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# Lead isotopic fingerprinting of 250-years of industrial era pollution in Greenland ice

Sophia M. Wensman [*,a], Alyssa E. Shiel [a], Joseph R. McConnell [b]

[a] College of Earth, Ocean, and Atmospheric Sciences, Oregon State University, 104 CEOAS Admin Bldg., Corvallis, OR 97331, USA
[b] Desert Research Institute, 2215 Raggio Pkwy, Reno, NV 89512, USA

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ABSTRACT

Emissions from mid-latitude industrial activities (e.g., mining, smelting, coal combustion) result in long-range atmospheric transport of lead (Pb) to the Arctic. While previous measurements of elemental concentrations and Pb isotopic ratios in ice and sediments have been used to suggest potential sources of toxic heavy metal pollution in these regions, high resolution Pb isotope records are largely unavailable due to the low Pb concentrations found in Arctic ice. Here we present and interpret a high-resolution, 1759–2008 record of Pb isotopes measured in a central Greenland ice core; the first high-resolution Pb isotope record for Greenland to include the First Industrial Revolution. Records of past industrial activities coupled with Pb isotopic signatures for regional ores and coals suggest Pb pollution prior to the mid-19th century was dominated by emissions from mining and combustion of coals in England, Scotland, and Wales. Rapid 1860s increases in Pb levels and decreases in $^{206}Pb/^{207}Pb$ ratios coincided with expansion of coal consumption in Europe and North America. Significant influence of 20th century smelting of Australian Broken Hill Pb ores in Europe resulted in a less radiogenic Pb isotope signature. The phase-out of leaded gasoline and other emissions reductions following passage of air-quality legislation in the United States had a pronounced effect on $^{206}Pb/^{207}Pb$ ratios, with values falling from 1.187 in 1978 to 1.154 in 1983. Increasing $^{208}Pb/^{207}Pb$ ratios through the 1990s and 2000s indicate rising influence of long-range transport from Asia countering declines in European emissions. This 250-year high-resolution Pb isotope reconstruction allows attribution of Pb sources to central Greenland with unprecedented detail.

## 1. Introduction

The global biogeochemical cycle of lead (Pb) has been dominated by anthropogenic emissions for centuries to millennia (Pacyna and Pacyna, 2001; Shirahata et al., 1980; Murozumi et al., 1969; Patterson, 1965). Because Pb can be transported great distances through the atmosphere (Settle and Patterson, 1991), elevated Pb levels from anthropogenic emissions have been detected in inhabited and uninhabited areas of the Northern Hemisphere for at least the past 2500 years (McConnell et al., 2019; McConnell and Edwards, 2008; Osterberg et al., 2008; Rosman et al., 1993, 1997; Candelone et al., 1995; Hong et al., 1994; Murozumi et al., 1969) and in the Antarctic for at least the past 130 years (McConnell et al., 2014; Van de Velde et al., 2005; Planchon et al., 2003; Vallelonga et al., 2002; Wolff and Suttie, 1994). However, the specific origins of natural and anthropogenic Pb in these remote environments, particularly prior to the mid-20th century, remain poorly constrained.

Isotopic fingerprinting techniques are uniquely suited to sourcing Pb. The stable Pb isotope system is comprised of both primordial Pb (204), and radiogenic Pb (206, 207, and 208) which forms from the radioactive decay of parent uranium and thorium isotopes ($^{238}U$, $^{235}U$, and $^{232}Th$, respectively). Lead isotopic signatures are preserved during rock formation resulting from the Pb source's age and geologic history (Sangster et al., 2000; Chow and Earl, 1972). Because Pb isotopic ratios are not measurably fractionated by physicochemical processes, industrial activities such as the mining and smelting of ores, as well as the combustion of fossil fuels (Pacyna and Pacyna, 2001), leads to atmospheric Pb emissions with the same Pb isotopic composition as the source. Major global sources of Pb have been characterized isotopically (e.g. Bollhöfer and Rosman, 2001) and these endmembers used to identify sources of Pb within environmental archives including glacial ice. However, such isotopic studies in ice have been limited (Lee et al., 2011; Vallelonga et al., 2002, 2010; Krachler et al., 2004; Rosman et al., 1993, 1997,

* Correspondence to: 2215 Raggio Pkwy, Reno, NV, USA.
*E-mail address:* sophia.wensman@dri.edu (S.M. Wensman).

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1998) by small sample size and low Pb concentrations (often only a few pg $g^{-1}$), leading to results characterized by poor precision or by low temporal resolution in exchange for improved precision. Most high-resolution studies in ice have been limited to the past few decades (Kang et al., 2017; Cimova et al., 2016; Bory et al., 2014; Liu et al., 2011; Barbante et al., 2004; Sherrell et al., 2000; Rosman et al., 1993, 1994, 1998).

Here we present a sub-annually resolved Pb isotope record for 1759–2008 from 138 discrete meltwater samples from a central Greenland ice core (Fig. 1), along with new protocols for isotopic measurements of low-level Pb samples by HR-ICP-MS developed as part of this study. Taking advantage of the high resolution and low uncertainties, we address the following research questions:

1. How did Pb isotopic ratios change in Greenland ice between 1759 and 2008? What portion of this Pb was from anthropogenic sources?
2. What were the primary sources of Pb within the Summit_2010 core? As this study constituted the first to analyze Pb isotopes in Greenland ice from the First Industrial Revolution, did Pb isotopic ratios during this period reflect emissions from primarily ore smelting or coal combustion?

