Lead isotopes and selected metals in ice from Law Dome, Antarctica

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ABSTRACT. The isotopic composition of Pb and the concentrations of Pb, Ba and Bi were measured in selected ice-core samples from Law Dome, East Antarctica, to a depth of 1196 m. The range of concentrations found in decontaminated ice was $0.03-1.5$ pg g^{-1} for Pb, $0.9-6.1$ pg g^{-1} for Ba and $0.4-17$ fg g^{-1} for Bi, excluding the deepest sample which contained ~1 ppm of rock dust. The abundances of all four stable lead isotopes were measured and gave $^{206}Pb/^{207}Pb$ ratios up to ~1.23. A value of $^{208}Pb/^{207}Pb = 2.78$ was measured in the deepest sample and is consistent with reported Pb isotope ratios of Antarctic granulites. Although the element concentrations in some samples were lower than have been reported elsewhere, geochemical and isotopic evidence indicated that a number of samples were contaminated with Pb not present in the original ice. However, it appears that the technical skills now available are approaching the level where careful sample selection, decontamination and analysis can yield accurate results for the concentration and isotopic composition of Pb in Earth's purest naturally occurring ice.

INTRODUCTION

The composition of the atmosphere to about 250 000 years ago can be investigated by analyzing the snow and ice archives of Greenland and Antarctica. The concentration of impurity aerosol species trapped in the snow changes significantly during the major glacial transitions and is an important record of global change. Snow and ice are an ideal matrix for trace element analysis because the impurities are preserved in an ultra-pure medium which can be accurately dated. However, because the concentrations of many elements are extremely low and the problems involved in making measurements at this level were not widely recognised by early analysts, a considerable quantity of inaccurate data exists in the literature. Ng and Patterson (1981) described the situation pertaining to lead, revealing that the only reliable measurements prior to the 1980s were those reported by Murozumi and others (1969).

The first reliable measurements of Pb in ice cores were reported by Ng and Patterson (1981), who developed a mechanical chiselling method for decontaminating the cores. Outer layers containing high Pb concentrations were successively removed, leaving uncontaminated ice at the centre. This method was then used by Boutron and Patterson (1986, 1987) and Boutron and others (1987) to analyze Antarctic ice cores. Subsequently, Boutron and others (1991), Candelone and others (1994, 1995) and Hong and others (1994) reported measurements of cores prepared at the Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE), Grenoble, France, using similar procedures.

Lead isotopes were first reported in snow cores from Summit, central Greenland, by Rosman and others (1993) who used them to identify and quantify contributions from the U.S.A. and Eurasia for two decades from the late 1960s. Although the concentration of lead in these samples was relatively low (up to ~200 pg g^{-1}) from an analytical standpoint, they reflected the highest concentrations encountered at Summit and corresponded to the time when Pb emissions to the atmosphere from gasoline were greatest. Since this time, concentrations in the Northern Hemisphere have fallen by about an order of magnitude in response to the reduction of leaded fuel consumption (Boutron and others, 1991). The concentration of lead in Antarctic snow and ice is lower still, and approaches the limit of current capability for lead-isotope abundance measurements. Results on Antarctic Holocene ice from a core at Dome C, Antarctica, containing ~2–10 pg g^{-1} lead have been reported by Rosman and others (1994) and Chisholm and others (1995).

This study reports preliminary measurements of lead isotopes and concentrations of Pb, Bi and Ba in two cores from Law Dome, East Antarctica, where the accumulation rate of snow is much higher than at Dome C (Boutron and Patterson, 1986). Barium concentrations have been included to indicate terrestrial dust levels, while bismuth is included because of its association with volcanic activity.

