

Lead Isotopes as Tracers of Pollution in Snow and Ice

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ABSTRACT. Careful measurements on ice from Greenland and Antarctica have shown that even the most remote locations on earth are polluted with lead (Pb). However, because anthropogenic Pb originates from ore bodies of known isotopic composition it is possible to identify the source of this Pb. Although Pb concentrations reach pg/g levels in older samples, the measurement sensitivity of modern mass spectrometers permits the isotopic composition to be measured and the source traced. This paper reviews recent measurements of Pb isotopes in Greenland and Antarctic ice and reports the isotopic composition of Pb reaching Dome C, Antarctica during the Last Glacial Maximum.

Key Words: Lead isotopes, pollution, snow, ice, Antarctica, Greenland

Introduction

Lead (Pb) is a toxic heavy metal whose abundance in the environment is closely associated with the development of civilizations. Early production occurred as a bi-product of smelting mixtures of native silver. However, the discovery of cupellation some five thousand years ago marked the beginning of the production of significant quantities of Pb, mainly associated with the production of silver from sulphide ores (Patterson 1980). Increasing Pb production also caused an increase in its concentration in the atmosphere. This was first demonstrated by Murozumi *et al.* (1969) who measured Pb concentrations in snow and ice dating from ~ 1965 AD to 800 BC and showed that modern snow at remote sites in Greenland was contaminated at least 100 fold above the natural background level.

Polar ice has proved to be a particularly useful matrix for measuring changes in the composition of the atmosphere. Since the natural abundance of Pb

in Greenland ice is extremely low (< 1 pg/g), small changes introduced by pollution can be easily resolved above the background level. These concentrations are however still extremely low and require highly sensitive measurement techniques. More importantly, great care needs to be exercised in the measurement process to avoid inadvertent contamination during sample collection, processing and analysis. Thus, Murozumi *et al.* (1969) minimised these problems by carefully processing very large quantities of ice (metre-sized blocks) and measuring the Pb concentration by thermal ionisation mass spectrometry (TIMS) using isotope dilution.

Since this time even cleaner sampling and processing procedures have been developed that allow surface snow and ice core samples, drilled at depths of more than 1 km in Greenland, to be reliably measured (Ng and Patterson 1981; Candelone *et al.* 1994; Hong *et al.* 1994). Evidence of high concentrations of Pb in the atmosphere in the recent past is well established, and there is now keen interest in identifying its origin. In this paper we describe how natural isotopic tracers are being used to probe the origin of the Pb preserved in the continental ice-caps.

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Lead Isotopes in Nature

Although Murozumi *et al.* (1969) used isotope dilution mass spectrometry (IDMS) to measure Pb concentrations, they did not report isotopic compositions for their samples. However, the measurement of the lead's isotopic composition is particularly important because it can be used to characterize sources and identify the origin of pollution.

Lead has four stable isotopes: ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb , with abundances typically 1.4, 24.1, 22.1 and 52.4 % respectively (Rosman and Taylor 1998). Lead displays large natural variations in isotopic composition depending on its origin, because the isotopes ^{206}Pb , ^{207}Pb and ^{208}Pb are the stable end products of three different radioactive decay series starting with ^{238}U (half-life 4.5×10^9 yr), ^{235}U (half-life 7.1×10^8 yr) and ^{232}Th (half-life 1.4×10^{10} yr), respectively. While the composition of Pb in crustal rocks containing U and Th steadily changes over geological time, it is constant in Pb ore bodies. This is due to the different geochemical properties of Pb and its parent elements resulting in their separation during the ore-forming process (Faure 1986). Consequently, young ores and crustal rocks will generally have a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio ~ 1.20 or greater while older Pb ores have significantly lower ratios (e.g. for Brocken Hill, Australia $^{206}\text{Pb}/^{207}\text{Pb}$ ratio ~ 1.04). Commonly available Pb ores can differ in their $^{206}\text{Pb}/^{207}\text{Pb}$ ratio by more than 30% (Chow *et al.* 1975).

