominated by a mixture of European and Asian sources, while low-Pb samples deposited early in the decade, and to a lesser degree later in the decade, appear to be more influenced by U.S. sources.

[34] The new Pb isotope data can also be evaluated in comparison to previously published records of Pb isotopes in central Greenland. The earlier Pb isotope measurements, for a discontinuous sample set from two nearby Summit snow cores spanning 1967–1989, showed a broad peak in  $^{206}\text{Pb}/^{207}\text{Pb}$  in the late 1970s [Rosman *et al.*, 1993, 1994]. Rosman *et al.* [1994] used a linear isotopic mixing model, assuming a fixed Eurasian-Canadian isotopic signature for 1960–1988, to argue that the trend is consistent with a substantial but decreasing U.S. Pb component after  $\sim 1972$ . They attributed  $52 \pm 7\%$  of Pb deposition to U.S. sources in 1980, followed by a fourfold decrease in the flux of the U.S. component to  $25 \pm 7\%$  of total Pb by 1989. The data of Rosman *et al.*

[1994] for the 1980s largely fall along a line consistent with a significant U.S. source mixing with somewhat variable European sources, while in our data set, only the low-Pb pre-1982 samples show a significant U.S. source (Figures 3 and 5). The reasons for the discrepancy between the mixing lines defined by Rosman *et al.*'s [1993, 1994] data and the bulk of our data probably lie in the relationship between relatively sharp temporal variations in Pb source signature and the integration time determined by sample length; these issues are discussed further below.

[35] On the basis of documented changes in European and North American Pb emissions over the 1980s, we can construct a crude model with which to predict changes in Summit Pb isotope signature over the decade. Emissions data from eastern Europe and the former Soviet Union are difficult to obtain; we assume that the magnitude and isotopic signature of Pb from these source regions did not change over the decade. While there is potential for significant reductions in total emissions in Europe, where a large fraction of Pb input is attributed to relatively easily controlled automotive sources (estimated 76% of total in 1982 [Pacyna *et al.*, 1991]), only a few countries enacted reductions measures during the 1980s. West Germany, United Kingdom, France, Sweden, Norway, and Switzerland legislated some reductions in Pb content of gasoline prior to the late 1980s [Pacyna *et al.*, 1991], but the European Community did not legislate low-Pb gasoline ( $0.15\text{g Pb L}^{-1}$ ) until 1988–1989 [Dörr *et al.*, 1991; Migon *et al.*, 1993]. As an upper bound estimate, decreasing total Pb emissions from these five countries would have decreased total western European emissions by only 14% [Pacyna *et al.*, 1991]. Because the present and previously published data indicate that western European Pb sources were a relatively small fraction of total Eurasian sources to central Greenland, we con-



clude that changes in the magnitude of Pb sources from Eurasia as a whole were negligible over the decade.

[36] In contrast, changes in U.S. Pb emissions were substantial over the 1980s and were probably accompanied by a shift in mean isotope signature. We can estimate the magnitude of these changes, driven by reductions in gasoline Pb consumption, using published records of Pb concentrations and isotopic composition in annually banded Bermuda corals, which indicate that gasoline and industrial sources contributed about equally to U.S. Pb emissions in 1980 [Shen and Boyle, 1987]. Thus the nearly 10-fold decrease in U.S. gasoline Pb consumption during the 1980s [Nriagu, 1989b] must have resulted in a decrease of about twofold in total U.S. Pb emissions, assuming no change in the industrial source. Allowing for some uncertainty in this source analysis and for small decreases in industrial emissions over the period, a reasonable upper limit estimate of the change in total U.S. Pb gasoline plus industrial emissions for the decade is a factor of 3. If U.S. Pb contributed  $\sim 50\%$  of Summit deposition in 1980 as suggested by Rosman *et al.* [1993, 1994], the above assumptions imply that the decrease in total Pb flux would be only 25–33% for the decade. Such a decrease is barely detectable against short-term variability for subseasonally resolved continuous records [Boyle *et al.*, 1994] but is consistent with a simple least squares regression on our snow pit Pb concentration data, showing a decrease of 28–55% for the decade at the 95% confidence interval [Boyle *et al.*, 1994].

[37] Isotopic composition trends resulting from this change in U.S. Pb contribution would likely be small relative to short-term variability but would be measurable over the decade. Assuming  $^{206}\text{Pb}/^{207}\text{Pb} = 1.21$  for mean U.S. Pb [Church *et al.*, 1990; Patterson and Settle,