## 2. Methods

### 2.1. Continuous analysis

Discrete melterwater samples dated to the period 1759–2008 were obtained from the Summit_2010 core collected near Summit Station in central Greenland (72.6 N, 38.3 W). Age dating for the Summit_2010 ice core has been described previously in Maselli et al. (2017), and the technique is described in detail in Sigl et al. (2013, 2015). Briefly, volcanic horizons in sulfur (S) from well-dated eruptions were first identified to constrain dating. Annual layer counting using seasonal changes in concentrations of sodium (Na) and calcium (Ca), as well as the ratio of non-sea-salt S/Na cycles were then used to robustly identify annual time horizons, with hydrogen peroxide used as an additional winter marker in the upper section of the core. The uncertainty on the age dating of the record is estimated to be ± 0.33 years.

Discrete samples from the ice core were collected for Pb isotope determinations during continuous chemical and elemental analysis with the melter-based system at Desert Research Institute (DRI). Lead and cerium (Ce) concentrations were measured in contiguous longitudinal samples on an Element2 (Thermo Scientific) high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) operating in low-slit resolution and electronic scan mode using previously published methods (McConnell et al., 2019, 2002b). Only meltwater from the innermost 10% of the ~33 by ~33 mm cross-section of the longitudinal samples was used for the HR-ICP-MS measurements. The continuously measured Pb and Ce concentrations, as well as enrichment factors have been published previously (McConnell et al., 2019) and are used here to inform interpretation of Pb isotope measurements. Enrichment factor (EF) was calculated following standard procedures (McConnell et al., 2018, 2019; McConnell and Edwards, 2008) from measured concentrations of Pb and the rock-forming element Ce which derives almost exclusively from crustal dust. In preparation for sample collection, 7 mL polypropylene vials were precleaned by soaking in 1% ultra-pure nitric acid ($HNO_3$) for at least three months. Discrete, ~5 mL samples used for Pb isotope analysis were collected by directing a portion of the acidified (1% ultra-pure $HNO_3$) continuous meltwater stream – just prior to injection into the HR-ICP-MS – to a Spectra-Chrome CF1 fraction collector equipped with the pre-cleaned vials. Discrete samples for the period 1817–1863 were used for another purpose and were therefore unavailable for Pb isotope analysis. Acidified meltwater samples were transferred to the University of British Columbia (UBC) for Pb isotopic analysis.

### 2.2. Sample preparation

All sample preparation for Pb isotopic analysis was completed in class 1000 cleanrooms at UBC in the Pacific Centre for Isotopic and Geochemical Research (PCIGR). Further care to avoid contamination was taken by working in class 100 laminar flow or exhaust hoods in these spaces. Nitric acid ($HNO_3$) used in this study was purified in-house from concentrated reagent grade acids by sub-boiling distillation.

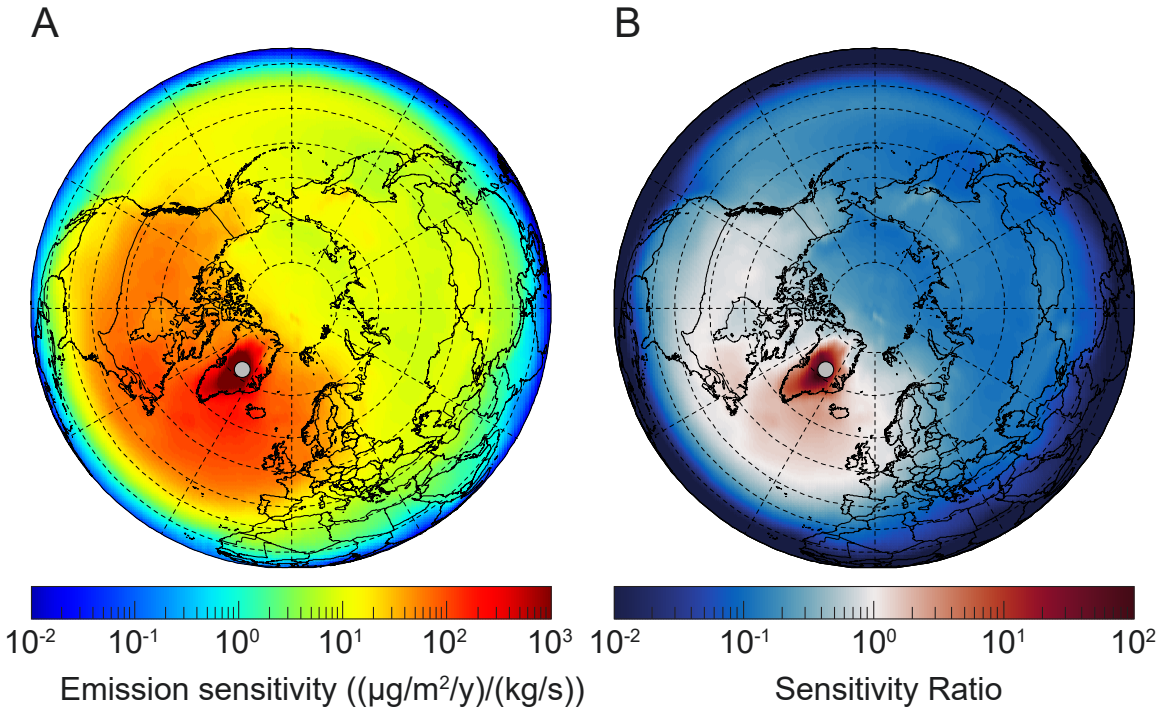


**Fig. 1.** A) Emission sensitivities for the Summit drilling location from FLEXPART model simulations, B) emission sensitivities normalized to Britain.

