

ATMOSPHERIC LEAD IN ANTARCTIC ICE DURING THE LAST CLIMATIC CYCLE

by

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ABSTRACT. Concentrations of lead (Pb) have been measured by the ultra-clean isotope dilution mass spectrometry technique in various sections of the Antarctic Dome C and Vostok deep ice cores, whose ages range from 3.85 to 155 ka B.P., in order to assess the natural, pre-human, sources of this toxic heavy metal in the global troposphere. Pb concentrations were very low, as low as about 0.3 pg Pb/g during the Holocene and probably during the last interglacial and part of the last ice age. On the other hand, they were quite high, up to about 40 pg Pb/g, during the Last Glacial Maximum and at the end of the penultimate ice age. Wind-blown dust from crustal rock and soil appears to be the main natural source of Pb in the global troposphere. Pb contribution from volcanoes is significant during periods of low Pb only. Contribution from the oceans is insignificant.

INTRODUCTION

For twenty years there have been great controversies about the reconstruction on a global scale of past natural tropospheric fluxes of lead (Pb) from analysis of the well-preserved ancient ice layers deposited within the Antarctic and Greenland ice sheets. Accurate knowledge of these fluxes is vital if modern Pb time trends are to be judged in the proper perspective (Wolff and Peel 1985, Boutron 1986, Peel 1986).

On the basis of the pioneering polar work of Murozumi and others (1969), which was confirmed 12 years later by Ng and Patterson (1981), Patterson and co-workers postulated that in ancient times there was no significant tropospheric Pb excess over Pb contributed by wind-blown dust from soil and rock. As a consequence, they ascribed the enormous Pb excess which is now indisputably present in the global troposphere of the Northern Hemisphere to emissions from automobile exhausts and smelteries (Murozumi and others 1969, Ng and Patterson 1981, Patterson and Settle 1987[a] and [b]). On the other hand, on the basis of the polar data published by Cragin and others (1975), Herron and others (1977), Herron (unpublished) and several other authors, various other investigators postulated that enormous Pb excesses over Pb contributed by dust from soil and rock was already present in ancient times (see, for instance, Herron and others 1977, Boutron 1980, Jaworowski and others 1981). It was claimed that these excesses were caused by emissions of huge quantities of Pb from various other sources, such as volcanoes, vegetation, rock volatilization and the oceans. Thus the enormous present-day Pb excess in the global troposphere of the Northern Hemisphere was claimed to be mainly natural, not anthropogenic.

The investigation of the occurrence of Pb in ice deposited within the Antarctic ice cap during the last 155 ka is a unique way of addressing this controversy. This period encompasses the Holocene, the last ice age, the last

interglacial, and the last part of the penultimate ice age. It was characterized by dramatic changes in the wind-entrained rock and soil dust content of the global troposphere, as evidenced by the very large changes in Al concentrations observed in the Byrd Station, Dome C and Vostok deep Antarctic ice cores. In particular, there have been three major peaks of Al (and therefore of rock and soil dust) during the last 155 ka (Cragin and others 1977, Legrand unpublished, De Angelis and others 1987, Legrand and others, in press). The first one occurred at the end of the penultimate ice age, about 150 ka ago; the second one occurred during the last ice age, about 60 ka ago; and the last one occurred at the end of the last ice age, about 20 ka ago (Fig.1a).

These three peaks allow testing of the two tropospheric Pb models outlined above. According to the model of Patterson and co-workers (the global lead-pollution model), changes in Pb concentrations should follow closely the changes in rock and soil dust concentrations, and therefore exhibit three major peaks, about 20, 60 and 150 ka ago. According to the other model (the natural sources of lead model), Pb concentrations would be expected not to exhibit such dependence on rock and soil dust concentrations, because contributions of Pb from dust would be insignificant with respect to contributions from other natural sources, and no large Pb concentration peaks should be observed over the past 155 ka.

We present here a discussion of the new data on the occurrence of Pb in Antarctic ice during the past 155 ka which have recently been obtained from analysis of various sections of the Dome C and Vostok deep ice cores (Boutron and Patterson 1986, Boutron and others 1987).