1987; Véron *et al.*, 1992, 1993] and 1.14 for Eurasia [Rosman *et al.*, 1993], Greenland  $^{206}\text{Pb}/^{207}\text{Pb}$  would change from 1.175 in 1980 to 1.158–1.163 in 1989. Corresponding changes would be observed for  $^{208}\text{Pb}/^{207}\text{Pb}$ . This decadal trend is roughly consistent with the small apparent trend in our data (Figure 3) and suggests that the 50% U.S. Pb component in 1980 [Rosman *et al.*, 1993] may be approximately correct. This limited range of values and the magnitude of seasonal and interannual variability during the decade means that quantification of changes in Pb sources during the 1980s is quite uncertain given any reasonable source trend scenario. Mean isotopic signatures for the source regions have likely also changed to some degree over the decade [Rosman *et al.*, 1994; Grousset *et al.*, 1994], and the mean western European signature is relatively poorly constrained [Hopper *et al.*, 1991], introducing further uncertainty. The U.S. isotopic signature is also geographically variable: note in Figure 5 that 1989–1990 aerosol data from different regions of the United States vary over a range of values similar to the temporal variations in Bermuda surface water during 1983–1986. A relative increase in the importance of industrial Pb may itself have introduced more variability in a U.S. endmember, since industrial sources are by nature more isotopically heterogeneous than gasoline Pb, and temporal trends are likely to be more regional [e.g., Chillrud *et al.*, 1999]. This exercise suggests that attempts to quantify the precise magnitude of any intradecadal trend in concentration [Boutron *et al.*, 1991] or source mixture [Rosman *et al.*, 1994] will be severely limited by high-frequency noise [Boyle *et al.*, 1994] and uncertainties in isotopic source signatures. A more prudent and fruitful approach may be to search for trends in well-established means for half-decade or decade intervals within longer records.

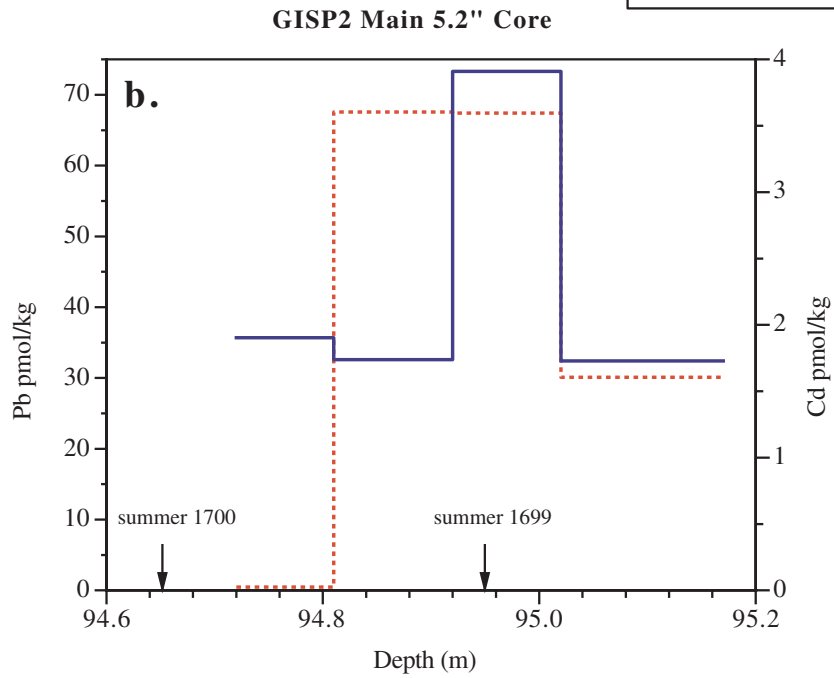
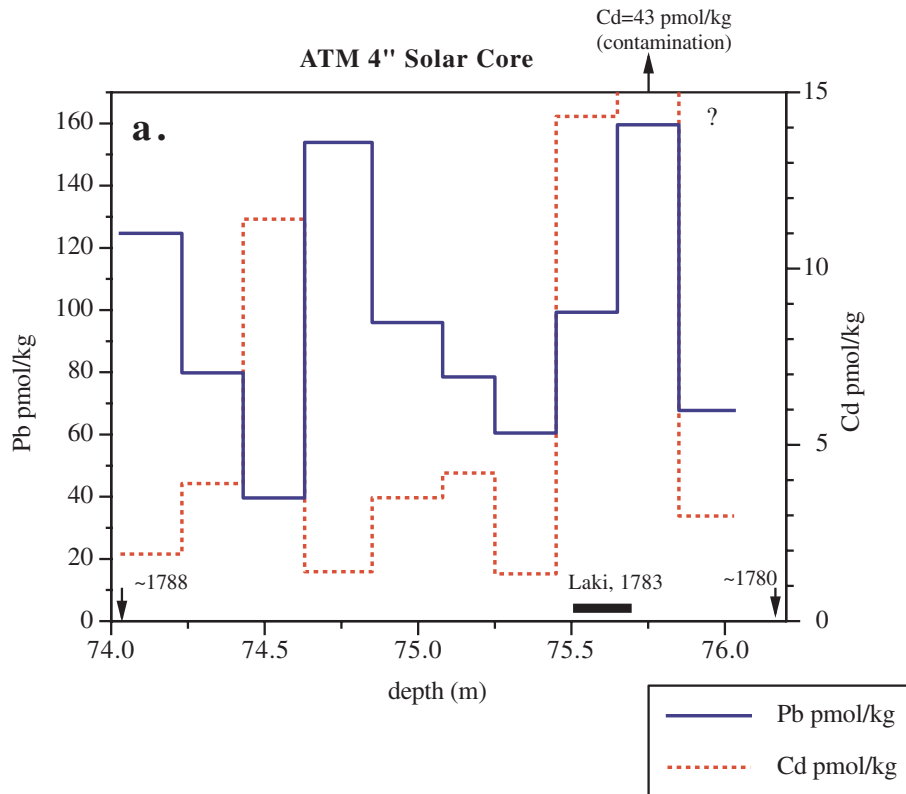
[38] Correlation of Pb isotopic signature with changes in Pb concentration, as seen in our