Tracing Pollution with Lead Isotopes

Greenland

The first measurements of Pb isotopes in Greenland snow were made in 1993 by Rosman *et al.* (1993, 1994a). Snow was sampled from two cores drilled at Summit, central Greenland. Decontaminated samples were evaporated to dryness in a teflon beaker under dust-free conditions. Before evaporation, the samples were acidified with nitric acid, then a silica gel-phosphoric acid mixture and a ^{205}Pb tracer (half-

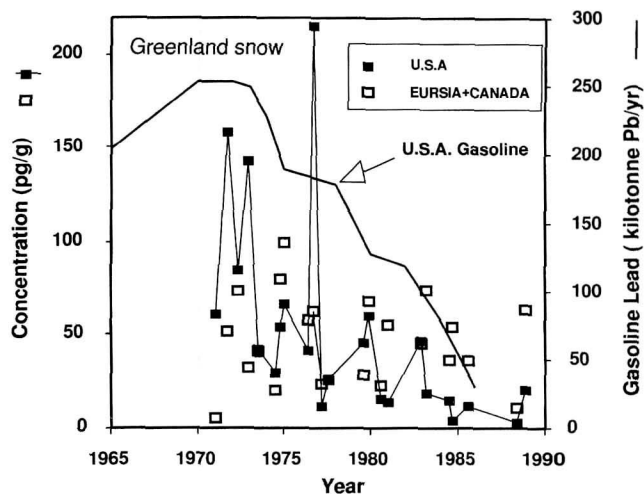


Fig. 1. The concentration of USA and Eurasian Pb in snow from Summit, Greenland. The proportional contributions were calculated using the measured $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in each snow sample and the corresponding values for USA and Eurasian Pb (Adapted from Rosman *et al.* 1994a). The proportions were converted to concentrations using the measured Pb concentration. Only from 1970 onwards are the two signatures sufficiently different to resolve the two Pb components. The decline in the use of Pb in gasoline in the USA can be seen to correlate with the concentration of USA Pb in the snow.

life 1.5×10^7 yr) were added. The samples were then transferred to rhenium filaments for thermal ionization. A VG354, 27 cm radius magnetic sector, direction focussing, mass spectrometer was used for the isotope analyses. Because the samples were small (~ 100 pg) and yielded ion currents of $\sim 1 \times 10^{-14}$ A, a Daly detector was used. The addition of a ^{205}Pb tracer to the sample during processing facilitated the measurement of both the concentration and isotopic composition at the same time (Chisholm *et al.* 1995). The results revealed that large variations in the isotopic ratios occurred over the period 1960 to 1989. Using published isotopic data for gasoline-Pb and aerosols in the United States and Eurasia, the signatures of the principal sources were characterized and used to estimate the relative contributions from these sources to the snow. The results of this study are shown in Figure 1. A high level of correlation with gasoline-Pb consumption was evident, with the bulk of the Pb originating from the USA in the early 1970s but decreasing following the removal of Pb from gasoline. By comparison there was a relatively steady contribution from Eurasia (Rosman *et al.*

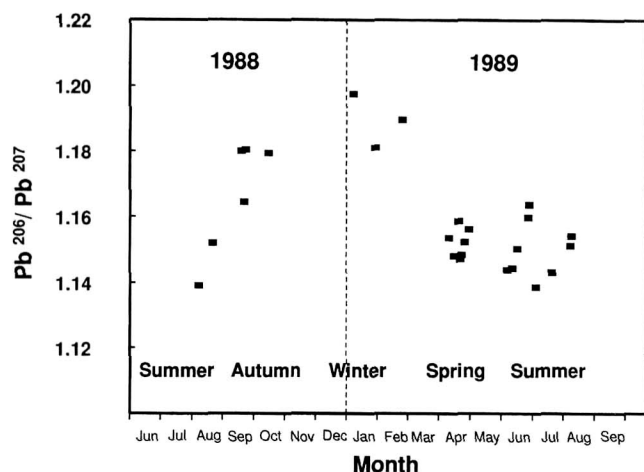


Fig. 2. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios measured in fresh snow collected at Dye 3, Greenland during 1988 and 1989. The ratios follow a seasonal cycle indicating that there is change in the relative amounts of Pb arriving from Eurasian (low ratio) and the USA (high ratio). Pb from the USA dominates in winter while in spring and summer Pb from Eurasia dominates.