DECONTAMINATION AND ANALYSIS OF SAMPLES

Description of samples

Fourteen sections of the 905 m Dome C ice core and six sections of the 2083 m Vostok ice core have been analyzed for Pb. The Dome C core (Lorius and others 1979) was thermally drilled during the austral summer 1977-78 in a dry hole which had not been filled with a wall-retaining fluid; it covers the past 32 ka, back to the beginning of the Last Glacial Maximum (LGM). The Vostok core (Lorius and others 1985) was thermally drilled in 1981-82 in a hole which had been filled with a hydrocarbon fluid; it was shown to cover the last 160 ka, back to the last part of the penultimate ice age (Jouzel and others 1987).

Sections selected for Pb analysis, packed in double-sealed polyethylene bags, were transported in a frozen state to California Institute of Technology (C.I.T.). Each section was 15-30 cm in length, which corresponds to about 3-10 years' accumulation. The diameter of those Vostok sections which were deeper than 1506 m was 9.1 cm; for all other sections, it was about 10.5 cm.

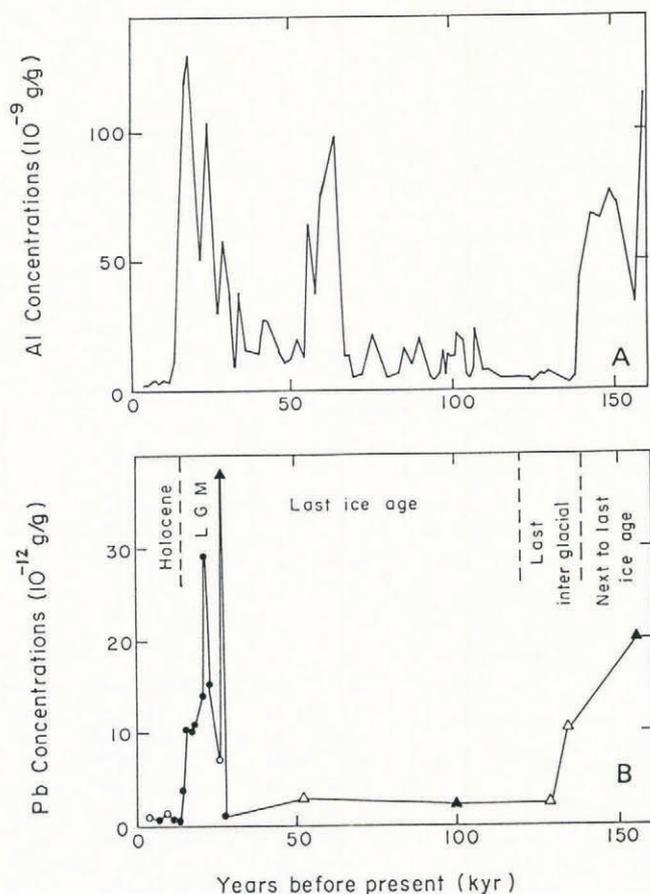


Fig.1. (a) Changes in aluminium concentrations in Antarctic ice during the past 155 ka, as seen in the Vostok deep ice core (from De Angelis and others 1987). (b) Changes in lead concentrations in Antarctic ice during the past 155 ka, as seen in the Dome C and Vostok deep ice cores (data from this study). Dots are used for data from the Dome C core sections, and triangles for data from the Vostok core sections. Open symbols indicate that the corresponding Pb concentration value is only an upper limit of the original concentration in the ice (see text). Approximate limits of the successive climatic stages described by Lorius and others (1985) are shown at the top of Figure 1b.

Mechanical decontamination of the core sections

Each section was cleaned by mechanically chiseling four–six successive veneers of ice, progressing from the outside to the interior, using ultra-clean stainless-steel chisels inside a cooled double-walled nitrogen-flushed polyethylene tray in the ultra-clean C.I.T. laboratory. The inner core so obtained was 2–4 cm in diameter. A detailed description of the chiseling technique and of the cleaning procedures is given in Boutron and Patterson (1983 and 1986).

IDMS Pb analysis

For each core section, the veneer layers and the remaining inner core were analyzed separately for Pb by the ultra-clean isotope dilution mass spectrometry (IDMS) technique (Boutron and Patterson 1983 and 1986, Boutron and others 1987). Each analysis was corrected for the total Pb contamination contributed by the mechanical chiseling and chemical treatment. This overall Pb contamination, which was accurately determined by performing numerous separate blank measurements (Boutron and Patterson 1983 and 1986) was found to range from 30 to 60 pg Pb (in this paper, the symbol pg represents 10⁻¹² g). When compared with the Pb content of the veneer layers and of the inner cores, this Pb contamination correction ranged from less than 1% for outer veneer layers (in which Pb concentrations were very high) to up to 75% for some of the Holocene inner cores (in which Pb concentrations were extremely low, as low as 0.3 pg Pb/g).