snow pit, suggests that a seasonal source variation may overlay decadal secular source changes. The present data, while limited in number, suggest that U.S.-influenced sources supply a significant fraction of Pb during low-Pb fall-winter periods, while Eurasian sources dominate the Pb peaks in spring. A possible explanation is that periodic short-term injections of pollutant rich low-latitude Arctic Basin air masses are mixed up to Summit altitude during late spring periods and are coincident with snow events often enough to provide sulfate- and Pb-rich snow accumulation. This is consistent with observations of elevated aerosol sulfate in spring over the Dye 3 site in southern Greenland [Davidson, 1993]. Because the winter-spring Arctic Basin air mass is a pollutant-rich and proximal aerosol source [Barrie and Barrie, 1990] only a few short-term events may provide inputs that are then smoothed by surface snow mixing [Hawley and Albert, 1998], producing consistent annual spring peaks in the snow pit. During the low-Pb summer-fall periods, air mass trajectories at 500-hPa cross North America more frequently [Kahl *et al.*, 1997] and transport of pollutant Pb from more distant U.S. sources may be enhanced. The climatological dominance of North America as the source of 10-day trajectories at 700-hPa for all seasons [Kahl *et al.*, 1997] is not reflected in a consistent U.S.-type Pb isotopic signature, perhaps because mean trajectories are over relatively unpopulated regions of Canada and do not intersect U.S. population centers. The range of Pb isotope composition defined by our high-Pb points and by most of the data of Rosman *et al.* [1993, 1994] is instead very similar to the mean composition of 1990 Arctic haze aerosols sampled in Barrow, Alaska [Sturges *et al.*, 1993] (Figure 5) and to aerosols collected in 1983–1984 for two Canadian high Arctic stations ( $^{206}\text{Pb}/^{207}\text{Pb}$  only [Sturges and Barrie, 1989]). Chemical evidence [Lowenthal and Rahn, 1985; Maenhaut *et al.*, 1989; Nriagu, 1989a; Rahn, 1985]

and meteorological investigations [Bowling and Shaw, 1992; Iversen and Joranger, 1985; Raatz, 1991] point to the former Soviet Union as the dominant contributor to low-altitude pollution in the Arctic vortex, with a lesser fraction from western European sources and negligible Canadian and U.S. contributions. For Pb in particular, a chemical transport model for 1979–1980 concluded that Pb flux to the Arctic during that year was split roughly equally between western European, eastern European, and former Soviet emissions sources (North American sources were not considered [Akeredolu *et al.*, 1994]). These lines of evidence suggest that Eurasian sources to the Arctic Basin haze phenomenon may also dominate Pb sources to Summit during the spring Pb maxima.

[39] Because the Pb maxima are relatively sharp through most of the record, lower concentrations characterize most of the pit depth. Our data suggest that Pb isotopes in these low-concentration intervals fall along a mixing line between U.S. and European sources. A blind and discontinuous sampling scheme that integrates periods longer than the typical spring peak duration is likely to miss the peaks much of the time and to mix the Pb from the peaks with off-peak Pb for samples that do include peaks. This scenario describes the samples of Rosman *et al.* [1993, 1994], which we infer were largely discontinuous sections  $\sim 20 \pm 10$  cm long, equivalent to pooling 2–6 of our samples, collected without knowledge of the fine-scale Pb concentration variability [Boyle *et al.*, 1994]. Therefore we expect that the Rosman *et al.* [1993, 1994] isotopic signatures represent a rough average of the depth (temporal) mean, while our high-Pb data are biased toward the signatures at the Pb flux maxima. Because the sharp Pb peaks account for a substantial fraction of the total Pb flux but are likely to be missed frequently in a discontinuous sampling scheme, the con-





centration-weighted annual mean isotopic signatures are probably not represented accurately by either data set and more likely fall between the lines defined by *Rosman et al.*'s [1993, 1994] and our high-Pb data. A more complete resolution of Pb source variations on all timescales would require a continuous, high-resolution Pb isotope data set with measurement precision as good or better than the present data.

### 5. Is There a Secular Trend in Pb or Cd Deposition During the 1980s?

[40] From the discussion in the previous section, it can be concluded that decreases in Eurasian Pb emissions were minor on a regional basis, exceeding a factor of 2 or more only locally (e.g., Federal Republic of Germany emissions decreased by a factor of  $\sim 2.5$  between 1980 and 1989 [*Dörr et al.*, 1991; *Pacyna et al.*, 1991]). Our interpretation of the snow pit results suggests that overall Eurasian sources must have decreased by less than a factor of 2. We argued above that a liberal estimate of U.S. influence would result in a decrease in total Pb flux at Summit of  $\sim 30\%$  over the decade. Thus, for Pb, a decadal change of a factor of 2 or less must be demonstrated against large-amplitude seasonal and interannual variability. We showed in detail elsewhere that a trend of this magnitude is difficult to prove for a single decade of high-resolution data [*Boyle et al.*, 1994].

