I. ANCIENT ARCTIC ICE DOES NOT CONTAIN LARGE EXCESSES OF NATURAL LEAD

II. CHRONOLOGICAL VARIATIONS IN LEAD AND BARIUM CONCENTRATIONS AND LEAD ISOTOPIC COMPOSITIONS IN SEDIMENTS OF FOUR SOUTHERN CALIFORNIA OFF-SHORE BASINS

Thesis by

Chihang Amy Ng

In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1982

(Submitted July 16, 1981)

ACKNOWLEDGMENTS

It gives me great pleasure to express my gratitude to members of the Caltech Biogeochemical Laboratory for providing the stimulating environment which has made this research possible. I gratefully acknowledge Biogeochemist Clair C. Patterson for his guidance, encouragement, and support throughout this work. Sincere thanks to Dorothy Settle for her friendship and generosity in giving her technical expertise. Discussions with Drs. Robert Elias, Yoshimitsu Hirao, Michael Burnett, Bernhard Schaule, and Russell Flegal were always challenging and constructive.

My special appreciation to Drs. George R. Rossman and James J. Morgan for their understanding, willingness to help, and encouragement.

I am indebted to Debbie Smith and Joanne Clark who typed the manuscript, and Jan Mayne who drafted all the figures.

This research was supported by the National Science Foundation and the Bureau of Land Management.

ABSTRACT

PART I This study settled the dispute and proved beyond doubt that excess lead today is 300-fold instead of the 5-fold, as proposed by other investigators, greater than prehistoric time. And, virtually all of the present-day excess of lead above natural levels was shown to be caused by industrial lead emissions to the atmosphere.

Concentrations of lead and potassium were determined in a series of ice samples taken in sequence from the outside to the interior of several >2000 year old ice cores drilled from the Greenland and Antarctic ice sheets. Concentrations of lead and potassium were observed to decrease continuously in going from the exterior to the interior of the cores, which indicated that surface contamination had penetrated to the interior of the core, making it impossible to determine the original concentration of lead in the ice. Concentrations measured at the centers of these cores must therefore represent upper limits of lead concentration originally present in the ice. There are 1.6 ng Pb/kg ice in 5000 year old Greenland ice and 1.4 ng Pb/kg in 2000 year old Antarctic ice.

These data verified the earlier findings reported by Murozumi et al. (1969) of <1 ng Pb/kg ice in 800 B.C. Greenland ice near Camp Tuto and also at New Byrd Station. Our findings also support their observation of a continual progressive increase of lead concentration with time even before 1900 A.D. These new data refuted the high concentration values of 45 ng Pb/kg ice and 70 ng Pb/kg ice reported by Herron et al. (1977) and Cragin et al. (1975) in pre-1900 Greenland ice and their claims of no concentration change with time before 1900. These new data also

refute the lead concentration values of 26 ng Pb/kg ice reported by Boutron and Lorius (1979) in snow strata of Dome C, Antarctica for the period 1914 to 1974 and their claims that this high lead concentration is natural and has been present since ancient times.

Potassium concentrations at the center of the ice core are 2x10^3 ng K/kg ice in 5000 year old Greenland ice and 9x10^2 ng K/kg ice in the 2000 year old Antarctic ice. The decrease in potassium concentrations within the central third of the core was, unlike that for lead, relatively small, indicating the potassium contamination effects were not large within the central portions of the cores.

Part II This study documented the chronological changes of lead and barium fluxes from the Los Angeles Urban Complex to adjacent San Nicolas, Santa Barbara, Santa Monica, and San Pedro coastal basins; and identified industry as the sources of the excess lead and barium.