1994a).

Changes in the origin of pollution between seasons has also been followed with Pb isotopes (Rosman *et al.* 1998a). This study was carried out at Dye 3, located south of Summit in Greenland. Individual snow-falls were sampled over a period of 12 months. During spring and summer the Pb had a Western European isotopic signature while during winter it had a U.S.A. signature, showing that Dye 3 was influenced by pollution from different source regions at different times of the year. The seasonal variation in the isotopic signature at Dye 3 is clearly evident in Figure 2.

The use of Pb isotopes to determine the provenance of ancient pollution was recently demonstrated in measurements on ice from the European GRIP (Greenland Ice-Core Program). Following a suggestion by Patterson (1980), Hong *et al.* (1994) analyzed 2 kyr old ice and detected a peak of Pb concentration that was attributed to emissions from Greek/Roman mining and smelting of Pb ores. Subsequent measurements of Pb isotopes in these samples by Rosman *et al.* (1997) showed that the Pb was anthropogenic. In addition, the same Pb was matched to Pb ores mined in Southern Spain during the same period. Because two main regions, Rio Tinto in south west Spain and Mazarron in south

east Spain, each with distinctive isotopic signatures, were being mined at this time, it was possible to quantify their relative contributions in the Greenland snow (Rosman *et al.* 1997).

Antarctica

There are very few measurements of Pb isotopes in Antarctic snow and ice. The first was carried out relatively recently by Rosman *et al.* (1994b) who measured snow sampled in 1983/84 along a transect from the coastal French base at Dumont d'Urville to a site 433 km inland. The isotopic composition of these samples showed that anthropogenic Pb was present, confirming earlier conclusions of Boutron and Patterson (1987) based on geochemical arguments. The analysis of snow collected 103 km and 433 km inland from the coast, led Rosman *et al.* (1994b) to suggest that the source of the anthropogenic Pb was South America, but source signatures were not available to test this hypothesis. The study also included a measurement on 7.5 kyr old ice from Dome C which displayed a surprisingly high $^{206}\text{Pb}/^{207}\text{Pb}$ ratio.

A second series of measurements was executed by Rosman *et al.* (1998). They measured Pb isotopes as well as Ba, Bi and Pb concentrations in snow and ice drilled at Law Dome, near Casey. Most snow and ice samples analyzed were less than ~150 years old, although one was dated ~946 BC. These samples were characterized by very high snow accumulation rates (600 and 1200 kg m⁻²yr⁻¹) and extremely low Pb concentrations, most < 1 pg/g. The low concentrations made the isotopic composition difficult to measure, but the precision on the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios was generally better than 1%. In addition, the final isotopic ratios were highly sensitive to the correction for the blank, which although small, became very significant at the lower concentrations encountered.

The latter study revealed the difficulty of obtaining reliable Pb isotopic ratios in Antarctic snow and ice. It showed that high sensitivity methods must be used and that extreme care must be taken to minimize contamination. However, the results presented in Figure 3 indicate that even when all precautions

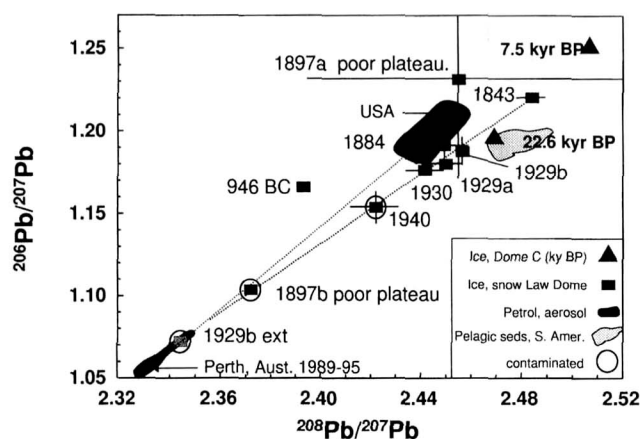


Fig. 3. The isotopic ratios of Pb in Antarctic ice. Shown are two samples from Dome C (triangles) with ages 7.5 kyr BP (Rosman *et al.* 1994b) and 22.6 kyr BP (THIS WORK), and samples of various ages from Law Dome (rectangles, Rosman *et al.* 1998). Also included are Pb data for USA gasoline and aerosols (Chow *et al.* 1975; A.R.Flegal, personnel communication), Australian gasoline (K.J.R. Rosman, unpublished data), and pelagic sediments adjacent to S. America (Chow and Patterson 1962).

