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Constraining recent lead pollution sources in the North Pacific using ice core stable lead isotopes

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[1] Trends and sources of lead (Pb) aerosol pollution in the North Pacific rim of North America from 1850 to 2001 are investigated using a high-resolution (subannual to annual) ice core record recovered from Eclipse Icefield (3017 masl; St. Elias Mountains, Canada). Beginning in the early 1940s, increasing Pb concentration at Eclipse Icefield occurs coevally with anthropogenic Pb deposition in central Greenland, suggesting that North American Pb pollution may have been in part or wholly responsible in both regions. Isotopic ratios ($^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$) from 1970 to 2001 confirm that a portion of the Pb deposited at Eclipse Icefield is anthropogenic, and that it represents a variable mixture of East Asian (Chinese and Japanese) emissions transported eastward across the Pacific Ocean and a North American component resulting from transient meridional atmospheric flow. Based on comparison with source material Pb isotope ratios, Chinese and North American coal combustion have likely been the primary sources of Eclipse Icefield Pb over the 1970–2001 time period. The Eclipse Icefield Pb isotope composition also implies that the North Pacific mid-troposphere is not directly impacted by transpolar atmospheric flow from Europe. Annually averaged Pb concentrations in the Eclipse Icefield ice core record show no long-term trend during 1970–2001; however, increasing $^{208}\text{Pb}/^{207}\text{Pb}$ and decreasing $^{206}\text{Pb}/^{207}\text{Pb}$ ratios reflect the progressive East Asian industrialization and increase in Asian pollutant outflow. The post-1970 decrease in North American Pb emissions is likely necessary to explain the Eclipse Icefield Pb concentration time series. When compared with low (lichen) and high (Mt. Logan ice core) elevation Pb data, the Eclipse ice core record suggests a gradual increase in pollutant deposition and stronger trans-Pacific Asian contribution with rising elevation in the mountains of the North Pacific rim.

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1. Introduction

[2] Lead (Pb) is a non-essential and potentially toxic metal whose principal atmospheric sources are crustal dust, volcanoes, mining, smelting, waste incineration, coal

combustion and combustion of leaded-gasoline [Nriagu, 1989; Pacyna and Pacyna, 2001]. Anthropogenic emissions are currently 1–2 orders of magnitude greater than those from natural (crustal and volcanic) sources [Komárek *et al.*, 2008]. Most anthropogenic Pb is emitted in the form of very fine (0.5–1 μm) particulates with an atmospheric residence time of ~ 10 days [Settle and Patterson, 1991], which can therefore be deposited thousands of kilometers from their source(s) of emission. Recent evidence also indicates that Pb-containing particulates are among the most efficient ice-forming substances in the atmosphere, and may play a crucial role in radiative forcing [Cziczo *et al.*, 2009]. Atmospheric archives from remote environments in the form of tree rings [e.g., Bellis *et al.*, 2004], ombrotrophic bog cores [e.g., Shotyik *et al.*, 1996; Kylander *et al.*, 2010], epiphytic lichens [e.g., Simonetti *et al.*, 2003] and ice cores [Rosman *et al.*, 1993; Zheng *et al.*, 2007; McConnell and Edwards, 2008] provide detailed histories of Pb concentrations in the atmosphere, and have demonstrated that humans have been polluting the atmosphere with Pb for over 2500

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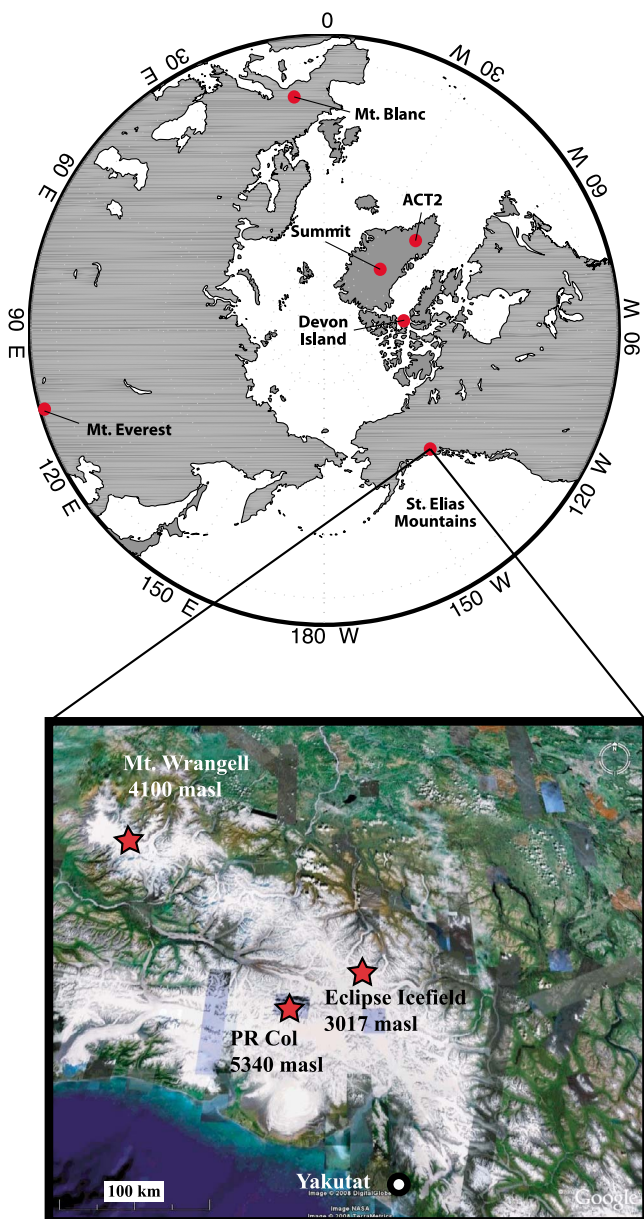


Figure 1. (top) Location map of ice core sites in the Northern Hemisphere with published Pb and Pb isotope records and (bottom) ice core sites in the St. Elias Mountains (Google Earth imagery © Google Inc. Used with permission).

years [Hong *et al.*, 1994; Shotyk *et al.*, 1996]. Ice and snow from Greenland, Antarctica, the European Alps, the Canadian Arctic, and recently the North Pacific have provided arguably the most well-preserved and highly resolved atmospheric Pb records [e.g., Boutron *et al.*, 1991; Rosman *et al.*, 2000; Schwikowski *et al.*, 2004; Shotyk *et al.*, 2005; Osterberg *et al.*, 2008]. For example, the pioneering work of Murozumi *et al.* [1969] demonstrated an ~ 500 -fold increase in Pb concentrations in Greenland ice since pre-anthropogenic time, with an unprecedented increase from 1933–1965. Based in part on these findings, and as a result of automobile engineering improvements, North American and European governments adopted regulations limiting vehicular and industrial Pb emissions [Boutron *et al.*, 1991]. These regulations have

been effective in reducing atmospheric Pb concentrations in these regions since circa 1976, and this reduction is apparent in ice core records from Greenland, Europe, and the Canadian Arctic [Boutron *et al.*, 1991; Schwikowski *et al.*, 2004; McConnell and Edwards, 2008].

[3] Determining the isotopic ratios of Pb preserved in snow and ice can be used to distinguish natural Pb from anthropogenic Pb and also to identify specific sources of anthropogenic pollution [Bollhöfer and Rosman, 2001; Rosman *et al.*, 1993, 1997, 2000; Shotyk *et al.*, 2005; Komárek *et al.*, 2008; Lee *et al.*, 2011]. Four isotopes (^{208}Pb , ^{207}Pb , ^{206}Pb and ^{204}Pb) comprise virtually all of Pb in the environment. ^{208}Pb , ^{207}Pb and ^{206}Pb result from the decay series of ^{232}Th , ^{235}U and ^{238}U , respectively, and ^{204}Pb is a primordial isotope. The isotopic composition of Pb, generally expressed in the form of a ratio (e.g., $^{208}\text{Pb}/^{207}\text{Pb}$, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$), depends on the age and geologic history of the Pb source as well as its initial concentrations of U, Th and ^{204}Pb . The Pb isotope composition of ores and other resources (i.e., coal) are globally variable, but, for the most part, are regionally consistent [Komárek *et al.*, 2008]. For example, Pb from the Mississippi Valley (USA) is more radiogenic (greater $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$) than Pb from the Broken Hills region of Australia [Bollhöfer and Rosman, 2001]. Furthermore, isotopic ratios in Pb are not measurably fractionated by physical and chemical processes so that anthropogenic Pb-aerosols transported thousands of kilometers retain the isotopic signature of their source material [Komárek *et al.*, 2008]. By comparing the Pb isotope ratios in natural archives (e.g., ice cores) to those of regional emission source(s), atmospheric transport pathways and mixing processes can be constrained, making Pb isotopes a powerful geochemical tracer.