[41] Although it has been argued that industrial abatement measures enacted since the 1960s and 1970s in the Northern Hemisphere likely resulted in decreased emissions of Cd (and Zn and Cu [*Candelone et al.*, 1995]), little in-

formation is available to suggest a significant decrease during the 1980s. Cadmium emissions result mainly from smelting of nonferrous metals and fossil fuel (coal, oil) burning [*Dörr et al.*, 1991; *Nriagu and Pacyna*, 1988]. An inventory of metals emissions sources in western Europe for 1982 noted industry predictions of negligible modernization for the coming years and concluded that 1982 levels would persist for many years [*Pacyna*, 1989]. This expectation is borne out by the snow pit data. A simple least squares regression on the snow pit Cd data shows no significant slope. While high-frequency noise in the record places large uncertainty on the regressed slope, we find the same conclusion for the trend in the annual flux data, which is affected by lower-frequency (interannual) noise (Figure 2), and for the 1–6 m interval of the firm core (Figure 1c). It would be difficult to argue convincingly for a significant trend in the 1980s Cd record. It is useful, however, to compare our results with those of a continuous record spanning spring 1990 to summer 1992, from a snow pit dug within a few kilometers of ours [*Candelone et al.*, 1996]. This more recent record shows mean Pb concentrations 60% lower, and Cd concentrations 30% lower than the mean for our 1980s record. A longer record of 1990s snow at Summit might help resolve long-term secular decreases against interannual variability.

### 6. Deposition of Pb and Cd 220 and 300 Years Before Present

[42] Analysis of Pb and Cd in deeper sections of the 108-m firm core and the main GISP2 “D” core were carried out as a preliminary investigation of short-term (seasonal to inter-

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**Figure 6.** (a) Pb and Cd in 12 roughly equal-length firm core sections spanning 8 years in the late eighteenth century. One sample is contaminated, certainly for Cd, and perhaps for Pb; (b) Pb and Cd in 4 samples from dry-drilled section of main GISP2 large-diameter core, roughly spanning the calendar year 1699. Summer depths are derived from visual stratigraphy of low-density hoar layers.



annual) variability during the period preceding the Industrial Revolution. Cleaning procedures for core samples are difficult and laborious and require extraction of a clean sample from the core, which is grossly contaminated on the exterior surface. Hence we sought to assess the validity of our core data. The strongest evidence that our core cleaning procedures were sufficiently rigorous is the excellent agreement between snow pit results and analyses of cleaned, sectioned core covering the same 0–6 m interval (Figures 1b and 1c) [Boyle *et al.*, 1994]. Details of the pit and core records differ, as expected from lateral variations in snow deposition over kilometer scales and from differences in sampling interval, but mean concentrations for both Pb and Cd are very similar (core: Pb = 217, Cd = 8.2 pmol kg<sup>-1</sup>; pit: Pb = 216, Cd = 11.4 pmol kg<sup>-1</sup>). This result lends confidence to the deep core results, obtained on samples cleaned by the same techniques. In addition, the data themselves suggest freedom from contamination artifact: the variability is on a scale expected from the seasonal and interannual variability observed in the pit record. Contamination, by contrast, typically produces a very spiky record with neighboring samples differing by more than 1 order of magnitude.

[43] A series of 10 samples near 75 m from the ATM firn core spans ~1780–1788 and shows fourfold variations in Pb and 10-fold in Cd, with mean concentrations of 93 and 5 pmol kg<sup>-1</sup> for Pb and Cd, respectively (Figure 6a). At this sampling interval, the variability is a combination of seasonal and interannual. These data span the period of the eruption of the Icelandic volcano Laki during 1783–1784, which is recorded in this core by ice acidity as measured by electrical conductivity [Taylor *et al.*, 1997; Zielinski *et al.*, 1997]. The sample most coincident with the conductivity peak shows no unusual Pb concentration but has

the highest Cd concentration for the 10-sample series (one sample obviously contaminated, traced to a leaking sample bag). A previous effort to define metal inputs associated with Laki found elevated sulfate, Pb, Cd, Cu, and Zn in a 7-cm-long sample representing ~3 months of deposition at Summit [Hong *et al.*, 1996]. Although the Pb peak was modest (less than twofold higher than neighboring samples), suggesting other important sources during this period, the Cd peak was 20-fold higher than the highest neighboring sample [Hong *et al.*, 1996]. Our results are consistent with this finding, although the magnitude of the Cd peak is ~2.7 times smaller than would be predicted on the basis of the previous results, assuming that the peak concentration in the previous data were attenuated by approximately threefold dilution associated with our longer sample interval. We attribute this difference to the highly variable nature in which short-term chemical inputs are recorded in snow and ice, even for nearby sites [Dibb, 1989; Wolff *et al.*, 1998]. For samples other than the Laki event our mean Pb and Cd values are about twice those reported previously for samples of similar age [Hong *et al.*, 1996]. The differences may be real lateral variations in recording of short-term inputs, but eliminating a few of our higher samples improves the agreement significantly, suggesting that minor contamination of some of our samples cannot be ruled out. Cleaning procedures are more difficult on dense firn and ice in deep core samples; hence the possible influence of some contamination is harder to refute than for the very recent firn samples.