EXPERIMENTAL

Samples

Ten ice-core sections of two drill cores taken from Law Dome were analyzed in this study. Four sections were taken

from Dome Summit South (DSS) and six from the DE08 ice cores. Law Dome is a 200 km diameter ice cap, located on the coast of the East Antarctic ice sheet, receiving mainly easterly atmospheric circulation, and having an exceptionally high accumulation rate. The DSS site is located 4.6 km south of the Law Dome summit (ice accumulation rate: $\sim$600 kg m^{-2}a^{-1}; mean annual temperature: $-21.8°$C). The upper 82 m section was drilled with a 200 mm diameter thermal drill, and the lower section with a 100 mm diameter electromechanical drill. All samples except the deepest one were dated by counting annual layers using δ^{18}O, peroxide and conductivity measurements. The lowest sample was dated by modelling the ice flow (Morgan and others, 1997). Silty ice containing small rock fragments was encountered at 1196 m. Morgan and others (1997) indicated that ice at the bottom of DSS has δ^{18}O values slightly more negative than for most of the Holocene, implying slightly lower temperatures than today, in turn implying that the ice is from the Last Interglacial, i.e. at least 110 000 years old. The DE08 core was thermally drilled at a site 16 km east of the summit where the accumulation rate was significantly higher ($\sim$1200 kg m^{-2}a^{-1}). Table 1 shows the depths at which samples were taken, as well as the corresponding year and season.

Core decontamination

All core sections were decontaminated at LGGE using the procedure described by Candelone and others (1994). The outer layers were mechanically removed with an acid-cleaned stainless-steel chisel, and each layer was analyzed using graphite furnace atomic absorption spectrophotometry (Görlach and Boutron, 1990). If a plateau of low concentration was not reached as the core centre was approached then the inner sample was considered to be definitely contaminated. The innermost sample was melted and aliquots were transferred to acid-cleaned low-density polyethylene (LDPE) bottles, triply sealed in acid-cleaned

LDPE bags then frozen awaiting transport. The samples were not acidified, to minimise the possibility of Pb being leached from the container walls. They were air-freighted to Perth, Australia, but although packed with dry ice, they melted in transit. A complete profile on the DE08 1929 section consisting of all layers was also analyzed at Curtin University, Perth, for lead isotopes. Tests carried out to simulate the possible contamination of the samples due to leaching from the bottles as a result of their melting during transport yielded a possible increase of Pb concentration by $\sim$0.01 pg g^{-1}.

Sample processing for isotopic analysis

At Curtin, samples were kept frozen until analyzed. Approximately 10 g amounts of each sample were analyzed using the procedures described by Chisholm and others (1995). Processing was minimised to avoid contaminating the samples. They were evaporated to dryness with a mixture of HNO_3, Si-gel and H_3PO_4, within Teflon enclosures, inside a clean-air laboratory supplied with HEPA-filtered air. The deposition rate of Pb onto surfaces within the laboratory was $\sim$0.1 pg cm^{-2}d^{-1}. Samples were transferred in a small drop of the Si-gel–H_3PO_4 mixture to a zone-refined, acid-cleaned rhenium mass-spectrometer filament and evaporated to dryness. They were transferred to the mass spectrometer within $\sim$6 hours of their preparation.

Mass spectrometry

The samples were analyzed on a VG354 Isotope Ratio Mass Spectrometer (Fisons Instruments) fitted with a thermal ion source and 16 sample turret. This instrument has a 90° magnetic sector and 27 cm radius-of-curvature ion path. The instrument is fitted with nine Faraday collectors and one Daly collector operating in analogue mode. The effective gain of the Daly collector system relative to the Faraday collectors is $\sim$100. Although the instrument was capable of fully auto-

Table 1. Lead isotopic ratios and Pb, Ba and Bi concentrations measured in ice from Law Dome