The precision of the data is associated mainly with these contamination corrections. It is estimated to range from a few per cent for high Pb concentrations to 50% for the lowest Pb concentrations.

Checking the quality of each individual core section and the efficiency of the decontamination procedure

As emphasized by Wolff and Peel (1985) and Boutron (1986), it is essential to study for each individual core section the variations in Pb concentrations from the outside to the center as a function of radius. Only if concentrations clearly level off to a fixed value in the central parts of a section for several consecutive veneer layers can data obtained from the center of this section be accepted. Variations in Pb concentrations as a function of radius were studied in detail for 14 of the 20 sections analyzed in this work.

Figure 2 shows the variations in Pb concentrations as a function of radius in three of the Dome C sections and one of the Vostok sections. For the 13.9 and 18.1 ka Dome C sections (Fig.2a and b), a clear plateau of concentrations is observed in several consecutive layers. This indicates that the mean Pb concentrations measured in the inner parts of these two sections (after correction for the total Pb contamination contributed by the mechanical chiseling and chemical treatment) do represent the original concentrations in the Antarctic ice: there was no significant contamination in the central parts of these two sections when we started to decontaminate them in the C.I.T. laboratory, and contamination which had previously affected the outside of the cores during drilling, handling and storage was not transferred to these central parts during the mechanical decontamination. On the other hand, no plateau is observed for the 38.5 ka Dome C section and for the 99.7 ka Vostok section (Fig.2c and d), which indicates that for these last two sections contamination has penetrated to the very center of the core either during drilling, transport and storage and/or during the mechanical decontamination in the laboratory. The Pb concentrations measured in the central parts of these last two sections must then be considered as upper limits of the original concentrations in the Antarctic ice only.

Excellent plateaus were obtained for nine of the ice sections analyzed in this work (seven Dome C sections and two Vostok sections). For five sections (three Dome C sections and two Vostok sections), no definite plateaus were obtained. For two Vostok sections, only the veneer next to the inner core was analyzed: for one section, Pb concentration in this layer was much higher than that in the inner core; for the other one, the concentrations were very similar. Finally, for four Dome C sections, only the inner core was analyzed. Pb concentrations measured in the

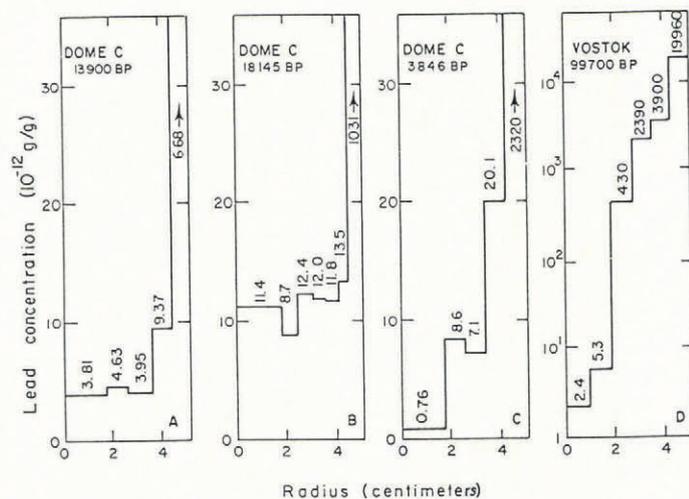


Fig.2. Variations in measured Pb concentrations as a function of radius in three sections of the 905 m Dome C Antarctic ice core (obtained by thermal drilling in a dry hole) and one section of the 2083 m Vostok Antarctic ice core (obtained by thermal drilling in a fluid-filled hole).

inner cores are then thought to be the original concentrations in Antarctic ice for ten sections; for six sections, they are considered to be only upper limits. For the last four sections, we cannot determine whether the inner-core Pb value is the original concentration or not.

RESULTS AND DISCUSSION

Concentrations of Pb measured in the inner core of the Dome C and Vostok sections are given in Table I.