[44] The shorter section of core near 95 m was split into four samples spanning the year 1699 and part of 1700 (dated on the basis of annual density layer counting [Alley *et al.*, 1997]). Pb shows factor of 2 variations and Cd shows larger variations including one sample with a concentration very close to our detection limit



(Figure 6b). Mean concentrations were 44 and 2.2 pmol kg<sup>-1</sup> for Pb and Cd, respectively, about half those measured for the 1780–1788 period in the solar core. Maxima for both metals in the 95 m record appear to occur roughly in spring-summer, suggesting seasonality in preindustrial input possibly similar to that seen in the 1980s. These preliminary core results suggest that Pb and Cd inputs to central Greenland may have doubled over the course of the eighteenth century, and doubled again by the 1980s (after a peak in the 1970s). Our interpretation of Pb sources, above, implies that future reductions to metal flux in central Greenland may depend most strongly on automotive and industrial pollution controls in Eurasia.

## 7. Summary

[45] 1. A 10-year high-resolution record shows coherent seasonal concentration cycles for Pb, Cd, and sulfate in central Greenland snow, with clear maxima in spring of each year, suggesting efficient transport of these anthropogenic species from lower altitude and/or lower-latitude sources with strong seasonal periodicity.

[46] 2. Trends in deposition for the decade 1981–1990 are difficult to quantify against large high-frequency noise. We estimate a decrease in Pb concentrations of <50% [Boyle *et al.*, 1994] and no significant trend for Cd.

[47] 3. The isotopic composition of Pb determined for a subset of samples over the decade, corresponding to seasonal Pb concentration maxima and minima, suggests both long-term and seasonal Pb source variations. Comparison to published data for the isotopic composition of anthropogenic Pb in North America, Europe, and Asia during this period suggests that North American Pb contributed significantly only early in the decade and during seasonal

Pb minima. The Pb maxima, which account for about half the total Pb flux despite their relatively short duration, have an isotopic composition consistent with a mixture of European and Asian sources. The decrease in U.S. gasoline emissions over the decade therefore likely had a relatively minor effect on the isotopic composition of the total Pb deposition flux at this site.

[48] 4. Pb and Cd data from two deep core sections for the eighteenth century demonstrate substantial seasonal and interannual concentration variations, and show mean concentrations for the years 1700 and 1780–1788 of roughly 25% and 50% the mean concentrations in the 1980s.

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## References

- Akeredolu, F. A., L. A. Barrie, M. P. Olson, K. K. Oikawa, J. M. Pacyna, and G. J. Keeler, The flux of anthropogenic trace metals into the Arctic from the mid-latitudes in 1979/80, *Atmos. Environ.*, 28, 1557–1572, 1994.
- Alleman, L. Y., A. J. Véron, T. M. Church, A. R. Flegal, and B. Hamelin, Invasion of the abyssal North Atlantic