[4] Using ice core records from the North Atlantic region, European and North American Pb pollution trends and sources have been well constrained (see summary in Kylander *et al.* [2010]). Comparatively little is known about Pb pollution in the North Pacific [e.g., Osterberg *et al.*, 2008]. In the past decade, considerable efforts have been made to quantify atmospheric pollution outflow from rapidly industrializing Asian countries and atmospheric monitoring stations in Western North America have observed the trans-Pacific transport of dust and pollution from Asia [e.g., Jaffe *et al.*, 1999; McKendry *et al.*, 2001; Jacob *et al.*, 2003; Liang *et al.*, 2004; Holzer *et al.*, 2005; Jacob *et al.*, 2009; Singh *et al.*, 2009]. An 8000 yearlong ice core record of atmospheric Pb deposition was developed by Osterberg *et al.* [2008] from a site (Prospector-Russell Col; PRC) at 5300 masl on the summit plateau of Mt. Logan in the St. Elias Mountains of the southwestern Yukon Territory (Figure 1). The PRC record registers an important rise in Pb deposition from 1981 to 1998, that likely reflects enhanced trans-Pacific transport of Pb pollution accompanying the rapid industrialization of China and other East Asian nations [Osterberg *et al.*, 2008]. However, other studies in the Canadian portion of the St. Elias Mountains have speculated that the influence of Asian air masses is minor at elevations below 3000 masl, thereby creating an elevational gradient of aerosol sources in the region [Yalcin and Wake, 2001; Wake *et al.*, 2002; Zdanowicz *et al.*, 2006]. Additional records from mid-tropospheric ice core sites are needed to test this hypothesis and better understand the history of Pb pollution

in the North Pacific. Here we present a 151 yearlong (1850–2001) record of Pb concentrations and a 31 yearlong (1970–2001) record of Pb isotopes from Eclipse Icefield (EI) (60.51°N, 139.47°W, 3017 masl), Yukon, Canada (Figure 1). Other ice core sites in the North Pacific [Osterberg *et al.*, 2008] and Asia [Lee *et al.*, 2011] are above 4000 masl and well into the free troposphere, but EI is within the planetary boundary layer (PBL) - free troposphere (FT) transition zone and therefore offers a unique perspective on Pb aerosols in the mid-troposphere. Using Pb concentration and isotopic data from the EI ice core, we provide direct geochemical evidence of the changing origin of Pb pollution to the North Pacific mid-troposphere through the 20th century.

2. Materials and Methods

[5] Several ice cores were recovered from EI (60.51°N, 139.47°W, 3017 masl) in the St. Elias Mountains, Yukon, Canada during the summer of 2002 (Figure 1): a 345 m core (core 2), a 130 m core (core 3), and a 100 m core (core 4). All cores were drilled within 3 m horizontal distance of each other. Stable O/H isotope ratios ($\delta^{18}\text{O}$, δD) and major ion data from all three cores have been previously published [Yalcin *et al.*, 2006a, 2006b, 2007]. The top 60 m of core 2 was drilled using the Geological Survey of Canada's ultra-clean, titanium drill barrel [Zheng *et al.*, 2006]. The drill barrel was lined with a pre-cleaned HDPE sleeve that was extruded with the core and sealed immediately to minimize potential contamination. Using a firn/ice core melting system and ultra-clean sample preparation and handling procedures [Osterberg *et al.*, 2006], all of this portion of core 2 was continuously sampled at the University of Maine at high resolution (10–15 cm sample⁻¹) to produce 492 discrete samples. For the determination of Pb isotope ratios, 4mm aliquots from the uncontaminated, inner portion of the ice core were poured from the acid-cleaned primary collection containers to acid-cleaned polypropylene vials in a HEPA filtered laminar flow bench [Gross, 2008]. Ultra-pure Optima™ HNO₃ was added to melted samples to make a 1% HNO₃ solution. Samples remained acidified and liquid for 4–8 weeks prior to analysis. All Pb measurements were measured at low resolution on a Thermo-Finnigan Element 2 single-collector inductively coupled plasma-sector field mass spectrometer (ICP-MS) equipped with a guard electrode, a Cetac ASX 260 autosampler and a high-efficiency APEX Q sample introduction system with a 1.5 mm (inner diameter) quartz injector tube, a heated spray chamber and a Peltier cooled condenser. Self-aspirated PFA nebulizers were run at 200 $\mu\text{L min}^{-1}$. Pb isotope ratios (²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb) were initially determined without a high-efficiency x-cone in order to minimize damage to the slits of the mass spectrometer [Krachler *et al.*, 2004]. Measurements with analytical errors greater than 0.4% were subsequently rerun with an x-cone to improve precision. Detector dead time was calculated by standard protocol to be 15 ns.

[6] National Institute of Standards and Technology (NIST) standard reference material (SRM) #981 was dissolved in heated Optima™ HNO₃ and serially diluted to create a solution of ~ 200 ng Pb L⁻¹. This standard was analyzed every 1–4 samples to correct for mass bias. An average mass bias correction of the two bracketing NIST SRM #981 measurements was applied to the measurements

performed between the bracketing standards. The accuracy of Pb isotope measurements was assessed by comparing corrected ²⁰⁸Pb/²⁰⁷Pb and ²⁰⁶Pb/²⁰⁷Pb measurements of SRM 981 to the certified values. Corrected ²⁰⁸Pb/²⁰⁷Pb and ²⁰⁶Pb/²⁰⁷Pb ratios differed from certified values by an average (n = 79) of 0.15% and 0.11% respectively. The analytical precision of individual samples (assessed by the standard deviation of >300 individual measurements per sample) averaged 0.24% and 0.25% for ²⁰⁸Pb/²⁰⁷Pb and ²⁰⁶Pb/²⁰⁷Pb respectively. Due to the precision necessary for source discrimination, any measurements with analytical error greater than 0.5% are discarded. The average procedural blank (10 samples of ultra-pure water (Milli-Q, 18 M Ω) subjected to the entire sampling procedure) is 1.6 ± 0.03 ppt [Osterberg *et al.*, 2006], an order of magnitude lower than the lowest value, and is considered negligible.

[7] The annual chronology of the EI ice core was constructed from seasonal oscillations of stable water isotopes, major ion concentrations, and the identification of over 60 volcanic horizons, six of which have been confirmed via geochemical fingerprinting of tephra samples from the EI cores [Yalcin, 2005; Yalcin *et al.*, 2003, 2006a, 2006b, 2007]. Additionally, ¹³⁷Cs marker horizons from the 1986 Chernobyl nuclear reactor accident and the 1963 atmospheric nuclear weapon test activity provides chronological tie-points. Error associated with the constructed chronology is estimated to be ± 1 year based on repeat layer counts [Yalcin, 2005; Yalcin *et al.*, 2003, 2006a, 2006b, 2007]. To construct seasonal divisions in the EI core record, δD minima are operationally defined as the middle of winter and δD maxima (within a given year) are operationally defined as the middle of summer. We then allocate samples between winter (summer) δD minima (maxima) into 4 bins, thereby creating 8 bins for an entire calendar year. We chose less than 12 bins to avoid implying monthly data resolution. The winter data set therefore represents the previous year's bin 8 and bin 1, spring is bins 2–3, summer bins 4–5, and fall bins 6–7. These seasonal divisions can only be approximate, because no ice core site receives constant snow accumulation throughout the year. However, meteorological data (snow surface height) from Divide Site (~ 15 km south of EI, ~ 2600 masl) demonstrate that, in this portion of the St. Elias Mountains, snow accumulation occurs during all months [Gross, 2008] with a maximum in the fall. We emphasize that our goal is not to correlate specific meteorological conditions to individual samples, but rather to identify persistent seasonal climate/geochemical relationships at EI.