Ultrapure water (18.2 MΩ cm) was used to dilute samples and standards. All plastics were cleaned using successive treatments of Citranox® detergent (Alconox, Inc., USA), reagent grade hydrochloric acid (HCl), and reagent grade $HNO_3$. Savillex® PFA vials were cleaned individually with an additional treatment with 15 M sub-boiled $HNO_3$.

In preparation for Pb isotopic analysis, the acidified meltwater samples were transferred to 15 mL Savillex® PFA vials, dried down overnight at ~90 °C, brought up in 0.5 mL of 2% $HNO_3$, and then heated at 90 °C for 1 h and sonicated for 20 min. Prior to analysis, samples were diluted further with 2% $HNO_3$ to obtain desired concentrations of Pb. Procedural blanks were prepared following the same method as samples and reference materials. Undiluted procedural blanks contained 8000–24,000 counts on a 350,000-count signal for samples. As samples were diluted prior to analysis, these procedural blanks are estimated to have contributed 1.3 ± 0.7% (SD) of the signal, with a maximum possible contribution of 5.0%.

### 2.3. Lead isotopic analyses

Lead isotopes were measured on an AttoM HR-ICP-MS (Nu Instruments) located in a class-1000 clean room in the PCIGR. Samples were introduced into the HR-ICP-MS using (1) the standard inlet configuration with a 100 μl $min^{-1}$ PFA nebulizer (Elemental Scientific) and glass spray chamber, or (2) an Aridus II desolvating C-flow nebulizer system (CETAC Technologies). The measurement protocol used for Pb isotopes was adapted from that presented in Smith et al. (Smith et al., 2019) for honey.

Samples, reference materials, and standards were analyzed at 0.2–0.4 ng $g^{-1}$ using the standard inlet configuration, and at 0.05–0.2 ng $g^{-1}$ using the Aridus II. Lead isotopic measurements were blank corrected online using the 2% $HNO_3$ solution used for sample dilution. This blank solution contributed an average of 0.7 ± 0.7% of the Pb signal measured, with a maximum of 2.6% determined from the ratio of the blank counts and average counts of the blank's bracketing standards, and therefore did not significantly impact interpretation of Summit_2010 samples. Measured uncertainties for samples were ~0.2% RSD for $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios and are thus comparable to previous studies using HR-ICP-MS (Zheng et al., 2007; Krachler et al., 2004).

We used National Institute of Standards and Technologies (NIST, USA) SRM 981 natural Pb (isotopic) standard for monitoring analytical run instrument drift and for normalization of all measured Pb isotopic ratios. A sample-standard measurement protocol was used where the standard was measured after each sample. At the start of each analytic session, nine successive runs of NBS 981 were included. Each session ended with five successive runs of NBS 981. For quality assurance, at least three reference materials were measured during each analytical session. While the reference materials do not have certified Pb isotopic compositions, measured Pb isotopic ratios were compared with published values (Weis et al., 2006 for BCR-2 Columbia River basalt, Souto-Oliveira et al., 2019 for NIST 2709a), and with other measurements of the same material made as a part of this study. Measured reference material (BCR-2 & NIST2709a) ratios differed from published values by an average (n = 85) of 0.27% ($^{206}Pb/^{207}Pb$) and 0.16% ($^{208}Pb/^{207}Pb$), respectively. Two in-house reference materials (bulk G and bulk J) were prepared from surface snow samples collected at Summit station in 2013 and measured ≥ 2 times per analytical session. Precision of the Pb isotopic measurements for these bulk samples is thought to best reflect that of meltwater from the Summit_2010 core.

Samples and reference materials were diluted with 2% $HNO_3$ to achieve run concentrations of Pb similar to those of bracketing standards. We included measured Pb isotopic ratios for samples and reference materials in this study when counts were within 60–175% of the bracketing standards. Tests with reference materials (BCR-2, NIST 2709a and NIST 1643f) were used to determine this range. No samples with concentrations between 60% and 175% of the standard bracket were outside of the 3 SD cutoff used to assess outliers.

All measurements for this study including samples, standard reference materials, bulk ice, analytical blanks, and procedural blanks can be found in SI Tables 1–10.

### 2.4. FLEXPART modeling

We used backward simulations of the FLEXPART atmospheric aerosol transport and deposition model (Eckhardt et al., 2017; Stohl et al., 2005) for identification of sources and source regions of Pb found in the ice. Such model simulations require detailed atmospheric fields so, following McConnell et al., (2018, 2019), we used 1920–1999 CE reanalysis data (CERA-20C) and assumed that atmospheric transport was similar during the past 250 years.

## 3. Results

The temporal records of Pb concentrations, EF values, and $^{206}Pb/^{207}Pb$ isotopic ratios are given in (Fig. 2). Between 1759 and 2008, Summit_2010 Pb concentrations varied between 0.007 ng $g^{-1}$ and 0.236 ng $g^{-1}$, with the highest concentrations observed in the 1960s and 70s. Pb isotopic ratios varied between 1.141 and 1.208 for $^{206}Pb/^{207}Pb$, and between 2.420 and 2.485 for $^{208}Pb/^{207}Pb$. While Pb concentrations and EF values generally increased until the 1970s, Pb isotopic ratios did not follow a consistent trend during this period suggesting multiple sources that varied through time. To evaluate sources, we divided the record into three periods: (1) the First Industrial Revolution (1759–1817), (2) the coal dominated industrial (1860–1922), and (3) expansion and phase out of leaded gasoline (1923–2008).