- by modern anthropogenic lead, *Geophys. Res. Lett.*, **26**, 1477–1480, 1999.
- Alley, R. B., C. A. Shuman, D. A. Meese, A. J. Gow, K. C. Taylor, K. M. Cuffey, J. J. Fitzpatrick, P. M. Grootes, G. A. Zielinski, M. Ram, G. Spinelli, and B. Elder, Visual-stratigraphic dating of the GISP2 ice core: Basis, reproducibility, and application, *J. Geophys. Res.*, **102**, 26,367–26,382, 1997.
- Arsenault, M. A., Soluble ionic composition of snow at Summit, Greenland from the 1997–1998 winter-over, *Eos Trans. AGU*, **79**(45), Fall Meet. Suppl., F297, 1998.
- Barrie, L. A., and M. L. Barrie, Chemical components of lower troposphere aerosols in the high Arctic: Six years of observations, *J. Atmos. Chem.*, **11**, 211–266, 1990.
- Bergin, M., J.-L. Jaffrezo, C. I. Davidson, J. E. Dibb, S. N. Pandis, R. Hillamo, W. Maenhaut, H. D. Kuhns, and T. Makela, The contributions of snow, fog, and dry deposition to the summer flux of anions and cations at Summit, Greenland, *J. Geophys. Res.*, **100**, 16,275–16,288, 1995.
- Boutron, C. F., and C. C. Patterson, Relative levels of natural and anthropogenic lead in recent Antarctic snow, *J. Geophys. Res.*, **92**, 8454–8464, 1987.
- Boutron, C. F., U. Gorlach, J.-P. Candelone, M. A. Bolshov, and R. J. Delmas, Decrease in anthropogenic lead, cadmium, and zinc in Greenland snows since the late 1960's, *Nature*, **353**, 153–156, 1991.
- Boutron, C. F., F. M. Ducroz, U. Gorlach, J.-L. Jaffrezo, C. I. Davidson, and M. A. Bolshov, Variations in heavy metals concentrations in fresh Greenland snow from January to July 1989, *Atmos. Environ., Part A*, **27**, 2773–2779, 1993.
- Boutron, C. F., J.-P. Candelone, and S. Hong, Greenland snow and ice cores: Unique archives of large-scale pollution of the troposphere of the Northern Hemisphere by lead and other heavy metals, *Sci. Total Environ.*, **160/161**, 233–241, 1995.
- Bowling, S. A., and G. E. Shaw, The thermodynamics of pollutant removal as an indicator of possible source areas for Arctic haze, *Atmos. Environ., Part A*, **26**, 2953–2961, 1992.
- Boyle, E. A., S. D. Chapnick, G. T. Shen, and M. Bacon, Temporal variability of lead in the western North Atlantic, *J. Geophys. Res.*, **91**, 8573–8593, 1986.
- Boyle, E. A., R. M. Sherrell, and M. P. Bacon, Lead variability in the western North Atlantic ocean and central Greenland ice: Implications for the search for decadal trends in anthropogenic emissions, *Geochim. Cosmochim. Acta*, **58**, 3227–3238, 1994.
- Candelone, J.-P., S. Hong, C. Pellone, and C. F. Boutron, 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, 1995.
- Candelone, J.-P., J.-L. Jaffrezo, S. Hong, C. I. Davidson, and C. F. Boutron, Seasonal variations in heavy metals concentrations in present day Greenland snow, *Sci. Total Environ.*, **193**, 101–110, 1996.
- Chillrud, S. N., R. F. Bopp, H. J. Simpson, J. M. Ross, E. L. Shuster, D. A. Chaky, D. C. Walsh, C. C. Choy, L.-R. Tolley, and A. Yarme, Twentieth century atmospheric metal fluxes into Central Park Lake, New York City, *Environ. Sci. Technol.*, **33**, 657–662, 1999.
- Church, T. M., A. Véron, C. C. Patterson, D. Settle, Y. Erel, H. R. Maring, and A. R. Flegal, Trace element sources, transport, and scavenging in the North Atlantic troposphere: Shipboard results of precipitation and aerosols, *Global Biogeochem. Cycles*, **4**, 431–443, 1990.
- Davidson, C. I., Chemical constituents in the air and snow at Dye 3, Greenland, 1, Seasonal variations, *Atmos. Environ.*, **27**, 2709–2722, 1993.
- Davidson, C. I., J.-L. Jaffrezo, M. J. Small, P. W. Summers, M. P. Olson, and R. D. Borys, Trajectory analysis of source regions influencing the south Greenland ice sheet during the Dye 3 gas and aerosol sampling program, *Atmos. Environ.*, **27**, 2739–2749, 1993.
- Dibb, J., The Chernobyl reference horizon (?) in the Greenland Ice Sheet, *Geophys. Res. Lett.*, **16**, 987–990, 1989.
- Dibb, J. E., and J.-L. Jaffrezo, Air-snow exchange investigations at Summit, Greenland: An overview, *J. Geophys. Res.*, **102**, 26,795–26,808, 1997.
- Dibb, J. E., R. Hawley, S. Sturges, P. Austin, and P. Smith, Air-snow relationships at Summit, Greenland: The 1997–1998 Winter-Over Experiment, *Eos Trans. AGU*, **79**(45), Fall Meet. Suppl., F296, 1998.
- Dörr, H., A. Mangini, W. Schmitz, F. Weber, and K. O. Münnich, Stable Pb and 210-Pb in German lake sediments and soils: A tracer for anthropogenic lead emission, in *Heavy Metals in the Environment*, edited by J.-P. Vernet, pp. 247–260, Elsevier Sci., New York, 1991.
- Gorlach, U., and C. F. Boutron, Preconcentration of lead, cadmium, copper and zinc in water at the pg/g level by non-boiling evaporation, *Anal. Chim. Acta*, **236**, 391–398, 1990.
- Gorlach, U., and C. F. Boutron, Variations in heavy metals concentrations in Antarctic snows from 1940 to 1980, *J. Atmos. Chem.*, **14**, 205–222, 1992.
- Grousset, F. E., C. R. Quétel, B. Thomas, P. Buat-Menard, O. F. X. Donard, and A. Bucher, Transient Pb isotopic signatures in the Western European atmosphere, *Environ. Sci. Technol.*, **28**, 1605–1608, 1994.
- Hamelin, B., G. Manhès, F. Albarede, and C. J. Allegre, Precise lead isotope measurements by the double spike