Drill-core section	Year[*]	Depth	Season[†]	$\frac{^{206}Pb}{^{207}Pb}$[‡]	$\frac{^{208}Pb}{^{207}Pb}$	$\frac{^{206}Pb}{^{204}Pb}$	Pb	Ba	Bi[§]
		m					pg g^{-1}	pg g^{-1}	fg g^{-1}
DSS 28A[‖]	1940	46.17–47.54	Sp/S	1.154 ± 0.004	2.422 ± 0.007	17.4 ± 0.5	<1.4 ± 0.3[††]	2.2 ± 0.2	0.4
DE08 55A[**]	1930	96.01–96.29	Sp/S	1.176 ± 0.005	2.442 ± 0.008	18.1 ± 0.3	0.8 ± 0.2	4.3 ± 0.4	1.4
DE08 55B-a	1929a	96.41–96.55	Sp	1.180 ± 0.003	2.450 ± 0.008	18.2 ± 0.6	0.9 ± 0.2	6.1 ± 0.6	15
DE08 55B-b	1929b	96.55–96.69	W/Sp	1.188 ± 0.08	2.457 ± 0.012	18.1 ± 0.5	1.5 ± 0.3	2.9 ± 0.3	17
DSS 41B	1908	72.95–73.20	W	1.3 ± 0.2	2.3 ± 0.2	12 ± 13	0.03 ± 0.02	1.1 ± 0.1	0.9
DE08 77A-a	1897a	135.02–136.16	A/W	1.231 ± 0.059	2.455 ± 0.067	19 ± 6	<0.09 ± 0.03[‡‡]	1.2 ± 0.1	5.3
DE08 77A-b	1897b	136.16–136.30	A	1.104 ± 0.006	2.372 ± 0.026	16.9 ± 0.4	<0.7 ± 0.1[‡‡]	1.1 ± 0.1	1.9
DE08 85A	1884	150.90–151.42	W	1.191 ± 0.007	2.449 ± 0.021	17.4 ± 1.1	0.17 ± 0.04	0.9 ± 0.1	1.5
DE08 108A	1843	192.80–193.08	S	1.221 ± 0.004	2.484 ± 0.005	18.6 ± 0.3	1.2 ± 0.2	2.3 ± 0.2	1.0
DSS 940	946 BC	895.74–895.99	~2 years	1.166 ± 0.010	2.393 ± 0.023	17.9 ± 1.5	0.21 ± 0.05	1.1 ± 0.1	9
DSS 1254	Preglacial	1196	–	1.189 ± 0.009	2.784 ± 0.015	18.5 ± 0.1	5 ± 1	30.4 ± 3.0	2.8

[*] The year is AD except where indicated. when an inner core was broken into two parts they were labelled "a" and "b". Dating methods are described by Morgan and others (1997).

[†] A, autumn; W, winter; Sp, spring; S, summer.

[‡] Uncertainties shown on isotopic ratios are 95% confidence intervals.

[§] Uncertainty on Bi concentrations is ~60%.

[‖] The shallower DSS core section was thermally drilled, and the two deep DSS cores were electromechanically drilled from a wet hole.

[**] All DE08 cores were thermally drilled. Details are given by Ethridge and others (1989).

[‡‡] Upper limits are given on these samples, as there was not a good plateau of concentration as a function of radius.

mated operation, the samples were generally analyzed manually.

Details of the complete analysis procedure are given by Chisholm and others (1995). Samples were analyzed at a temperature of $\sim 1500°C$ after a preliminary degas to remove any volatile material.

Isotope dilution mass spectrometry (IDMS): Pb and Ba

IDMS was used to measure the concentration of Pb and Ba. The technique is well established (Webster, 1960), provides high sensitivity and is the most accurate technique currently available for concentration measurements. It involves the addition of a measured quantity of an enriched isotope of the element to the sample. The quantity of the element present can then be determined from the isotopic composition of the mixed spectrum. In the present work a solution containing both ^{205}Pb (half-life 1.5×10^7 a) and ^{137}Ba spikes was added to each sample. The ^{205}Pb and ^{137}Ba spikes were calibrated against lead metal (NIST SRM 981) and a barium nitrate (Johnson-Matthey, Spec-pure), respectively (unpublished information from S. Jimi, 1996). Corrections made for the analytical blank amounted to 0.10 ± 0.05 pg for Pb and 0.6 ± 0.2 pg for Ba. The final uncertainties shown on each concentration are 95% confidence intervals and take account of uncertainties in weighings, spike calibrations and the isotopic ratios.

Bi determination

The technique used to measure Bi concentration is described in detail by Chisholm and others (1997) and takes advantage of the simultaneous ionisation of Bi and Pb. A comparison of the $^{209}Bi^+$ current with $^{208}Pb^+$ ion current which is determined by isotope dilution allows Bi concentrations to be determined. Bi concentrations are determined with an accuracy of $\sim 50\%$ (95% confidence interval). In this study Bi, Pb and Ba were measured simultaneously.