[8] To produce a longer, continuous 1850 to 2002 Pb concentration record from the Eclipse Icefield, contiguous (with respect to chronology), longitudinal samples with cross-sections of 3 cm² were cut from remaining portions of cores 2, 3, and 4 and analyzed at the Desert Research Institute using a continuous flow analysis with trace elements (CFA-TE) system [McConnell *et al.*, 2002b, 2007a, 2007b; McConnell and Edwards, 2008]. Chronologies developed using stable O/H isotopes, major ions, and trace elements for each core were compared to ensure accurate matching of the DRI and UMaine measurements with depth, and the high-resolution DRI measurements were combined to produce annually averaged Pb concentrations. Overlapping portions (1970–2001) of EI Pb annual concentration data produced at UMaine and DRI Pb data have mean values of 66.3 ± 19.3

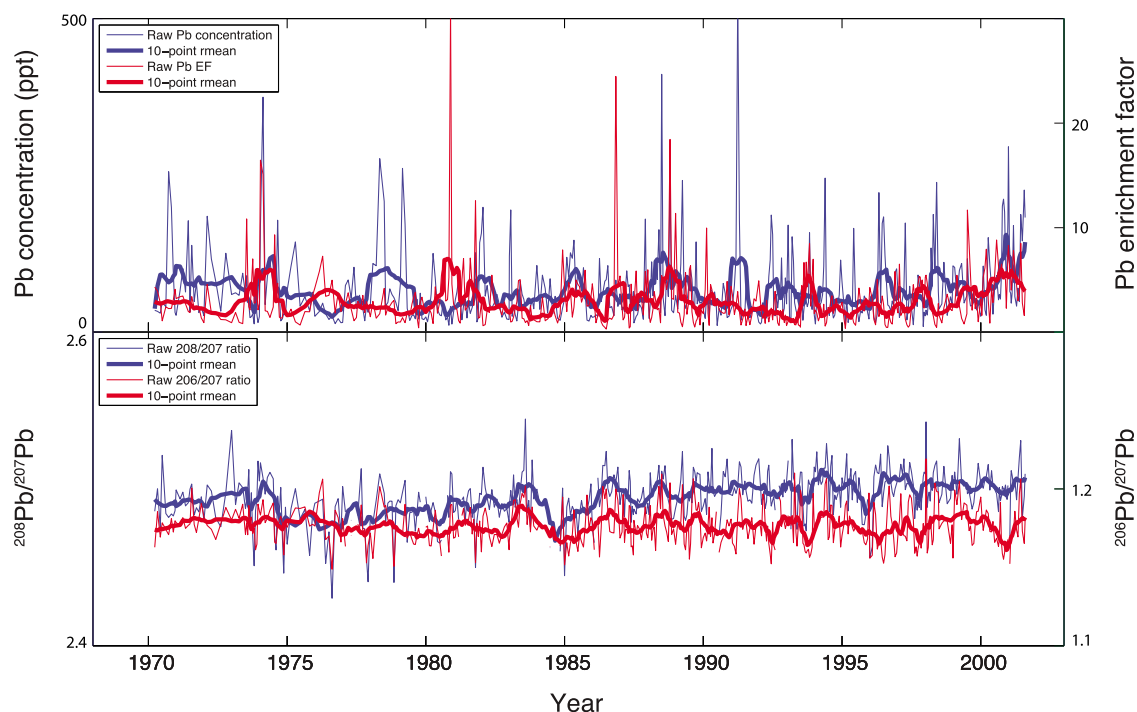


Figure 2. Pb concentration, Pb enrichment factor, and Pb isotope ratio ($^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$) data from the Eclipse Icefield ice core. Raw data (thin lines) represent the full 492-sample data set, and thick lines are 10-point running mean smoothed data.

and 44.7 ± 14.2 ppt, respectively, which are statistically different based on a simple two sided t-test. We note, however, that the higher mean Pb value obtained at UMaine is consistent with recent work demonstrating that measured concentrations of trace elements leached from environmental samples and from rock standards are strongly dependent on the strength of acid used and on the length of acidification prior to analysis. Differences in the measured concentrations of trace elements between continuous injection ICP-MS and discretely analyzed ICP-MS systems are well-documented; for example, *Knüsel et al.* [2003] enumerate elements that show good and poor agreement between continuous-flow and conventional analyses. *Rhodes et al.* [2011] similarly found dramatic increases in trace elemental concentrations through time for four different rock standards. Importantly, different elements behaved quite differently through time, complicating the calculation and use of enrichment factors in ice core studies. They found that Pb increased on the order of 50% from 10 min to 12 h of leaching for a given standard (Nod-P-1), and that the concentration continued to increase up to 7 weeks (the length of the study). Finally, experimental data from UMaine (B. Koffman et al., manuscript in preparation, 2012) are consistent with existing evidence: for example, from 20 min to 28 days, *Koffman et al.* observe a 250% increase in measured Pb concentrations in Antarctic snow, acidified at 1% nitric acid. We therefore believe that the $\sim 30\%$ high mean Pb value in UMaine samples is within the uncertainty introduced by different sample acidification schemes. The two Pb concentration time series (5-year average) are significantly correlated ($r = 0.55$, $p = 0.001$; Figure 7) and when compared in time series the trends in the UMaine and DRI Pb concentration data sets are roughly similar with decreasing concentrations through the 1970s

and slightly increasing concentrations in the 1990s. We are not aware of any similar research investigating the effects of acidification strength and time on Pb isotope ratios, and thus it is more difficult to assess the reliability of comparisons between various snow and ice core Pb isotope studies. We note that to date, all snow/ice core Pb isotope data have come from discrete sample processing, and determined either via thermal ionization mass spectrometry (TIMS) or ICP-MS techniques that utilize different processing schemes. Individual Pb isotopes may leach at constant rates, such that isotope ratios are preserved even at different overall Pb concentrations, thereby negating the importance of acidification technique on Pb isotope ratio data. In the absence of any compelling evidence regarding this idea, we proceed with the assumption that the new Eclipse Pb isotope data can be directly compared to other snow/ice core Pb isotope data.

3. Results and Discussion

3.1. Pb Concentration and Enrichment Factor

[9] Figure 2 shows the EI ice core subannual Pb concentration time series, which contains a high degree of intra and interannual variability over the 1970–2001 time period. A portion of the Pb deposition is likely from crustal dust aerosol, and indeed several studies have observed an increase in deposition/concentration of anthropogenic pollutants concurrent with certain dust deposition events [*Han et al.*, 2004; *Jaffe et al.*, 2003; *Mori et al.*, 2003; *Marx et al.*, 2005, 2008]. Crustal Pb enrichment factors (EF_{Pb}) estimate the amount of non-crustal Pb in a sample by dividing the ratio of Pb to a crustal reference element in a sample by the ratio of the same elements in the upper

continental crust (UCC [Wedepohl, 1995]; $EF_{Pb} = \text{average} ([Pb]/[r]_{\text{sample}} \div [Pb]/[r]_{\text{UCC}})$). Following the method described in Osterberg *et al.* [2008], we use the average EF_{Pb} calculated using seven crustal reference elements (Sr, Cs, U, Al, Fe, La, and Ce) to reduce potential bias from any one crustal reference element. While the seven crustal reference element time series are highly correlated ($r > 0.64$, $p < 0.0001$), they are not identical nor are the calculated EF_{Pb} values (average EF_{Pb} for Sr = 1.8, Cs = 1.7, U = 1.5, Al = 4.6, Fe = 2.4, La = 4.6, and Ce = 4.7) because of mineralogical and geochemical considerations, solubility and fractionation during transport, and measurement uncertainty. The average EF_{Pb} at EI calculated from all seven reference elements for 1970–2001 is 3.0, which indicates that roughly a third of the Pb deposited at EI is anthropogenic, assuming approximately equal natural contributions from crustal and volcanic sources based on the reported average EF_{Pb} value of 2.1 for pre-anthropogenic ice from Mt. Logan [Osterberg *et al.*, 2008]. For comparison, over the same time period the EF_{Pb} in the Mt. Logan ice core is >30 [Osterberg *et al.*, 2008], suggesting a greater proportion of anthropogenic pollutant deposition at high elevations in the St. Elias range. The EI EF_{Pb} time series (Figure 2) shows a similar degree of variability to the Pb concentration time series, but with different maxima as expected based on anthropogenic versus crustal inputs. We note that there is no obvious change in either Pb concentration or Pb EF during or after the 1976/77 Pacific Decadal Oscillation (PDO) shift observed in the North Pacific Ocean [e.g., Mantua and Hare, 2002]. While the PDO mode shift had clear effects on North Pacific regional temperature and precipitation variability, it is less clear how the shift may have impacted trans-Pacific aerosol transport to Eclipse, particularly given the effect of aerosol emission strength and vertical aerosol distribution [Zhao *et al.*, 2006]. A 40-year transport simulation study did not show any significant shift in dust transport from Asia during the mid-1970s [Zhao *et al.*, 2006], however there is clear evidence for the impact of the PDO on trans-Pacific aerosol transport [e.g., Gong *et al.*, 2006]. We speculate that the lack of an obvious correlation of the PDO and Eclipse Pb deposition may be related to the vertical nature of aerosol transport, and the influence of North American Pb at the Eclipse elevation.