## 4. Discussion

### 4.1. First industrial revolution (1759–1817)

Summit_2010 Pb concentrations during the First Industrial Revolution period showed relatively small variations, with an average value of 0.016 ng $g^{-1}$ (Fig. 2). Despite lower levels compared to the remainder of the record, the median annual EF was 17 and ranged from 8 to 50 (Fig. 2), indicating that ~96% of the deposited Pb was pollution related – well above enrichments of ~1 measured in central Greenland ice at the

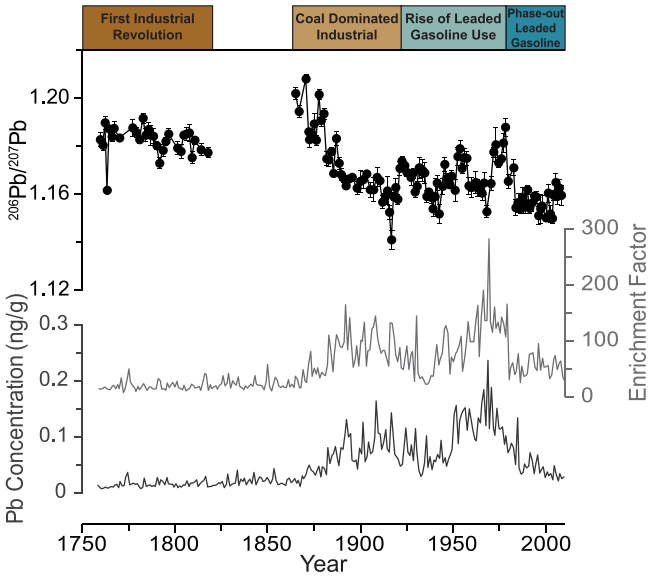


**Fig. 2.** The $^{206}Pb/^{207}Pb$ ratios (this study), Pb concentrations and EFs (McConnell et al., 2019) of the Summit_2010 core from 1759 to 2008. Uncertainties shown for $^{206}Pb/^{207}Pb$ represent 2SE.

~500 CE start of the Early Middle Ages when anthropogenic emissions were negligible (McConnell et al., 2019). Similar to the Pb concentrations, the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios during this time period were relatively stable, with average values of 1.182 ± 0.006 (2SD) and 2.462 ± 0.006, respectively (Figs. 2, 3).

Mining and coal combustion are well-known sources of Pb pollution (e.g., Pacyna and Pacyna, 2001). The invention of the steam powered Newcomen engine in 1712 that was used to pump water out of regularly flooded coal mines revolutionized and expanded coal mining operations in Britain by allowing mining at greater depths than previously possible (Flinn, 1984). The Pb isotopic ratios in the ice during this period were consistent with emissions from mining and combustion of British coal as a primary source of Pb pollution (Fig. 3). In addition, mining and smelting of British Isles Pb ores produced approximately 31,000 tons of Pb in 1755, and up to 59,000 tons in 1769 (Burt, 1969), and likely represented an important, but minor source of Pb pollution. High relative emission sensitivities indicated by FLEXPART model simulations for central Britain compared to other potential United States (U.S.) and European sources further support this interpretation (Fig. 1B).

Because there were relatively few anthropogenic sources during the First Industrial Revolution, we used a three-endmember mixing model to estimate the relative contributions of (1) English and Welsh coal, (2) Scottish coal, and (3) British Isles Pb ores. English and Welsh coals exhibit similar Pb isotopic compositions and thus were combined to simplify the model. In addition, we assumed the contribution of natural Pb (1.201 ± 0.005 for $^{206}Pb/^{207}Pb$ and 2.472 ± 0.009 for $^{208}Pb/^{207}Pb$; Rosman et al., 1997) to be negligible because anthropogenic sources dominated total Pb deposition. Development and details behind Pb isotope mixing models have been described previously (e.g., Faure and Mensing, 2005; Gobeil et al., 1995). In a three-endmember mixing model it is assumed that Pb can be represented as a mixture of endmember 1 ($f_1$), endmember 2 ($f_2$) and endmember 3 ($f_3$), such that the combined total of these fractions equals 1 (Eq. 1). As a result, the isotopic ratio of the sample ($X_S$) is determined by the isotopic ratios of the endmembers ($X_1$, $X_2$, and $X_3$) multiplied by the fraction of Pb each endmember contributes (Eq. 2).

$$f_1 + f_2 + f_3 = 1 \quad (1)$$

$$f_1X_1 + f_2X_2 + f_3X_3 = X_S \quad (2)$$

In our model, $^{206}Pb/^{207}Pb$ ($^{208}Pb/^{207}Pb$) ratios for English and Welsh coal, Scottish coal, and British Isles Pb ores were 1.184 (2.458), 1.181 (2.479), and 1.171 (2.453), respectively (Farmer et al., 1999; Rohl, 1996; Hamilton and Clifton, 1979), with isotopic ratios of each Pb endmember assumed to be constant during this time period. Given these assumptions, calculated endmember contributions should be viewed as estimates of relative proportions of Pb contributed from each source. Model results suggest that emissions from combustion of English and Welsh coal dominated Pb pollution through most of the First Industrial Revolution, contributing ~85% of Pb in the ice until 1789. After this, the fraction from English and Welsh coal combustion decreased slightly to ~50%. Scottish coal combustion also contributed a significant fraction of Pb, rising from ~15% to ~25% after 1793. Although contributions from British Isles Pb ore smelting were relatively small, variability in these contributions led to significant shifts in the Pb isotopic composition in the ice over time. For example, the dip in the $^{206}Pb/^{207}Pb$ ratio in 1763 appears to have been strongly controlled by British Isles Pb ores, as were smaller dips in 1791 and 1809. In summary, the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios in the ice during the First Industrial Revolution suggest that Pb pollution resulted predominantly from emissions from English and Welsh coal combustion, with significant contributions of Scottish coal burning particularly later in the period, and smaller contributions from British Isles Pb ore smelting (Fig. 3). However, caution should be exercised in over-interpretation of the three-endmember mixing model results, as there is significant overlap in the source Pb isotopic ratios. Rather, the model is used to support the overall interpretation that British Isles sources dominated the Pb pollution record during the course of the First Industrial Revolution. Our findings further support interpretations in earlier studies, which identified British Isles coal mining and combustion emissions as primary sources of Pb pollution in lake sediments from Northern Scotland and a peat core from the Faroe Islands (Shotyk et al., 2005; Eades et al., 2002) dated to this period.