RESULTS AND DISCUSSION

The results of measuring the isotopic composition and metal concentrations at Curtin are shown in Table 1.

Decontamination and contamination

A good plateau of concentration for lead was found in most cores except where concentrations are indicated as an upper limit in Table 1. One complete decontamination profile on DE08 1929, measured by mass spectrometry, is displayed in Figure 1. This profile shows that the two outer layers were severely contaminated by Pb with an isotopic composition similar to that used in Perth petrol during and since the drilling operation (K. Rosman, unpublished data). The $^{206}Pb/^{207}Pb$ ratio in petrol varied between 1.052 and 1.078 during the period 1989–95 and is expected to be typical of that supplied to the southern Australian cities (Adelaide, Hobart, Melbourne, Perth and Sydney).

The most noticeable feature of the data is the very low concentration of Pb in all cores. Both the measured concentrations and the $^{206}Pb/^{207}Pb$ ratios are displayed in Figure 2. Apart from the preglacial sample, the highest concentration was 1.5 pg g^{-1}, while the lowest was 0.03 pg g^{-1}. However, there is evidence to suggest that a number of these samples
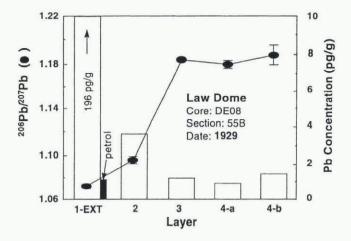

Fig. 1. Decontamination profile for sample 1929 from the DE08 ice core, showing the concentration and $^{206}Pb/^{207}Pb$ isotopic ratio for each concentric layer of the core. The range of isotopic ratios in Australian petrol sampled in Perth between 1989 and 1995 is also shown.

were contaminated. For instance, a comparison of samples 1897a (<0.09 pg g^{-1}) and 1897b (<0.7 pg g^{-1}) suggests that at least 80% of the latter concentration is due to contamination prior to transportation to Perth. This conclusion is supported by a poor decontamination profile and a low $^{206}Pb/^{207}Pb$ ratio indicative of contamination with Australian petrol lead. Sample DSS 1940 also yielded a poor profile which casts doubt on the reliability of the results from this sample. The relatively low $^{206}Pb/^{207}Pb$ ratio in this sample is consistent with the addition of ~ 0.4 pg g^{-1} of lead typical of Australian leaded petrol. This estimation used only isotopic ratios and assumed the original ice to contain lead similar to that in DE08 1929a and b.

Some confirmation that Australian petrol lead is the primary source of the contamination is indicated in Figure 3, where all the data are plotted on a three-isotope plot. On such a plot, binary mixtures will lie along a line with the sources as the end-points. The contaminated samples already discussed are circled on this plot, and their positions
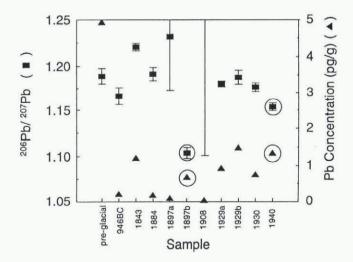

Fig. 2. Isotopic composition of lead and its concentration in selected samples from Law Dome. Only the measurements made on the central ice taken from the ice cores are shown. Samples which did not yield a good decontamination plateau for lead are circled. Squares identify the isotopic ratios, and triangles identify the concentration measurements.

are consistent with petrol Pb as one end-point, with a second source further up the trend. Most data points lie on the line joining petrol lead with 5505 BC ice from Dome C (Rosman and others, 1994). Because of uncertainty about the level of contamination in the samples, it is not possible to say if the position of a sample reflects its true isotopic composition or it has been significantly modified by contaminant lead.
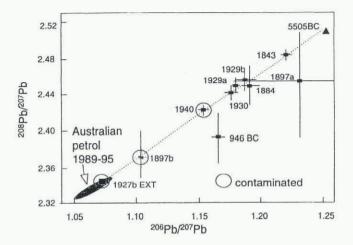

Fig. 3. A three-isotope plot for ice from Law Dome (square symbols). The dotted line is drawn through the higher-precision measurements. Samples which yielded a poor decontamination plateau are circled. Also included are data for Holocene ice from Dome C (Rosman and others, 1994) (triangle) and Australian petrol (elliptical field).