[10] A seasonal maximum in dust aerosol deposition during spring in the St. Elias has been noted by several studies [Goto-Azuma *et al.*, 2006; Osterberg *et al.*, 2008; Gross, 2008]. The seasonal pattern of Pb concentration at Eclipse is less coherent than that of marine (Na^+) and dust (Al) aerosol species [Yalcin, 2005; Gross, 2008], but nonetheless does show increases in Pb deposition during portions of the year (Figure 3) [Gross, 2008]. Concentrations between the 25th and 75th percentiles and the median are highest during spring and early summer and gradually decline to their lowest during autumn and winter. Concentrations above the 75th percentile are highest during spring and early summer, but are also slightly elevated during winter. The elevated concentrations during late spring and early summer are concomitant with the peak in ice core dust concentration [Gross, 2008] and maximum springtime Asian dust outflow [e.g., Uno *et al.*, 2009], suggesting that dust is acting as a vector for Pb and/or that Pb and dust are being transported independently by the same synoptic systems. We are unable

to resolve the relative importance of these processes, but assume that they are both significant based on previous dust-Pb interaction studies [Fukuda and Tsunogai, 1975; Marx *et al.*, 2008], satellite imagery depicting dust and pollution in the same frontal system, and observations from the National Oceanic and Atmospheric Administration's (NOAA) Mauna Loa observatory (R. Schnell, personal communication, 2009). The slightly elevated levels of Pb concentration during winter could be a result of increased transport efficiency (e.g., a deepened Aleutian Low and increased trans-Pacific outflow of pollutants and/or dust in the lower troposphere; Liang *et al.*, 2004, 2005; Osterberg *et al.*, 2008). EF_{Pb} values show no distinct seasonality, but values are somewhat lower in late winter and spring (Figure 3). This observation appears consistent with the general picture of anthropogenic emissions from coal burning for electrical generation, waste-incineration, smelting and mining that have only minor seasonal variation [Van de Velde *et al.*, 1998], and increased dust transport in spring.

3.2. Pb Isotopes

[11] Figure 4a shows the Pb isotope data set from the several northern hemisphere ice cores (including EI) compared with regional Pb isotope fields constructed from in situ measurements of atmospheric aerosol Pb in urban centers around the world [Bollhöfer and Rosman, 2001]. The aerosol fields are derived from spatially and temporally limited measurements (particularly for China and Russia) and thus may not capture the full range of Pb isotope ratios in aerosols from all regions. Nonetheless, they provide a baseline for comparison and interpretation of the ice core Pb isotope data. The Pb isotope ratios from EI are less radiogenic than those of upper continental crust (UCC; $^{206}\text{Pb}/^{207}\text{Pb} = 1.21$, and $^{208}\text{Pb}/^{207}\text{Pb} = 2.50$, using river sediments from major river basins [Millot *et al.*, 2004] (Figure 4b), confirming the influence of anthropogenic Pb. In a three-isotope plot, a binary mixture would plot as a linear array between the two end-member ratios. The EI data set does not form a linear array, suggesting that more than two sources contribute Pb to EI. In general, EI samples fall within and between the fields defining North American (primarily U.S.), Asian (Japanese and Chinese) and Russia/Eastern Europe aerosols (Figure 4a). Figure 4b compares the EI Pb isotope data set to various source region fuel data (i.e., Pb isotope data from coal and leaded gasoline). As a whole, Pb isotope ratios from EI show very little evidence of Pb from Russian or Chinese leaded gasoline, which generally has a very low Pb isotope ratios (typically <2.415 and <1.125 for $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$, respectively; Bollhöfer and Rosman, 2001]. Although leaded gasoline was phased out in North America and Europe beginning the 1970s, some influence from North American gasoline may be discernable in the EI Pb isotope record for the 1970s and 1980s (Figure 4b). As with Pb EF values, there is no obvious seasonality in the EI Pb isotope ratios (Figure 5).

[12] The published Chinese Pb aerosol isotope signature [Bollhöfer and Rosman, 2001] and high elevation ice core Pb isotope data from Mt. Everest [Lee *et al.*, 2011] (Figure 4a) form an end-member that cannot be obtained by a combination of other potential Pb-aerosol sources. Thus, Pb isotope ratios at EI provide geochemical evidence of trans-Pacific transport of Asian pollutants to lower elevations

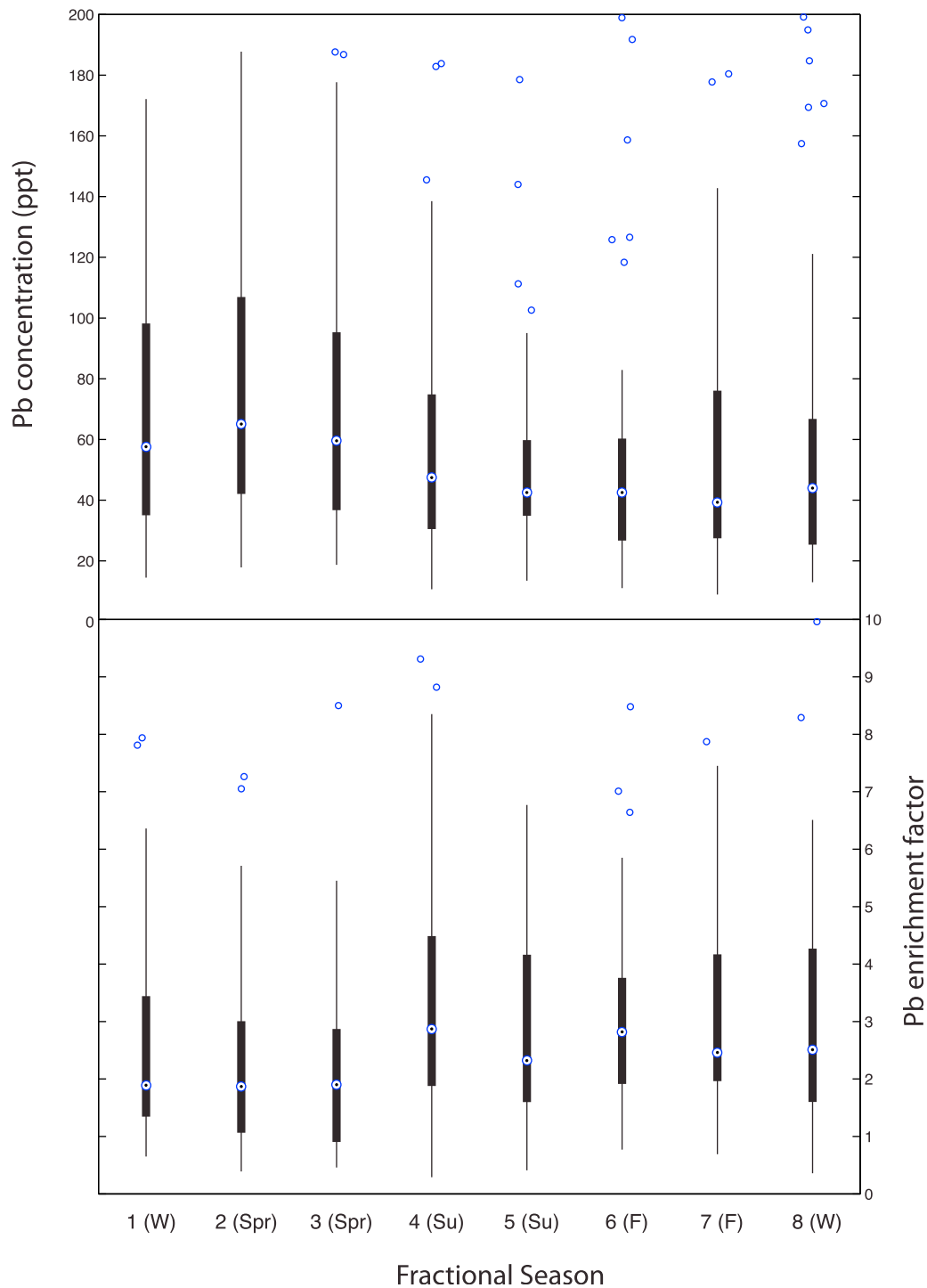


Figure 3. Pb concentration and Pb enrichment factor data from the Eclipse Icefield ice core, grouped as described in section 2 according to fractional season (2–3, spring; 4–5; summer; 6–7 fall; 8 and 1, winter). Circles within the blue boxes are median values for all data in that bin, the edges of the boxes are the 25th and 75th percentiles, and the whiskers extend to the most extreme data points not considered outliers (circles).