Variations in Pb concentrations during the last 155 ka

Figure 1b shows the variations in Pb concentrations in Antarctic ice as a function of the age of the ice for the 3.85–155 ka period. The 3.85–27 ka part of this Pb temporal curve is quite detailed: it demonstrates clearly that Pb concentrations were very low during the Holocene (from 0.32 to less than 0.94 pg Pb/g), but that they rose to very high values (up to 38 pg Pb/g) during the LGM. The pre-27 ka part of the curve, on the other hand, is only preliminary, since the Vostok data are very sparse: there are only six concentration values for the 27–155 ka period, and three of these six values are given as upper limits only. This part of the curve, however, suggests that Pb concentrations were low during the last interglacial and during several periods in the last ice age, but, on the other hand, the concentrations were high (20 pg Pb/g) at the end of the penultimate ice age. Obviously, new and detailed data for the 27–155 ka period will be greatly needed in the future, which emphasizes the importance of analyzing for

Pb various additional core sections from the Vostok deep ice core.

Changes in Antarctic precipitation rates can explain only a small fraction of the Pb temporal changes of two orders of magnitude shown in Figure 1b. Indeed, precipitation rates have probably not varied by more than a factor of 2 during the periods which have been investigated in central East Antarctica: according to Yiou and others (1985), precipitation rates during the last interglacial and during the Holocene were similar to present-day ones, whereas during the last ice age they were only about half as much.

The two periods during which we observe high Pb values (during the LGM and at the end of the penultimate ice age) are the periods about 20 and 150 ka ago, during which De Angelis and others (1987) and Legrand and others (1987) observed their first and third Al peaks, described in the Introduction (see Fig. 1a). On the other hand, we cannot determine whether or not Pb values were high during the period when they observed their second Al peak (about 60 ka ago), since we have unfortunately not analyzed core sections which correspond to this second Al peak; these core sections will need to be analyzed in the near future.

More generally, changes in Pb concentrations during the past 155 ka are found to follow closely the changes in Al concentrations and therefore the changes in crustal rock and soil dust concentrations. It appears, then, that these new Pb data are in excellent agreement with the tropospheric Pb model of Patterson and co-workers (the global-pollution lead model). On the other hand, they definitely disagree with the natural sources of lead model.

TABLE I. ANTARCTIC DOME C AND VOSTOK DEEP ICE CORES: MEASURED CONCENTRATIONS OF Pb IN THE INNER CORES AND EVALUATION OF RELATIVE Pb CONTRIBUTIONS FROM ROCK AND SOIL DUST, VOLCANOES AND THE OCEANS.

Depth ^a (m)	Estimated ^b age (years B.P.)	Pb in pg/g (10^{-12} g/g)			
		Total measured	Rock and soil dust contribution ^g	Volcanic contribution ^h	Oceanic contribution ⁱ
Dome C					
172.8	3846	<0.76 c	0.38	0.22	0.00009
300.6	7587	0.47 d	0.44	0.30	0.00008
373.8	9785	<0.94 c	0.37	0.27	0.00006
451.9	12160	0.43 d	1.1	0.33	0.00020
476.3	13020	≤0.32 e	0.88	0.33	0.00020
500.5	13900	3.8 d	2.1	0.35	0.00033
527.2	14950	≤10.5 e	7.3	0.47	0.00040
545.1	15705	10.2 d	13	0.48	0.00054
602.2	18145	11.4 d	11	0.40	0.00045
658.2	20590	≤14.0 e	12	0.56	0.00051
670.5	21120	29.3 d	6.9	0.47	0.00047
704.2	22640	≤15.2 e	7.3	0.45	0.00050
775.7	25860	<7.2 c	3.2	0.35	0.00038
796.9	26830	1.25 d	1.4	0.35	0.00035
Vostok					
499.1	26200	38 d	10	0.44	0.00043
851.6	53600	≤3.1 f	3.9	0.54	0.00029
1425.3	99700	≤2.4 c	1.4	0.41	0.00017
1775.4	129000	<2.6 f	0.5	0.34	0.00007
1850.5	134000	<10.6 c	0.5	0.30	0.00004
2026.3	155000	20 d	14	0.59	0.00049

(a) Depths are given as real depths; they are not expressed as meters of ice equivalent. (b) From Lorius and others (1979 and 1985), personal communication from J.P. Benoist and C. Ritz. (c) For this section, no plateau was obtained. (d) For this section, a good plateau was obtained. (e) For this section only the inner core was analysed. (f) For this section, only the veneer next to the inner core was analyzed. (g) Calculated from interpolated Al values (Legrand 1985, De Angelis and others 1987, Legrand and others 1987); soil dust Pb = 1.7×10^{-4} Al (Patterson and Settle 1987[b]). (h) Calculated from interpolated SO_4 values (Legrand 1985, Legrand and others 1987); volcanic Pb = 0.32×10^{-5} non-sea-salt SO_4 (Boutron and Patterson 1986, Patterson and Settle 1987[a] and [b]). (i) Calculated from interpolated Na values (Legrand 1985, Legrand and others 1987); oceanic Pb = 0.46×10^{-8} Na (Boutron and Patterson 1986).