- technique: A reconsideration, *Geochim. Cosmochim. Acta*, **49**, 173–182, 1985.
- Hawley, R., and M. R. Albert, Physical snow surface characteristics during the 1997–98 winter-over experiment at Summit, Greenland, *Eos Trans. AGU*, **79**(45), Fall Meet. Suppl., F298, 1998.
- Hinkley, T. K., P. J. Lamothe, S. A. Wilson, D. L. Finnegan, and T. M. Gerlach, Metal emissions from Kilauea, and a suggested revision of the estimated worldwide metal output by quiescent degassing of volcanoes, *Earth Planet. Sci. Lett.*, **170**, 315–325, 1999.
- Hong, S., J.-P. Candelone, C. C. Patterson, and C. F. Boutron, Greenland ice evidence of hemispheric lead pollution two millennia ago by Greek and Roman Civilizations, *Science*, **265**, 1841–1843, 1994.
- Hong, S., J.-P. Candelone, and C. F. Boutron, Deposition of atmospheric heavy metals to the Greenland ice sheet from the 1783–1784 volcanic eruption of Laki, Greenland, *Earth Planet. Sci. Lett.*, **144**, 605–610, 1996.
- Hong, S., J.-P. Candelone, and C. F. Boutron, Changes in zinc and cadmium concentrations in Greenland ice during the past 7760 years, *Atmos. Environ.*, **31**, 2235–2242, 1997.
- Hopper, J. F., H. B. Ross, W. T. Sturges, and L. A. Barrie, Regional source discrimination of atmospheric aerosols in Europe using the isotopic composition of lead, *Tellus Ser. B*, **43**, 45–60, 1991.
- Iversen, T., and E. Joranger, Arctic air pollution and large scale atmospheric flows, *Atm. Environ.*, **19**, 2099–2108, 1985.
- Jickells, T. D., A. H. Knap, and T. M. Church, Trace metals in Bermuda rainwater, *J. Geophys. Res.*, **89**, 1423–1428, 1984.
- Kahl, J. D. W., D. A. Martinez, H. Kuhns, C. I. Davidson, J.-L. Jaffrezo, and J. M. Harris, Air mass trajectories to Summit, Greenland: A 44-year climatology and some episodic events, *J. Geophys. Res.*, **102**, 26,861–26,875, 1997.
- Krogh, T. E., A low-contamination method for hydrothermal decomposition of zircon and extraction of U and Pb for isotopic age determinations, *Geochim. Cosmochim. Acta*, **37**, 485–494, 1973.
- Landy, M. P., and D. A. Peel, Short-term fluctuations in heavy metal concentrations in Antarctic snow, *Nature*, **291**, 144–146, 1981.
- Lowenthal, D. H., and K. A. Rahn, Regional sources of pollution at Barrow, Alaska during winter 1979–80 as deduced from elemental tracers, *Atmos. Environ.*, **19**, 2011–2024, 1985.
- Maenhaut, W., P. Cornille, J. M. Pacyna, and V. Vitols, Trace element composition and origin of the atmospheric aerosol in the Norwegian Arctic, *Atm. Environ.*, **23**, 2551–2569, 1989.
- Manhes, G., Ph. D. thesis, Université de Paris, 1978.
- Manhes, G., J. F. Minster, and C. J. Allegre, Comparative uranium-thorium-lead and rubidium strontium study of the Saint Severin amphoterite: Consequences for early solar system chronology, *Earth Planet. Sci. Lett.*, **39**, 14–24, 1982.
- Mart, L., Seasonal variations of Cd, Pb, Cu and Ni levels in snow from the eastern Arctic Ocean, *Tellus Ser. B*, **35**, 131–141, 1983.
- Martínez-Cortizas, A., X. Pontevedra-Pombal, E. García-Rodeja, J. D. Nóvoa-Muñoz, and W. Shotyk, Mercury in a Spanish peat bog: Archive of climate change and atmospheric metal deposition, *Science*, **284**, 939–942, 1999.
- Mayewski, P. A., W. B. Lyons, M. J. Spencer, M. S. Twickler, C. F. Buck, and S. Whitlow, An ice-core record of atmospheric response to anthropogenic sulphate and nitrate, *Nature*, **346**, 554–556, 1990.
- 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, The Greenland Ice Sheet Project 2 depth-age scale: Methods and results, *J. Geophys. Res.*, **102**, 26,411–26,424, 1997.
- Migon, C., L. Alleman, N. Leblond, and E. Nicolas, Evolution of atmospheric lead over the northwestern Mediterranean between 1986 and 1992, *Atmos. Environ.*, **27A**, 2161–2167, 1993.
- Murozumi, M., T. J. Chow, and C. Patterson, Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata, *Geochim. Cosmochim. Acta*, **33**, 1247–1294, 1969.
- Neffel, A., J. Beer, H. Oeschger, F. Zurcher, and R. C. Finkel, Sulphate and nitrate concentrations in snow from South Greenland 1895–1978, *Nature*, **314**, 611–613, 1985.
- Ng, A., and C. Patterson, Natural concentrations of lead in ancient Arctic and Antarctic ice, *Geochim. Cosmochim. Acta*, **45**, 2109–2121, 1981.
- Nriagu, J. O., A global assessment of natural sources of atmospheric trace metals, *Nature*, **338**, 47–49, 1989a.
- Nriagu, J. O., The history of leaded gasoline, in *Heavy Metals in the Environment*, edited by J.-P. Vernet, pp. 361–366, Elsevier Sci., New York, 1989b.
- Nriagu, J. O., and J. M. Pacyna, Quantitative assessment of worldwide contamination of air, water and soils by trace metals, *Nature*, **333**, 134–139, 1988.
- Nriagu, J. O., R. D. Coker, and L. A. Barrie, Origin of sulphur in Canadian Arctic haze from isotopic measurements, *Nature*, **349**, 142–145, 1991.
- Pacyna, J. M., Technological parameters affecting atmospheric emissions of trace elements from major anthropogenic sources, in *Control and Fate of Atmospheric*