(~3000 masl) in the St. Elias Mountains. Several airborne sampling campaigns have documented pollutant outflow from Asia, and in particular have noted the layered structure of atmospheric chemistry over the North Pacific [Jacob *et al.* 2003; Singh *et al.*, 2009]. The EI samples within the Chinese

Pb isotope field are similar to aerosol values from Mukai *et al.* [1993] and are similar to Pb isotope ratios in coal from Northern China (Figure 4b), which is consistent with coal being the dominant source of Pb aerosols in parts of China despite the fact that leaded gasoline was not banned in

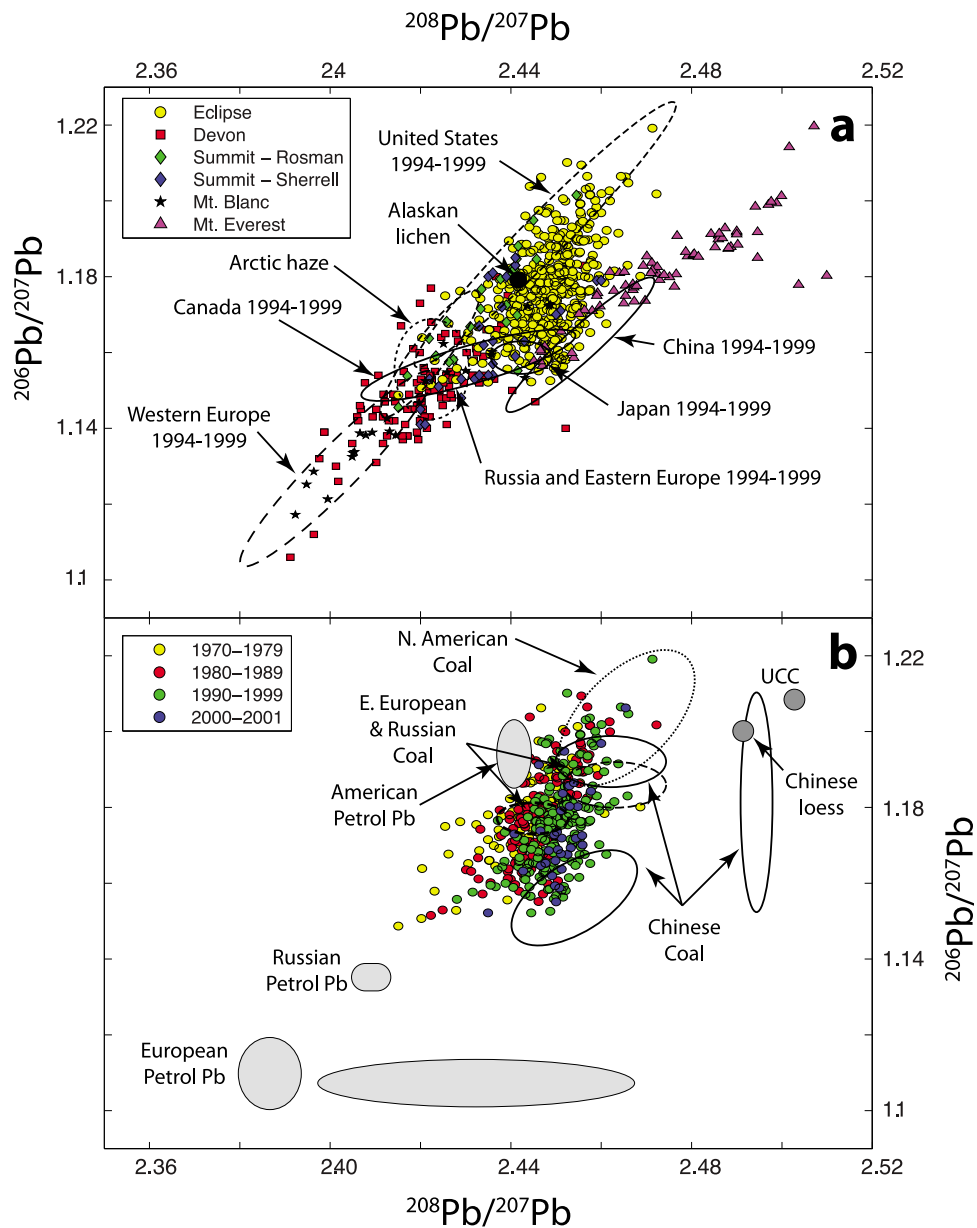


Figure 4. (a) Pb isotope composition of all samples from the Eclipse Icefield ice core compared to other recent (post-1970) Northern Hemisphere snow and ice core data (Devon Island ice core [Shotyk *et al.*, 2005], Summit Greenland [Rosman *et al.*, 1993], Mt. Blanc [Rosman *et al.*, 2000], and Mt. Everest [Lee *et al.*, 2011]), and nearby Alaska lichen [Simonetti *et al.*, 2003]. Ellipses are fields of regionally characteristic Pb isotope ratios, determined from atmospheric aerosols [Bollhöfer and Rosman, 2001; Sturges *et al.*, 1993]. (b) Pb isotope ratios of decadal binned samples from Eclipse Icefield ice core compared to Pb isotope ratios from Chinese leaded petrol [Chen *et al.*, 2005], Chinese coal [Mukai *et al.*, 1993; Komárek *et al.*, 2008], Russian leaded petrol [Kober *et al.*, 1999], Eastern European coal and Russian coal [Kober *et al.*, 1999], North American coal [Chow and Earl, 1972], American leaded petrol [Sherrell *et al.*, 1992; Teutsch *et al.*, 2001], upper continental crust (UCC) [Millot *et al.*, 2004], and Chinese loess [Jones *et al.*, 2000].

China until 1997 [Chen *et al.*, 2005]. Furthermore, the presence of Chinese Pb at EI is consistent with several studies that have observed the transport of Asian pollution to the Western U.S. by midlatitude westerlies [e.g., Jaffe *et al.*, 1999]. Japanese Pb aerosols are isotopically indistinguishable from a combination of Eurasian and Chinese sources, and the meteorological conditions that transport Chinese Pb

to EI would likely also transport Pb from Japan. Likewise, easterly transport from northern Asia may incorporate aerosol from Russia, resulting in the partial overlap of the EI and Russia/E. Europe Pb isotope fields. However, since 1991 total emissions of most pollutants from northern Asia (Russia) have been comparably small [Shindell *et al.*, 2008]. While we cannot rule out a possible contribution from