It must be noted that the Pb concentrations observed in Antarctic ice during the LGM and the end of the penultimate ice age are only about one-tenth of the concentrations which are found in present-day Arctic surface snow. And the low concentrations observed during the other periods are only about one-five-hundredth of those in present-day Arctic surface snow.

Sources of natural Pb during the past 155 ka

Na, sulfate and Al have not yet been measured in the 20 core sections which were analyzed for Pb in this study. But values of these constituents have already been obtained for numerous other sections of the Dome C and Vostok cores by Legrand (1985), De Angelis and others (1987) and Legrand and others (1987), which allows us to obtain interpolated Al, sulfate and Na concentration values for the core sections analyzed for Pb.

The interpolated Na concentration values in our core sections varied by up to a factor of about 12 during the past 155 ka (from about 10 up to 120 ng Na/g). After subtracting the Na fraction contributed by rock and soil dust (calculated from the Al concentrations), these Na values can be used to obtain estimates of the Pb fraction contributed by the oceans in each of our core sections, using the relation: oceanic Pb = 0.46×10^{-8} Na (Boutron and Patterson 1986). This last equation combines the Pb/Na ratio which occurred in surface sea-waters in ancient times with the Pb enrichment which occurred during the formation of sea spray in ancient times (Patterson and Settle 1987[b], Patterson and others 1985). As shown in Table I, the calculated oceanic contribution is always insignificant (less than one-thousandth of measured Pb), which indicates that the oceans were not a significant source of natural Pb in the global troposphere during the last 155 ka.

Interpolated sulfate concentration values have not varied by more than a factor of about 3 during the past 155 ka (from about 75 to 210 ng SO₄/g). After subtracting the SO₄ fraction contributed by sea salts, these SO₄ values can be used to obtain estimates of the Pb fraction contributed by volcanoes in each core section, by combining them with the known global fraction of volcanic sulfates (determined from the global sulfur cycle) and the known global (volcanic Pb/volcanic S) ratio (determined from measurements in volcanic gases; Patterson and Settle 1987[a]). The volcanic contribution calculated in Table I is found to represent only a few per cent of the measured total Pb during the periods of high Pb (LGM and the end of the penultimate ice age); on the other hand, it accounts for about half of the measured total Pb during the periods of low Pb (Holocene, pre-LGM part of the last ice age, and last interglacial) (see Table I).

Interpolated Al concentration values varied by a factor of about 40 during the past 155 ka (from about 2 to 80 ng Al/g). These Al values allow us to obtain estimates of the Pb fraction contributed by crustal rock and soil dust, from the mean Pb/Al ratio in crustal rock and soil (Pb/Al = 1.7×10^{-4} , Patterson and Settle 1987[b]). This last contribution is found to represent most of the measured total Pb during the periods of high Pb, and about half of it during the periods of low Pb, as shown in Table I.

It must be noted that for part of the core sections, the sum of the Pb contributions from oceans, volcanoes and rock and soil are either significantly higher or significantly lower than the total measured Pb concentrations (Table I). These differences are thought to be mainly due to the fact that we use interpolated Na, sulfate and Al values for the calculation of these contributions. The use of interpolated values can result in errors of up to a factor of 3, since Na, sulfate and (in particular) Al exhibit within distances of decimeters or meters quite large variations along the Dome C and the Vostok cores.

CONCLUSIONS

During the 3.85–155 ka period, the observed levels of Pb in Antarctic ice can be accounted for simply by contributions from rock and soil dust and from volcanoes. This last contribution, however, is shown to be significant only during periods of low Pb. These new Pb data confirm that in ancient times there was no large excess of Pb over that contributed by wind-blown dust from crustal rock and soil, in accordance with the tropospheric Pb model of

Patterson and co-workers (the global lead-pollution model). Thus it is no longer possible to claim that the enormous Pb excess which is now present in the global troposphere of the Northern Hemisphere is not caused by human activity (automobile exhausts and smelteries).

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