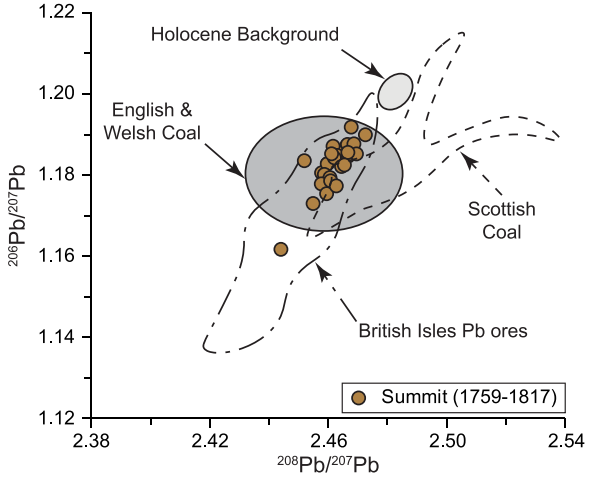


**Fig. 3.** Lead isotopic ratios in Summit_2010 samples corresponding to the First Industrial Revolution (1759–1817) compared to Pb isotopic ratios from British Isles Pb ores (Rohl, 1996; Hamilton and Clifton, 1979), British Isles coals (Farmer et al., 1999), and Holocene background (Rosman et al., 1997).

### 4.2. Coal dominated industrial (1860–1922)

Between 1817 and the early 1860 s, Pb concentrations remained largely constant with values averaging 0.02 ng $g^{-1}$, although Summit_2010 core samples were not available for Pb isotope analysis between 1817 and 1863. Beginning in the 1860 s, Pb concentrations increased approximately 10-fold from ~0.02 ng $g^{-1}$ to a maximum of ~0.14 ng $g^{-1}$ in 1916, with median annual enrichments increasing from ~25, between 1860 and 1870, to ~80, between 1910 and 1920 (Fig. 2). During this same period, the $^{206}Pb/^{207}Pb$ ratios decreased from 1.201 to 1.141 (Fig. 2). The higher $^{206}Pb/^{207}Pb$ ratios observed between the 1860 s and 70 s likely resulted from a high proportion of U.S. coal burning emissions since U.S. coal values are more radiogenic than European coal emissions (Díaz-Somoano et al., 2009; Farmer et al., 1999; Walraven et al., 1997; Chow and Earl, 1972). Due to the lack of discrete samples available for Pb isotope analysis between 1817 and 1863, we cannot identify when fallout from U.S. emissions began to overwhelm European pollution at Summit. However, due to the rapid increase in Pb concentrations that occurred in the mid-1860s, it is likely the transition to more radiogenic signatures occurred around the same time. Previous studies have indicated coal burning as the primary source of Pb pollution in Greenland during this time largely based on covariation with source tracers such as non-sea-salt sulfur and black carbon (Pérez-Rodríguez et al., 2018; McConnell and Edwards, 2008; McConnell et al., 2002a). The rise in Pb pollution also tracked the rapid expansion of coal consumption in Europe and North America (Bond et al., 2007; Novakov et al., 2003) in the late 19th century. A three-endmember mixing model was insufficient to capture the complexity of this or subsequent time periods because of the large number of potential sources, and therefore was not employed to estimate relative contributions during the coal-dominated period of the Second Industrial Revolution in the late 19th and early 20th centuries, or during the use and phase-out of leaded gasoline.

In the Faroe Islands (Shotyk et al., 2005) and Denmark (Shotyk et al., 2003), coals from the British Isles have been identified as a primary

source of Pb pollution well into the 20th century. In the Summit_2010 core, fallout from combustion of British Isles coals likely dominated much of the European signature through the late 19th century as production outpaced that of Germany, the next largest European coal producer (Mitchell, 1992). By the early 1900s, however, Germany's production largely matched that of the British Isles (Mitchell, 1992), thus contributing to a more mixed European pollution signature.