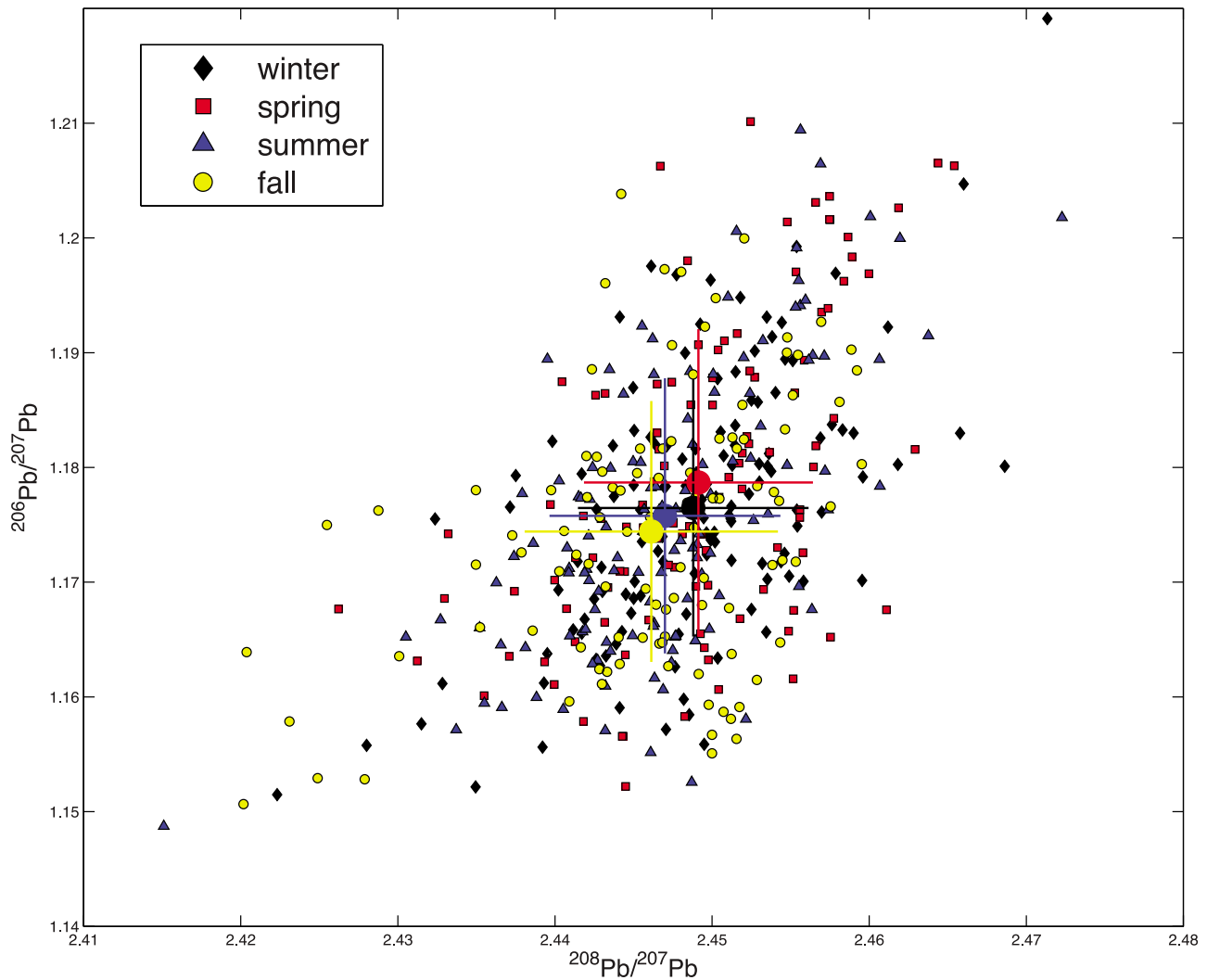


Figure 5. Pb isotope data from the Eclipse Icefield ice core plotted by season of deposition. Grouping into seasonal bins is described in section 2. Large circles represent mean values for each season, and error bars represent one standard deviation.

northern Asia based on available data, we infer that the majority of Asian Pb is derived from East Asia.

[13] The EI samples that plot within the North American (U.S.) Pb isotope field have similar Pb isotope ratios to North American Pb detected in Summit, Greenland [Rosman *et al.*, 1993; Sherrell *et al.*, 2000], Lake Erie [Graney *et al.*, 1995] and the Sargasso Sea [Hamelin *et al.*, 1997]. Prevailing mid-latitude westerlies (Figure 6) suggest that North American air masses may not strongly and consistently contribute to atmospheric pollutant deposition in the North Pacific. During all seasons the atmosphere of the St. Elias Mountains is characterized by predominantly southerly flow from the Gulf of Alaska, which in turn, receives westerly flow from the North Pacific Ocean (Figure 6). However, these time-averaged views of atmospheric flow may obscure transient meridional patterns along the North American west coast that could affect the St. Elias Mountains. Modeling and backtrajectory studies during the 2008 ARCTAS mission indicate that, particularly during summer, airflow from the contiguous U.S. into the Arctic via the Northeast Pacific occurs on synoptic timescales and is responsible for significant pollutant transport [Fuelberg *et al.*,

2010]. Blocking of flow by high elevation Western North American topography may be responsible for flow from the Southwestern U.S., and results in Alaska being one of the primary entrance points to the Arctic for air departing near the surface [Fuelberg *et al.*, 2010]. We therefore expect that the overlap of EI and North American (U.S.) Pb isotope fields, as well as the mixed EI composition between North American (U.S.) and East Asian fields results from this Southwestern U.S. pollutant contribution.

[14] Comparing Pb isotopic data from EI to those from Devon Island and Mt. Blanc (Figure 1 for location) is particularly useful (Figure 4a) for evaluating the role of Western European pollution in the Northeast Pacific. Using Pb isotopes and the seasonality of Pb deposition, Shotyk *et al.* [2005] concluded that Pb in recent snow (1994–2004) on Devon Island is derived from pollutant laden surface and upper air from Eurasia that dominates the winter atmosphere of the Arctic, known as Arctic Haze [Shaw, 1982, 1995; Quinn *et al.*, 2007]. Similarly, on the basis of the seasonality of deposition, regional emissions trends, and correlations with ice core sulfate time series, Yalcin and Wake [2001]

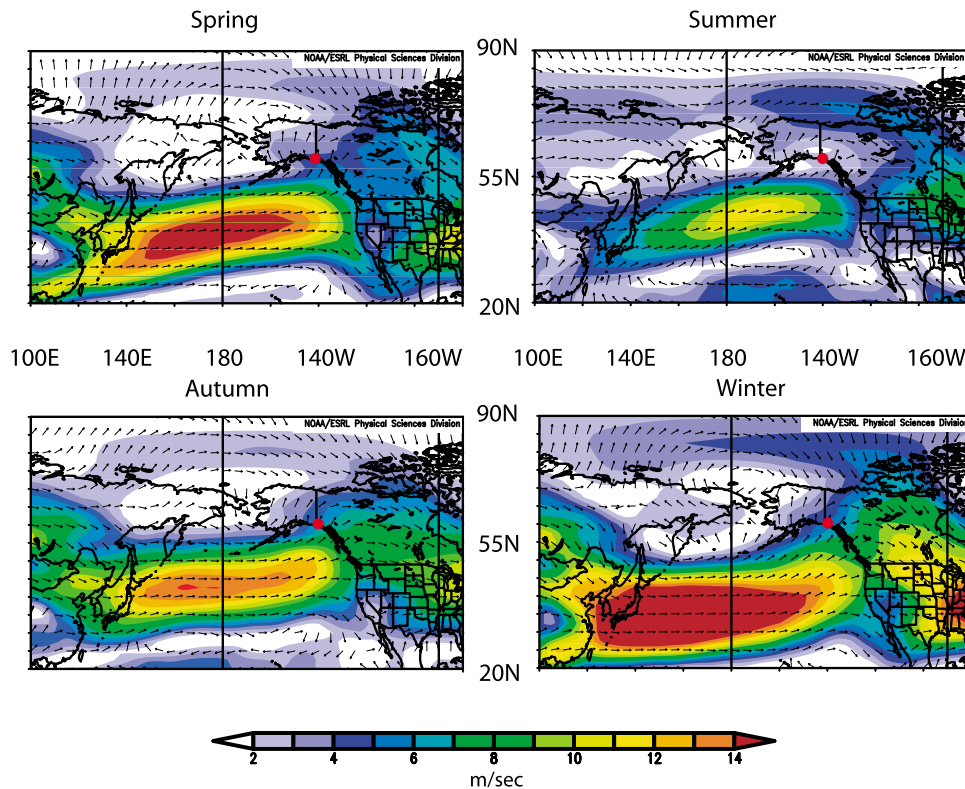


Figure 6. Seasonal average wind vectors (m/sec) at 700 mb from 1971–2001 from NCEP/NCAR reanalysis [Kalnay *et al.*, 1996]. Spring = JFM, Summer = JJA, Autumn = SON, Winter = DJF. The location of Eclipse Icefield is noted with a red circle.

suggested that sulfate at EI is predominantly comprised of Arctic Haze. However, Pb isotope ratios from EI are significantly more radiogenic (higher $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$) than those measured in polluted air in Barrow, Alaska [Sturges *et al.*, 1993] and on Devon Island and Mt. Blanc [Shotyk *et al.*, 2005; Rosman *et al.*, 2000]. Arctic Haze was originally understood to contain a significant amount of pollution from Western Europe and northern Eurasia [e.g., Sturges *et al.*, 1993; Quinn *et al.*, 2007], particularly for aerosol species, which in the case of Pb are less radiogenic than East Asian or North American emissions (Figure 4a). In this sense, the EI Pb isotope data show a distinct difference from those sites in the North Atlantic sector of the Arctic (Devon Ice Cap) and the European Alps (Mt. Blanc), namely a lesser influence of Western Europe emissions. This finding is consistent with the relative influence of trans-Pacific westerly flow (Figure 6) at EI, and circumpolar (northerly/northwesterly) flow at sites in Northern Alaska and the Canadian Arctic. Recent observational [Stohl, 2006] and modeling [Shindell *et al.*, 2008] studies have demonstrated that pollutant transport into the Arctic occurs along numerous pathways which have both spatial and vertical heterogeneity, and which can be unique for various pollutant types (e.g., gases, sulfate, metal, and black carbon aerosols). Therefore, the Arctic Haze signal at a particular site may contain a distinct mixture of pollutant type and source contribution (generalized as North America, East Asia, South Asia, and Europe by Shindell *et al.* [2008]). Based on the EI Pb isotope data, we suggest that Arctic Haze at EI has a composition and

mixture of sources unique among Northern Hemisphere ice core sites thus far studied.