The natural deposition fluxes of acid leachable lead in Santa Barbara, Santa Monica, and San Pedro basins were about 0.7, 0.1 and 0.2 μg Pb/cm^2 yr respectively. A model, using clay as a major transport vehicle for soluble lead, was proposed to explain the large lead flux within the Santa Barbara basin compared to the other basins. Sedimentation fluxes of industrial and natural leachable lead within these three basins today are 3- to 10-fold greater, being about 2.1, 1.1 and 1.8 μg Pb/cm^2 yr respectively. Directly deposited large sewage particles account for 0%, 66%, and 75% of the industrial lead deposition fluxes respectively. Isotopic compositions of the excess leachable lead change in accordance with corresponding known changes of isotopic compositions of industrial

lead in the Los Angeles atmosphere. Lead remaining in acid leached sediment residues originates from igneous and clay minerals, exhibiting no change in concentration or isotopic composition since pre-industrial times.

Deposition fluxes of total barium among the three basins were proportional to mass deposition fluxes before 1950. Afterwards, there are barium concentration maxima with time in both Santa Monica and San Pedro basin sediments that are attributable to industrial sewage rather than to erosion from barium-rich sedimentary evaporite strata exposed locally along the shore. A slight increase of barium concentration in present-day Santa Barbara basin sediments may reflect dispersal of barium-rich drilling mud from local drilling operations.

PREFACE

Lead, a metallic element existing naturally in trace quantities, is a highly toxic biochemical poison. It causes biochemical dysfunction in the hematopoietic, nervous and renal systems. Besides acute poisoning effects, lead can act in a slow and subtle manner. Long term exposure can cause irreversible degradation of mental abilities, while maintaining general well-being without causing the victim to be conscious of the dysfunction within himself. (Needleman *et al.* 1969, Gilfillan 1965, Douglass-Wilson and Munro 1966, Environmental Protection Agency 1977). In the native state, lead is relatively unavailable to the biosphere. However, with the large scale mining and usage of lead which began 4500 years ago (production increased from 5 tons to 4 million tons annually at present), lead pollution becomes a world-wide phenomenon as a result of the dispersal of industrial aerosols. Although the pollution effects have existed for a long time, and analyses for lead in plants, animals and other substances have been carried out in thousands of laboratories for nearly a century, the existence of this intense pollution effect became recognized only within the last decade. The seriousness of the situation had been overlooked because industrial lead contamination added to samples during sampling and analyses were mistakenly believed to be the "natural" lead in the samples. By wrongly concluding there is a huge amount of natural lead in our environment, these researchers claim that the additional input of industrial lead, even though large, is not enough to cause worldwide concern.

The pioneering studies of C.C. Patterson and other investigators, employing elaborate clean laboratory techniques to reduce, control and measure industrial lead contamination added to the samples before and during analyses, begin to show that an enormous difference exists between present-day flows of lead through air, plants and animals and those that have occurred through prehistoric times. In the same light as their research, the two studies presented here documented the contrast which existed between the natural geochemical distribution of lead and the distribution of lead in typical human environments, and called attention to the existence of marked, widespread lead pollution from industrial sources. Part I, a study of the lead pollution history recorded in the Polar ice sheets, presented primary evidence of the anthropogenic origin of eolian fluxes of lead to our environment measured on a global scale. This work verified earlier findings by Murozumi et al. (1969) and extended to a broader geographical significance the general validity of their observation of a ~300-fold increase of lead concentrations in the Polar ice sheets during the past 3000 years. This work also showed virtually all present day excesses of lead above crustal levels were caused by industrial lead emissions to the atmosphere. Part II presents a lead pollution history of a large urban complex, through the study of the sedimentary records. We were able to observe the drastic alternation of the natural lead flux pattern by disproportionately greater deposition fluxes of industrial lead. By combining changes of lead concentrations with changes of lead isotopic compositions in the stratigraphic column, we were able to distinguish the effect of atmospheric depositions and the more direct industrial sewage inputs.

Douglass-Wilson I. and Munro I. A. H. (1969) Lead absorption and lead poisoning. Lancet, 1: 1307-1308

Environmental Protection Agency (1977) Air quality criteria for lead. Publication EPA-600/8-77-017, Washington D.C.

Gilfillan S. C. (1965) Lead poisoning and the fall of Rome. J. Occupational Medicine, 7: 53-60.