Anthropogenic lead in Antarctica

Boutron and Patterson (1987) using geochemical arguments and Rosman and others (1994) using isotope systematics showed that Antarctic snow collected at a site 433 km inland from the coastal station at Dumont d'Urville, Terre Adélie, East Antarctica in the early 1980s contained a significant amount of anthropogenic lead. Wolff and Suttie (1994) also measured lead concentrations in snow from a pit in Coats Land, West Antarctica, which showed there was an increase from ~2.5 pg g^{-1} between 1920 and 1950 to ~6 pg g^{-1} in 1980. The data reported here for Law Dome are sparse, making it difficult to discern a regular trend over the last 100 years. If
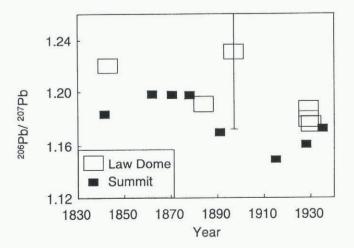
samples 1897b and 1940 are disregarded because of contamination then the samples analyzed fall into three time intervals: 1843 with a concentration of 1.2 pg g^{-1}; 1884, 1897a and 1908 with values below ~0.2 pg g^{-1}; and 1929a, 1929b and 1930 which averaged ~1.1 pg g^{-1}. No convincing trend is evident in these data.

The isotopic data from Law Dome are also too few to make any sensible comparison of the lead from the two hemispheres, but the available data suggest that the isotopic ratios are similar if the level of contamination of the samples is taken to be negligible. A comparison of data from Law Dome with data from Summit, Greenland, for the same time period (K. Rosman, unpublished data) is shown in Figure 4.

Bismuth, barium and volcanism

The concentrations of Ba and Bi are extremely low in the Law Dome samples, as expected from the high accumulation rate. In Table 1 the concentrations are given in pg g^{-1} and fg g^{-1}, respectively. Using a Ba/Al ratio of 5.5×10^{-3}, which is an average taken from published compilations (Taylor, 1964; Mason and Moore, 1982; Taylor and McLennan, 1985; Wedepohl, 1995), the Ba concentrations are consistent, in general, with Al concentrations measured at LGGE on the same samples (S. Hong, unpublished data).

Since in volcanic emissions Bi is concentrated relative to other crustal species (Patterson and Settle, 1987), it may be possible to detect volcanic events by identifying periods when the Bi concentration in the snow is high. However, a more reliable approach is to measure element ratios such as Bi/Pb. The average global Bi/Pb flux ratio for volcanic emissions probably lies in the range 0.2–0.6, compared with $\sim1.3 \times 10^{-2}$ for crustal rock (Chisholm and others, 1997). However, because anthropogenic Pb can significantly alter the Bi/Pb ratio it is best avoided as the reference element. Chisholm and others (1997) recently used Bi/Al ratios to seek evidence of volcanic events archived in an 11 m snow core from Summit, central Greenland. In the present study we use Ba instead of Al to monitor terrestrial dust levels in the
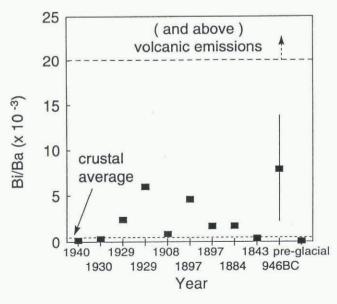

Fig. 4. Comparison of the isotopic composition in ice at Summit, central Greenland, and Law Dome, Antarctica.

Fig. 5. The Bi/Ba concentration ratio in samples of different age from Law Dome. The uncertainty on all points is ~60%, although it is only shown on one. The crustal average value and the range for volcanic emissions are indicated by dashed lines.

samples (Settle and Patterson, 1991) because it can be measured with high sensitivity in a Thermal Ionisation Mass Spectrometer (TIMS) instrument.