While European and North American Pb coal signatures in the ice dominated at the end of the 19th century (Fig. 4), beginning in the 1890s, and extending through 1916, isotopic ratios exhibited lower $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ values than can be fully accounted for with only these sources. This shift in Pb isotopic composition may be suggestive of emissions from the smelting of Pb and zinc (Zn) ores imported to Europe from the Australian Broken Hill mine (1.04 for $^{206}Pb/^{207}Pb$ and 2.32 for $^{208}Pb/^{207}Pb$; Sangster et al., 2000) and to a lesser extent from European ores (Farmer et al., 1999). Broken Hill ores were processed in England as early as 1826 (Day and Tylecote, 1991). By the 1850 s, British ores were deemed uneconomical and gradually replaced (Day and Tylecote, 1991). Influence of Broken Hill ores during this period has been observed in lake and peat records from Loch Laxford, Scotland (Kylander et al., 2009), as well as the Jura Mountains, Switzerland (Shotyk, 1998). Although signatures of coal combustion continued to dominate, the comparatively low radiogenic signature of Broken Hill ores resulted in a significant drop in both the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios in the Summit_2010 core. After 1916, Pb levels in ice rapidly declined and remained low through the Great Depression until 1949. $^{206}Pb/^{207}Pb$ ratios sharply increased between 1916 and 1922 coincident with the drop in Pb levels. This may in part represent a reduction of Broken Hill ore smelting in Europe in response to the concurrent production declines from the mine (Mudd, 2007).

### 4.3. Leaded gasoline use and phase-out (1923–2008)

Tetraethyl Pb additive was first developed as an antiknock agent in internal combustion engines in 1921, with commercial use beginning around 1923 (Nriagu, 1990). By 1936, tetraethyl Pb had been added to 90% of gasoline in the U.S. (Nriagu, 1990). The Summit_2010 record shows no significant influence of U.S. leaded gasoline combustion until the 1950s, likely due to the lower consumption levels observed between the 1930s and 1940s (less than ~100,000 metric tonnes per year) compared to higher levels beginning in the 1950s (~100,000–270,000 metric tonnes) (Nriagu, 1990). The reduction in Pb concentrations observed in the ice from the early 1920s through the late 1940s suggests changes in coal, oil, and gasoline consumption patterns during and following the Great Depression. Coal consumption in the U.S. decreased by 30% between 1920 and 1935 (U.S. EIA, 2012), with rapid, additional changes during the 1940s and 50s as oil became a more common source of home heating. The share of households using coal for heating fell from 55% in 1940 to 35% in 1950, while oil and gas usage rose from a combined 20–52% in the same period (U.S. Census Bureau, 1940, 1950). The shift towards heating oil also has been identified as a cause of changing Pb concentration profiles in Swiss peat bog cores (Shotyk et al., 1998). Fluctuating $^{206}Pb/^{207}Pb$ ratios (1.15–1.17) between the late 1920 s and the late 1940 s support dynamic changes in Pb emissions corresponding to changes in production and consumption of coal in the U.S. and Europe.

Consumption and the associated production of leaded gasoline in the U.S. increased steadily from ~1930 until its peak in the early 1970s (Fig. S2) (Reuer and Weiss, 2002; Nriagu, 1990). The influence of leaded gasoline in the Summit_2010 core was clear by the 1950s. Lead concentrations rose rapidly after 1949 in parallel with increases in leaded gasoline use in the U.S., peaking in 1968 (Fig. 2; Fig. S2), with depositional fluxes reaching levels 15 × those seen during the First Industrial Revolution (1759–1817). Increases in annual enrichments were large but less pronounced than concentrations because of a doubling in the dust tracer Ce during the late 1960s. Enrichments increased ~8-fold from a median of 17 during the First Industrial Revolution to 135 during the height of leaded gasoline use, with a maximum of 280 in 1968 (Fig. 2). While leaded gasoline use in Europe began around the same period, U.S. levels remained far higher through the period of extensive leaded gasoline consumption (Reuer and Weiss, 2002).

The Summit_2010 record largely demonstrates the influence of U.S. consumption patterns on Arctic environments during this period. This is consistent with previous studies of Greenland peat and ice cores (Pérez-Rodríguez et al., 2018; Rosman et al., 1993) and is supported by the Pb isotopic shift towards more radiogenic U.S. leaded gasoline emissions. Between 1967 and 1978, the Summit_2010 record shows an increase in $^{206}Pb/^{207}Pb$ ratios from 1.152 to 1.188 (Fig. 2). U.S. aerosol measurements during this period demonstrated a similar shift, with an increase from 1.151 to 1.211 between 1967 and 1974 (Chow et al., 1975) to 1.220 by 1980 (Shirahata et al., 1980). This shift has been attributed to the transition towards leaded gasoline additives derived from SE Missouri ores that are characterized by a more radiogenic signature (Chow et al., 1975). Unlike the variability in U.S. aerosols, isotopic ratios in European aerosols between 1970 and 1984 were relatively stable, with a comparatively lower radiogenic signature ($^{206}Pb/^{207}Pb$ ratios averaging 1.11 ± 0.02) due to the pervasive use of Broken Hill ores as a leaded gasoline additive (Grousset et al., 1994).