[15] To investigate temporal variability in EI data, the Pb isotope values are grouped decadal (Figure 4b). The frequency of samples with Pb isotope ratios characteristic of Chinese aerosols increases from the 1970s to 1990s, which can also be seen in the progressively more radiogenic character of the $^{208}\text{Pb}/^{207}\text{Pb}$ ratio with time (Figure 2). During the 1980s and 1990s, Pb emissions from China increased in response to higher energy demands resulting from rapid industrialization, while Pb emissions from North America, Europe and Russia decreased with increased regulation (North America, Europe) and decreasing economic output (Russia; Pacyna and Pacyna, 2001). Thus, the shift in Pb isotopic composition observed at EI from 1970 to 2000 is likely the result of a progressively larger contribution from Chinese aerosols to the Pb flux at EI.

3.3. Pb Concentration Time Series

[16] The annually resolved EI Pb concentration data set from 1850 to 2001 provides a longer context within which to evaluate changes in North Pacific pollutant transport relative to the North Atlantic (Figure 7). Changes in Greenland Pb concentration over the past 150 years have been well documented, and include a pronounced increase beginning in the 1940s [e.g., McConnell and Edwards, 2008]. Comparison of the Southern Greenland ACT2 and EI Pb data sets reveals a nearly identical rise in mid-tropospheric North Pacific Pb deposition, which is consistent with Pb isotope results implying North American influence in the Gulf of Alaska

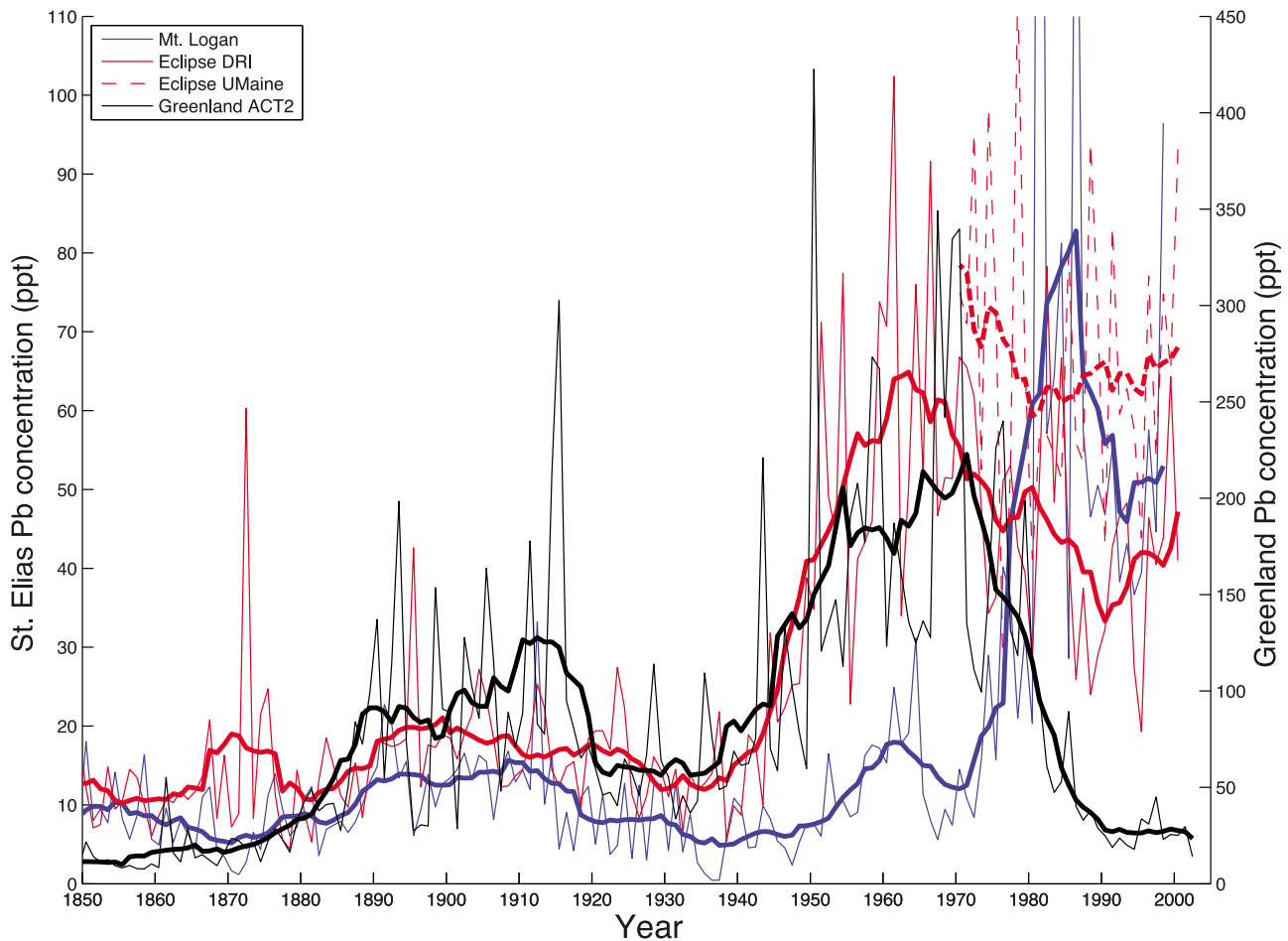


Figure 7. Comparison of annual and 5-year smoothed, 1850 to 2002 Pb concentration data from EI with the Mt. Logan (PR Col) summit [Osterberg *et al.*, 2008] and the Greenland ACT2 ice core records [McConnell and Edwards, 2008].

region. The decline in North Atlantic Pb concentration, typically attributed to phase-out of leaded gasoline in the early 1970s, begins concomitantly in the North Pacific. However, beginning around 1970, the trends in the two regions clearly diverge, with North Atlantic concentrations returning to pre-industrial background levels, and EI concentrations remaining elevated above background.

[17] Previous work with the Mt. Logan summit ice core has shown an obvious disparity between Pb concentration time series from high elevation (>5000 masl) North Pacific sites and the North Atlantic (Figure 7). Osterberg *et al.* [2008] attributed the sharp rise in Pb concentration starting in the late 1970s as reflecting increased East Asian economic activity and pollutant emission. The rise in presumably Asian Pb in the Mt. Logan record begins essentially at the time when the EI and Greenland trends diverge (Figure 7). The increase in East Asian Pb emissions is not obvious in the EI Pb concentration time series from 1970 to 2001 (Figure 8; the period with Pb isotope data). Annually averaged EI Pb concentrations range from 25.6 ppt in 1976 to 96.7 ppt in 1978 (mean 67.6 ± 20.6 ppt (1σ)), with no discernable long-term trend in annual flux or interannual variability over the 1970–2001 period. For comparison we also plot (Figure 8) annual Pb flux in the Eclipse record,

calculated using annual concentration and accumulation rate data [e.g., Alley *et al.*, 1995]. While there is an increasing trend in the Pb flux data, the trend is clearly being driven by an increase in accumulation rate during 1970–2001 (Figure 8). Because it is generally accepted that ice core concentration data likely provide the best representation of atmospheric concentration at sites (such as EI, with an annual accumulation rate of ~ 1.5 mwe yr^{-1}) dominated by wet deposition [Alley *et al.*, 1995], we choose to use the EI Pb concentration time series for comparison with other ice core data. The lack of trend in EI Pb concentration is in contrast to the records from Greenland (Figure 7) and Devon Island [Shotykh *et al.*, 2005] not shown]. The Greenland and Devon Island Pb concentration records exhibit a dramatic decline beginning circa 1970 in response to North American and European Pb emissions regulations [McConnell *et al.*, 2002a; Shotykh *et al.*, 2005; McConnell and Edwards, 2008], while PR Col Pb concentrations drastically increase during the 1980s in response to Chinese industrialization [Osterberg *et al.*, 2008]. This distinction is further evidence that anthropogenic Pb at EI in the latter part of the 20th century is neither predominantly from North American, European, and Eurasian sources (as at Devon Island and ACT2) nor from predominantly Asian sources (as at PR Col), but likely