- Trace Metals*, edited by J. M. Pacyna and B. Ottar, pp. 15–31, Kluwer Acad., Norwell, Mass., 1989.
- Pacyna, J. M., J. Munch, and F. Axenfeld, European inventory of trace metal emissions to the atmosphere, in *Heavy Metals in the Environment*, edited by J.-P. Vernet, pp. 17–20, Elsevier Sci., New York, 1991.
- Patterson, C. C., and D. M. Settle, Review of data on eolian fluxes of industrial and natural lead to the lands and seas in remote regions on a global scale, *Mar. Chem.*, **22**, 137–162, 1987.
- Patterson, T. L., and R. A. Duce, The cycle of atmospheric cadmium over the North Pacific ocean, *Tellus Ser. B*, **43**, 12–29, 1991.
- Raatz, W. E., Meteorological conditions over Eurasia and the Arctic contributing to the March 1983 Arctic Haze episode, *Atmos. Environ.*, **19**, 2121–2126, 1985.
- Raatz, W. E., The climatology and meteorology of arctic air pollution, in *Pollution of the Arctic Atmosphere*, edited by W. T. Sturges, pp. 334, Elsevier Sci., New York, 1991.
- Raatz, W. E., R. E. Schnell, and B. A. Bodhaine, The distribution of transport of pollution aerosols over the Norwegian Arctic on 31 March and 4 April 1983, *Atmos. Environ.*, **19**, 2135–2142, 1985.
- Rahn, K. A., Progress in Arctic air chemistry, 1980–1984, *Atmos. Environ.*, **19**, 1987–1994, 1985.
- Rosman, K. J. R., W. Chisholm, C. F. Boutron, J. P. Candelone, and U. Gorlach, Isotopic evidence for the source of lead in Greenland snows since the late 1960s, *Nature*, **362**, 333–335, 1993.
- Rosman, K. J. R., W. Chisholm, C. F. Boutron, J.-P. Candelone, and S. Hong, Isotopic evidence to account for changes in the concentration of lead in Greenland snow between 1960 and 1988, *Geochim. Cosmochim. Acta*, **58**, 3265–3269, 1994.
- Savarino, J., C. F. Boutron, and J.-L. Jaffrezo, Short-term variations of Pb, Cd, Zn, and Cu in recent Greenland snow, *Atmos. Environ.*, **28**, 1731–1737, 1994.
- Shen, G. T., and E. A. Boyle, Lead in corals: Reconstruction of historical industrial fluxes to the surface ocean, *Earth Planet. Sci. Lett.*, **82**, 289–304, 1987.
- Shen, G. T., and E. A. Boyle, Thermocline ventilation of anthropogenic lead in the western North Atlantic, *J. Geophys. Res.*, **93**, 15,715–15,732, 1988.
- Sturges, W. T., and L. A. Barrie, Stable lead isotope ratios in arctic aerosols: evidence for the origin of arctic air pollution, *Atmos. Environ.*, **23**, 2513–2519, 1989.
- Sturges, W. T., J. F. Hopper, L. A. Barrie, and R. C. Schnell, Stable lead isotope ratios in Alaskan Arctic aerosols, *Atm. Environ.*, **27A**, 2865–2871, 1993.
- Suttie, E. D., and E. W. Wolff, Seasonal input of heavy metals to Antarctic snow, *Tellus Ser. B*, **44**, 351–357, 1992.
- Taylor, K. C., R. B. Alley, G. W. Lamorey, and P. Mayewski, Electrical measurements on the Greenland Ice Sheet Project 2 core, *J. Geophys. Res.*, **102**, 26,511–26,518, 1997.
- Véron, A., T. M. Church, C. C. Patterson, Y. Erel, and J. T. Merrill, Continental origin and industrial sources of trace metals in the northwest Atlantic troposphere, *J. Atmos. Chem.*, **14**, 339–351, 1992.
- Véron, A. J., T. M. Church, A. R. Flegal, C. C. Patterson, and Y. Erel, Response of lead cycling in the surface Sargasso Sea to changes in tropospheric input, *J. Geophys. Res.*, **98**, 18,269–18,276, 1993.
- Wedepohl, K. H., The composition of the continental crust, *Geochim. Cosmochim. Acta*, **59**, 1217–1232, 1995.
- Whitlow, S., P. A. Mayewski, and J. E. Dibb, A comparison of major chemical species seasonal concentration and accumulation at the South Pole and Summit, Greenland, *Atmos. Environ.*, **26**, 2045–2054, 1992.
- Wolff, E. W., and D. A. Peel, Concentrations of cadmium, copper, lead and zinc in snow from near Dye 3 in South Greenland, *Ann. Glaciol.*, **10**, 193–197, 1988.
- Wolff, E. W., J. S. Hall, R. Mulvaney, E. C. Pasteur, D. Wagenbach, and M. Legrand, Relationship between chemistry of air, fresh snow and firn cores for aerosol species in coastal Antarctica, *J. Geophys. Res.*, **103**, 11,057–11,070, 1998.
- Wolff, E. W., E. D. Suttie, and D. A. Peel, Antarctic snow record of cadmium, copper, and zinc content during the twentieth century, *Atmos. Environ.*, **33**, 1535–1541, 1999.
- Zielinski, G. A., P. A. Mayewski, L. D. Meeker, K. Grönvold, M. S. Germani, S. Whitlow, M. S. Twickler, and K. Taylor, Volcanic aerosol records and tephrochronology of the Summit, Greenland, ice cores, *J. Geophys. Res.*, **102**, 26,625–26,640, 1997.