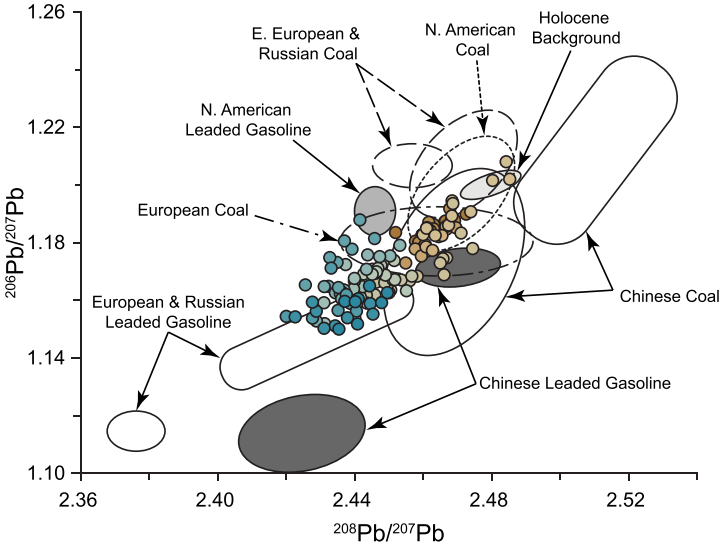


**Fig. 4.** Comparison of decadally binned Pb isotopic ratios from Summit_2010 to source materials. Ellipses represent isotope ratios from Chinese leaded gasoline (Díaz-Somoano et al., 2009), Chinese Coal (Bi et al., 2017; Mukai et al., 1993), European Coal (Díaz-Somoano et al., 2009; Farmer et al., 1999; Walraven et al., 1997; Chow and Earl, 1972), European leaded gasoline (Teutsch et al., 2001; Monna et al., 1997; Hopper and Ross, 1991; Chow et al., 1975), N. American coal (Chow and Earl, 1972), N. American leaded gasoline (Teutsch et al., 2001; Chow et al., 1975), Russian coal (Mukai et al., 2001), Russian leaded gasoline (Kober et al., 1999; Mukai et al., 1993), and Greenland Holocene background (Rosman et al., 1997). Comparison of isotopic ratios with Broken Hill Pb ore can be found in Fig. S1.

While other regions of the globe also used leaded gasoline during this period, FLEXPART model simulations suggest that the primary source regions were Europe and North America where emission sensitivities were much higher (Fig. 1A).

Just as the rise of leaded gasoline in the U.S. was recorded in the ice core, phase-out of leaded gasoline in response to the U.S. Clean Air Act also was clearly observed, with Pb concentrations dropping by 80% during this period. The $^{206}Pb/^{207}Pb$ ratio mirrors this decline in Pb pollution and U.S. leaded gasoline consumption (Fig. S2), falling from 1.188 in 1978 to 1.154 in 1983, as relative influence of the more radiogenic U.S. leaded gasoline isotopic signature declined. Following declines in leaded gasoline use in the U.S., the Summit_2010 record is characterized by a period of relatively little variation in $^{206}Pb/^{207}Pb$ ratios (1.150–1.165). The change in the ratio following phase-out of leaded gasoline in the U.S. is consistent with a decline in the relative importance of U.S. emissions until the end of the record (Fig. 5). This mid-1980s Pb signature is consistent with European aerosols of the time (Bollhöfer and Rosman, 2001). The phase-out of leaded gasoline in Europe occurred.

from 1984 to 2000 but it appears to have had little impact on Pb pollution in central Greenland indicating influence of an additional Pb source. Beginning in the 1990s there is a trend towards increasing $^{208}Pb/^{207}Pb$ observed through the end of the record, with ratios increasing from ~2.33–2.45 during this period (Fig. 5). This trend suggests the rising influence of Chinese Pb pollution. Indeed, Summit_2010 samples fall on a mixing line between European and Chinese aerosols following phase-out of leaded gasoline in the U.S. as is seen in Fig. 5.

FLEXPART modeling suggests that for Chinese emissions to significantly influence the Summit_2010 record, levels must be at least an order of magnitude higher than European or North American emissions (Fig. 1A). Following the ban of leaded gasoline in China, Pb concentrations in Chinese aerosols averaged 188 ng $m^{-3}$, significantly higher than levels found in European and North American aerosols (<20 ng $m^{-3}$) (Bi et al., 2017), with higher levels attributed to coal combustion and non-ferrous metal smelting in the region (Bi et al., 2017). Thus, these results demonstrate the importance of Chinese emissions following the reduction of U.S. and European emissions. Previous studies in Greenland ice have indicated Chinese emissions as likely sources beginning in the early 2000s (Kang et al., 2017; Bory et al., 2014).

### 4.4. Comparisons to other Greenland records

No other Greenland ice studies of Pb isotopes have covered the same 250-year period. Four previous studies presented Pb isotopes from Greenland snow and ice cores (Kang et al., 2017; Bory et al., 2014; Sherrell et al., 2000; Rosman et al., 1994), however, these studies focused on shorter time periods of ~10–30 years and only extended back as far as 1960. The new Pb isotope ratios for Greenland ice from Summit are presented with previously published Pb ratios of Greenland snow and ice in Fig. 6 (expanded record observed Fig. S3). The Summit Pb isotope record reconstructed in this study shows good agreement with other records obtained at or near Summit Station (Sherrell et al., 2000; Rosman et al., 1993, 1994). However, we found lower $^{206}Pb/^{207}Pb$ values than were observed in the insoluble particulate matter measured in NGRIP snow samples (Bory et al., 2014) (Fig. 6). These differences may be the result of the 300 km distance between Summit (72.6 N, 38.3 W) and NGRIP (75.1 N, 42.3 W), or may be due to methodological differences. Lead isotopes were measured only on insoluble particulate matter for NGRIP samples (Bory et al., 2014), while here we measured Pb isotopes of total Pb. Bory et al. (2014) suggested industrial sources of Pb including coal combustion and smelting were the primary sources of insoluble Pb, attributing the more radiogenic signature to North American sources from 1989 to 1995, and to Chinese sources from 1998 to 2001. Indeed, Pb isotope ratios suggest that the NGRIP samples were more sensitive to emissions from European coal combustion, while Summit_2010 samples were more sensitive to leaded gasoline emissions during this period (Fig. S4).