An average of four tabulated values gives a Bi/Ba ratio of $\sim 3.2 \times 10^{-4}$ for crustal rock (Taylor, 1964; Mason and Moore, 1982; Taylor and McLennan, 1985; Wederpohl, 1995), while that in volcanic emissions can be estimated as follows. The product of the average global Bi/Pb flux ratio given previously, with the average Pb/Ba ratio based on element concentrations in plumes from the Augustine volcano (Lepel and others, 1978), gives a range of ~ 0.02–0.3. Figure 5 shows the Bi/Ba ratios measured in the Law Dome cores. The highest value was registered by the Holocene sample at 8×10^{-3}. It should be noted that the uncertainty on the ratios is $\sim 60\%$, mainly due to the Bi measurement. Although the uncertainty is high, the Bi concentration is exceedingly low. To quantify the volcanic contribution to each sample, it will be necessary to establish the Bi/Ba ratio for volcanic emissions much more precisely, but some indication of the relative significance of eruptions to the Antarctic atmosphere can be obtained from the ratio (Fig. 5).

The late Holocene and pre-Holocene

Only the sample from 946 BC is likely to provide geogenic Holocene data. This sample has a Pb concentration of $0.21 \, \text{pg g}^{-1}$, which is one-tenth the concentration reported by Rosman and others (1994) for 5505 BC ice. However, an estimate of expected natural contributions from terrestrial dust (based on Ba) and volcanic emissions (based on Bi) suggests that the concentration should be less than half of this value. Also the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio is unexpectedly low since a value of 1.252 has been measured in Holocene ice from Dome C, which suggests the sample may be contaminated. However, this shift could also be due to a molecular interference in the mass spectrum at the position of the ^{207}Pb isotope which could alter the isotopic ratio without changing the Pb concentration significantly. The position of the sample point below the trend in Figure 3 is consistent with interference in the mass spectrum. Further evidence for contamination comes from Pb concentrations of 0.03 and $0.09 \, \text{pg g}^{-1}$ measured at shallower depths (samples 1908 and 1897a). Hence there is evidence to suggest that this sample may have been contaminated.

The preglacial sample has a high Pb concentration with an interesting isotopic composition. Although the $^{206}\text{Pb}/^{207}\text{Pb}$ is at the lower limit expected for natural aerosols, the $^{208}\text{Pb}/^{207}\text{Pb}$ ratio is highly anomalous and cannot be displayed in Figure 3 without drastically compressing the scale. None of the other samples show evidence of this anomaly, and since it is not found in commercial Pb ore deposits anthropogenic contamination can be ruled out. The high $^{208}\text{Pb}/^{207}\text{Pb}$ ratio is indicative of a thorium-rich source rock since ^{208}Pb is produced by the radioactive decay of ^{232}Th (half life 1.4×10^9 years). De Paolo and others (1982) reported similar enrichments in Antarctic granulites from the Fyfe Hills, Enderby Land. It therefore appears that this ice sample is contaminated with a significant quantity of Antarctic granulite. Morgan and others (1997) reported visible impurities in ice from the bottom of the core only 5 m below our sample. Contamination with rock particles is therefore not unexpected. Based on the Pb concentration of the ice, a concentration of $\sim 1 \, \text{ppm}$ of rock material was es-

timated, assuming the granulite to contain $\sim 6 \, \mu\text{g g}^{-1}$ Pb (De Paolo and others, 1982) with a Pb/Ba ratio of ~ 0.029.

CONCLUSION

Measurements have been made of Pb isotopes and Pb, Ba and Bi concentrations in selected ice cores from Law Dome. Extremely low concentrations of these elements were detected, which is consistent with a very high ice-accumulation rate. The Bi concentrations are the first to be reported in Antarctic ice and when referenced to Ba may serve as an indicator of volcanic events because of the relative enrichment of Bi in volcanic emissions. The Pb concentrations are the lowest reported to date in any ice core, but there is strong evidence from both geochemical and isotopic systematics to show that a number of the samples contain anthropogenic lead not present in the original ice. A profile of the isotopic composition of the lead across one core indicates the effectiveness of the decontamination process and has revealed that the most contaminated outer layers of the cores contained lead whose isotopic composition was the same as that used in Australian petrol. This was probably also the origin of the contamination detected in the other samples.

This paper indicates the state of current measurement capability for Pb isotopes and Pb, Ba and Bi concentrations in polar ice. More accurate determinations will require better-quality samples.

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