are taken the samples may still contain Pb not present in the original ice. Results for sample '1897b' illustrate this point. The data fall close to the composition of the contaminated outer layer of '1929b' which, as expected, was highly contaminated. Because the isotopic composition is similar to gasoline-lead used in Australia during the late 1980s and early 1990s (K.J.R. Rosman, unpublished data), it is likely that this external contamination was added during storage or handling in Australia or Antarctica. In the case of sample '1897b', however, some of this Pb appears to have penetrated the core, probably via small cracks.

Figure 3 also includes a measurement of Pb isotopes in 22.6 kyr old ice (depth 704.06-704.27 m) from Dome C. This is a new measurement and the first on ice close to the LGM (Last Glacial Maximum). This is an aliquot of a sample analysed for Pb, Al, Na and SO_4 by Boutron and Patterson (1986). The Pb concentration was found to be ~ 16 pg/g, which is consistent with the value of 15 pg/g found by Boutron and Patterson (1986). The isotopic composition was $^{206}\text{Pb}/^{207}\text{Pb} = 1.196 \pm 0.002$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.469 \pm 0.004$, and $^{206}\text{Pb}/^{204}\text{Pb} = 18.72 \pm 0.07$. Only 2.3 g of decontaminated ice was consumed for this analysis. Procedures described by Chisholm *et*

al. (1995) were used for this measurement. Uncertainties are 95% confidence intervals that include known sources of measurement bias. This Pb is less radiogenic than that found in Holocene ice (Rosman *et al.* 1994b) but is similar to the pelagic sediments found near southern South America (Chow and Patterson 1962) and volcanic rocks from central Chile (Hildreth and Moorbath 1988).

Grousset *et al.* (1992) analyzed dust in ice from Dome C for Sr and Nd isotopes. Their study compared Dome C dust with a variety of different dust samples from Australia, Africa, Argentina, shelf sediments and moraines from Antarctica, and basalts from the South Sandwich Islands. The analysis provided strong evidence for an Argentine (Patagonian) loess source for the dust reaching Dome C during the LGM. It was also suggested that the surrounding continental shelf had received eroded Patagonian rocks via rivers which, with the lowering of the sea level during the LGM, provided a larger source area for this material. Basile *et al.* (1997) extended the Sr and Nd measurements to include ~ 60 kyr and ~ 160 kyr old ice from Vostok, as well as Argentine continental shelf material. These samples gave a good match for Dome C Sr and Nd isotopes with Patagonian loess, but not with the marine shelf sediments. These two studies present strong evidence that Patagonian loess is the source of most of the Dome C dust during the LGM.

A comparison of the Pb isotope data presented here for Dome C with that measured by Rosman *et al.* (1994b) shows that the isotopic composition changed with the climatic conditions. The dry and windy conditions, believed to have prevailed during the LGM, led to a relatively high Pb concentration at Dome C and an isotopic composition that was similar to the pelagic sediments near southern South America. We do not have Pb isotope data for Patagonian loess, however, the Andean volcanics in Chile from which the loess is believed to have derived has a similar composition to the pelagic sediments, and presumably the Pb in the latter originated from the former. The Dome C LGM Pb isotope data are therefore consistent with a South American origin of this Pb via Patagonian loess.

Summary

Lead isotopes can be used as tracers of sources because of the large variations in the isotopic composition of Pb encountered in nature. However, only in the last decade has this approach been effectively used to trace sources of pollution archived in Greenland and Antarctic ice. Both ancient and modern sources of Pb have now been successfully traced and seasonal variations in sources detected.

This paper also reports a measurement of the isotopic composition of the Pb reaching Antarctica during the LGM. This composition is consistent with a Patagonian origin, discovered previously using Sr and Nd isotopic tracers.

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