## 5. Conclusions

This study provides a high-resolution examination of the Pb pollution record for central Greenland during the last 250 years. This is the first Greenland ice Pb isotope record to cover the First Industrial Revolution through the mid-20th century. We were able to identify and, in some cases, quantify the relative contribution of sources to the Arctic using Pb isotopic fingerprinting techniques. In response to the questions raised in the introduction:

1. Anthropogenic emissions dominated the Pb pollution record during the 250-year record. By the start of the First Industrial Revolution, more than 95% of Pb present in the record stemmed from anthropogenic sources. The Pb isotope record demonstrated the strong influence of European and North American emissions between 1759 and 2008. The importance of these influences resulted from a combination of the ice core collection location (Summit, Greenland) and the magnitude of emissions produced by these two regions during this time.

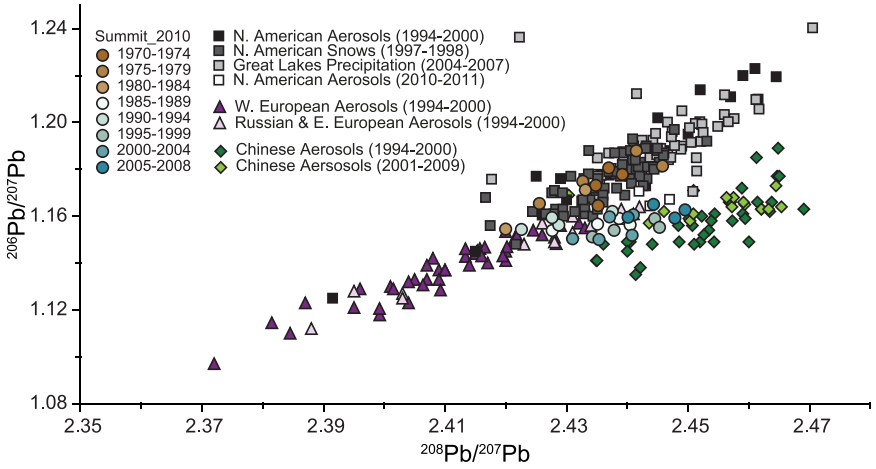


**Fig. 5.** Lead isotopic ratios of Summit_2010 samples between 1970 and 2008, compared to other recent (post-1994) Northern Hemisphere aerosols (Noble et al., 2015; Bollhöfer and Rosman, 2001), snows (Simonetti et al., 2000b,a) and precipitation (Sherman et al., 2015), European and Russian aerosols (Bollhöfer and Rosman, 2001), and Chinese aerosols (Bi et al., 2017).

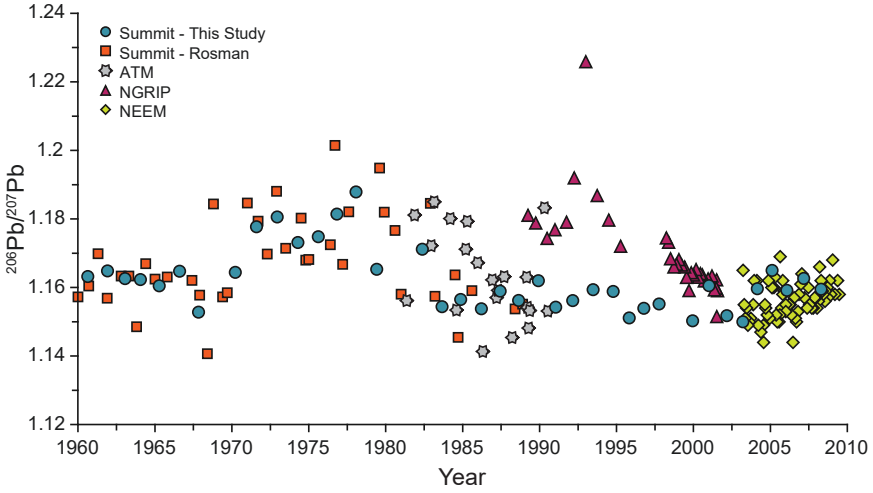


**Fig. 6.** Compilation of Pb isotope ratios from the Greenland Ice Sheet (1960–2008) including Summit Station ice (this study) and snow (Rosman et al., 1994) cores, ATM snow pit (Sherrell et al., 2000), NGRIP insoluble particles (Bory et al., 2014), and NEEM snow (Kang et al., 2017).

2. During the First Industrial Revolution (1759–1817), Pb isotopes identify coal burning in the British Isles as the dominant source, with lesser contributions from Pb ore smelting in the British Isles. By the start of the 20th century, the Pb isotopic record indicates significant contributions of Pb from expanded coal burning in North America and Europe, as well as smelting of Australian Broken Hill Pb ores in Europe. Leaded gasoline use in North America was the dominant driver of the Pb isotopic trends observed between the 1960s and 1980s. The subsequent phase out of leaded gasoline and decline of associated emissions first in North America during the 1970s and 1980s and later in Europe is seen clearly in the Summit_2010 Pb isotope record, while Chinese emissions emerge as an important source beginning in the 1990s.

Use of HR-ICP-MS techniques allowed us to perform Pb isotope analyses on sub ng $g^{-1}$ level ice with uncertainties comparable to other ice core studies using HR-ICP-MS instrumentation (SI Table 11). Uncertainties are equal to or better than studies using thermal ionization mass spectrometry (TIMS; SI Table 11) but required substantially lower volumes (typically 15–30 mL for TIMS, ~5 mL for this study). This provides evidence that these methods may be applied to other ice cores and media where low Pb levels make precise Pb isotopic measurements analytically challenging.

## Declaration of Competing Interest

The authors declare no competing interests.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ancene.2022.100340.

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