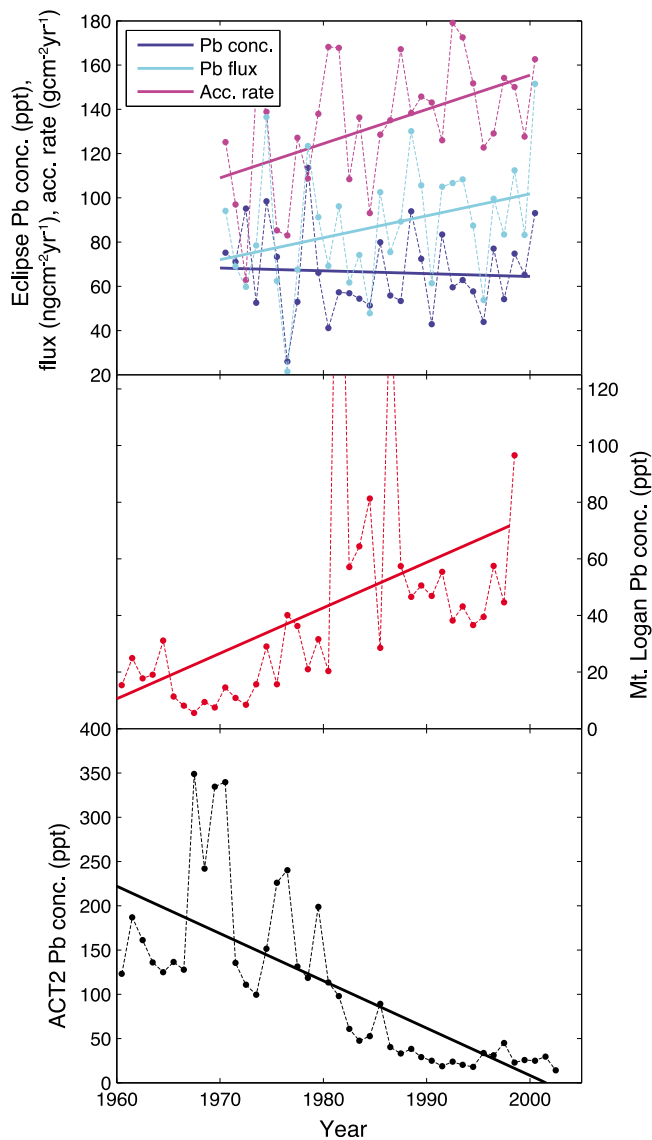


Figure 8. Comparison of Pb concentration records. (top) Eclipse Icefield ice core Pb concentration (1-year averages in ppt; linear regression slope = -0.12 ppt/yr, $p = 0.75$), including annual accumulation rate (in $\text{ng cm}^{-2} \text{yr}^{-1}$; linear regression slope = 1.5 $\text{ng cm}^{-2} \text{yr}^{-1} / \text{yr}$, $p = 0.005$) and annual Pb flux (in $\text{ng cm}^{-2} \text{yr}^{-1}$; linear regression slope = 1.0 $\text{ng cm}^{-2} \text{yr}^{-1}$, $p = 0.08$). (middle) Prospectors - Russell (PR) Col ice core on the summit plateau of Mt. Logan, Yukon, Canada (1-year average [Osterberg et al., 2008]; linear regression slope = 1.6 ppt/yr, $p = 0.008$). (bottom) Greenland ACT2 site (1-year average [McConnell and Edwards, 2008]; linear regression slope = -5.3 ppt/yr, $p = 0.00001$). Trend lines in all plots are one-dimensional least squares linear regression.

represents a mixture of decreasing North American and increasing East Asian sources with the importance of East Asian sources increasing with time.

[18] We return now to the hypothesis that there is a distinct vertical separation of pollutant aerosol deposition in the St. Elias, such that sites above 5000 masl receive predominantly Chinese pollution [Osterberg et al., 2008], and sites below receive predominately Eurasian pollution [Yalcin and

Wake, 2001; Wake et al., 2002]. Based on the Pb isotope and concentration data presented here, we conclude that the Asian influence is clear at both sites, however additional pollutant contributions from North America affect lower elevations. A similar conclusion was reached by other sampling campaigns, including those looking at vertical changes in snow chemistry in the St. Elias Mountains [Zdanowicz et al., 2006], low elevation aerosol and lichen sampling in Alaska [Cahill, 2003; Simonetti et al., 2003] (Figure 4a), and airborne dust and pollutant aerosol sampling over the North Pacific [Bahreini et al., 2003; Oshima et al., 2004; Huang et al., 2008]. Each of these studies has demonstrated the influence of Chinese aerosols at all levels of the North Pacific atmosphere, albeit with significant complexity with respect to layered aerosol distribution. Low elevation sites (e.g., Adak Island, SE Alaska) demonstrate the additional influence of North American, Northern Europe and Russian aerosols [Cahill, 2003; Simonetti et al., 2003]. Given the overall dominance of Asian pollution in the North Pacific, the more perplexing issue is why there is not an increasing trend in Pb concentration (flux) in the EI record. The PR Col ice core clearly shows a large increase in Pb deposition over the past several decades that is not matched in the EI record, and EF_{Pb} values at PR Col an order of magnitude higher than at EI. Answering this question likely requires, at a minimum, a Pb isotope time series from the PR Col ice core. However, insight may come from the conceptual model of Holdsworth [2008], whereby the three dimensional nature of cyclones impacting the St. Elias Mountains lead to a complex vertical profile of local moisture (and presumably aerosol) flux. Indeed, during a single large Asian outflow event in 2001, Zdanowicz et al. [2006] found that dust aerosol deposited above ~ 3000 masl had an Asian geochemical signature and large (4 μm) diameter, suggesting rapid trans-Pacific transport, while dust below 3000 masl had a mixed local/exotic source, consistent with dust-related trace element data in the EI record [Gross, 2008]. Therefore, the combined influence of aerosol source, vertical and horizontal transport, and synoptic-scale processes likely play a role in determining the relative importance of East Asian aerosols in the North Pacific across a range of altitudes. These observations are consistent with model results focused on the Arctic that show that for pollutant aerosols, European emissions dominate at the surface, but Asian emissions become progressively more important with altitude and are dominant in the upper troposphere [Shindell et al., 2008; Jacob et al., 2009]. The transport from East Asia at higher altitudes is often a function of warm conveyor belts (WCBs) associated with storm tracks on the east coast of continents [Koch and Hansen, 2005; Stohl, 2006]. We infer, based on our results and those of Pacific airborne sampling campaigns [Jacob et al., 2003; Singh et al., 2009], that a similar vertical gradient between a mixture of North American/Eurasian and East Asian sources at lower altitude to solely East Asian sources at higher altitudes also exists in the North Pacific region.

4. Summary and Conclusions

[19] The data presented here represent the first ice core time series of stable Pb isotopes from the North Pacific and provide direct geochemical evidence of trans-Pacific transport of Pb pollutants to the St. Elias Mountains. Several

important conclusions can be drawn from the combination of the Pb isotope ratios and concentrations from EI. First, EF_{Pb} and ²⁰⁸Pb/²⁰⁷Pb and ²⁰⁶Pb/²⁰⁷Pb ratios suggest that the deposition of anthropogenic Pb is roughly equal to that of crustal and volcanic sources. Second, the Pb concentration time series from EI is significantly different from other Northern Hemisphere ice core Pb records in the latter part of the 20th century and suggests multiple sources of anthropogenic Pb. Time series of Pb isotope ratios and concentrations in conjunction with meteorological data are used to identify the most important contributing Pb source regions as East Asia (China and/or Japan) and North America (U.S.). Third, Pb isotopes from EI shed new light on depositional variability as a function of elevation in the St. Elias Mountains. Pb isotope ratios from EI indicate significant deposition of Chinese Pb at ~3000 m, as was found at the nearby, higher (~5000 m) PR Col site [Osterberg et al., 2008]. We contend that there is a vertical source gradient between EI and PR Col defined by a lack of North American aerosols at PR Col (and a much more significant Asian influence), rather than a lack of East Asian aerosols at EI. Additionally, the presence of East Asian Pb at EI makes it likely that a component of dust deposited at EI is also of East Asian provenance. Fourth, Pb deposited at EI is isotopically distinct from Pb at Barrow, Alaska [Sturges et al., 1993], Devon Island [Shotyk et al., 2005], Greenland [Rosman et al., 1993; Sherrell et al., 2000], Mt. Blanc [Rosman et al., 2000] and Mt. Everest [Lee et al., 2011]. This observation, combined with the lack of clear seasonality in Pb EF and Pb isotope ratios and the relatively radiogenic EI Pb isotope data argue against a significant input of Western Europe pollution at EI. Fifth, the contribution of East Asian Pb to EI increased from the 1970s to the 1990s, consistent with rising Pb emissions from East Asia noted in the Mt. Logan summit record. The isotopic composition of Pb at EI is consistent with coal combustion being the preeminent source of atmospheric Pb to the North Pacific from 1970 – 2001 [Chen et al., 2005], despite the fact that leaded gasoline was only banned in China in 1997. The difference in Pb time series from EI and PR Col exists despite the proximity of the two sites, and the apparent lack of significant contribution of North American Pb to PR Col illustrates that elevation-dependent variability exists and must be accounted for when attempting to interpret regional/global climate signals in records from regions of high relief.

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