Needleman H. L., Gunnoe C., Leviton A., Reed R., Peresie H., Mahen C., and Burrett P. (1969) Deficits in psychologic and classroom performance of children with elevated dentine lead levels. New England Journal of Medicine, 300: 689-695.

TABLE OF CONTENTS

6. TABLES

7. FIGURES

PART I

ANCIENT ARCTIC ICE DOES NOT CONTAIN LARGE EXCESS OF NATURAL LEAD

1. INTRODUCTION

Scientists may wonder why it should be so crucial to distinguish between one situation in which 70% of the excess lead in present-day polar snow originates from industrial sources and another situation in which 99.7% does so; because in terms of mass fluxes, about the same enormous amounts of industrial lead are involved in either case. This is not the matter of concern. Instead, it is the magnitude of the mass flux of natural lead that we are trying to measure, and if the former case were true the mass flux of natural lead would also be enormous, so large in fact that we could no longer explain why there has been a large increase of lead input fluxes from the atmosphere to the oceans and to terrestrial ecosystems during the past century and why bones of humans who lived thousands of years ago contained so little lead compared to those in present-day humans.

Murozumi *et al*. (1969) showed that surface snow in polar regions today contains much more lead than can be accounted for by natural lead in silicate dusts and sea salts in these snows. Their measurements of lead in polar ice as a function of time showed that an increase of ~ 300-fold in concentrations of lead in polar atmospheres has been recorded in Greenland snow strata and that the present excess of lead in aerosols above natural levels of lead contained in silicate dusts and sea salts did not exist in ancient atmospheres and snow and is of recent anthropogenic origin. This observation disclosed the widespread and intense occurrence of the most pervasive and significant central nervous system poison known to exist in human environments. It supports the interpretation of other evidence which show that many natural cellular biochemical processes involving calcium of most people living in industrialized countries have probably been detrimentally perturbed by an average 500-fold excess of industrial lead above natural levels in their bodies. (Ericson *et al*. 1979, Elias and Patterson 1980). This has important implications concerning the health of billions of people, the developmental history of engineering technology, and the survival of our civilization.

Murozumi *et al*. (1969) reported less than 1 ng Pb/kg in two 2800 year old blocks of Greenland ice (about 35 cm per edge), which had high mass/surface ratios and were collected under ultra-clean field conditions from the western edge of the ice sheet at 76°N. Their upper limit was set by uncertainty in determination of laboratory lead contamination. They also reported 210 ng Pb/kg in surface snow accumulated throughout one year (1964-1965) at a remote virgin location in the western interior of the ice sheet at 77°N, and they found that lead concentrations increased progressively with time in older ice blocks collected manually under ultra-clean conditions in the western interior from 11 ng Pb/kg at 1750 A.D. to 160 ng Pb/kg at 1963 A.D. They observed no corresponding increases in concentrations of salts and dusts, and ascribed the entire ~ 300-fold increase of lead concentrations to industrial atmospheric lead emissions because they found that natural lead contained in dust and salt in the 1964-1965 ice firn layer could account for only 1/300th of the total lead present.

In the Antarctic they reported lead concentrations in virgin snow near and at the surface for the period 1947-1966 to be about 15 ng Pb/kg snow which was 1/10th that in Arctic surface snow of the same age, and observed that centuries-old Antarctic firn contained, as an upper limit, less than 1/10th of the lead found in surface snow. Their upper limit was determined by uncertainty in determination of lead contamination in the laboratory. They found that salt and dust concentrations in Antarctic snow were too small to account for the lead in the snow.

Before 1968 investigators had reported erroneously high concentrations of such elements as Na, K, Cl, Mg, Ca, and Si in polar ices (Langway 1967, Hanappe _et al_. 1968, Wilson and House 1965). Accurate measurements of salts and dusts in polar snows were made in the Murozumi _et al_. (1969) study so that the amounts of lead in excess of sea salt and crustal silicate compositions in the ice could be correctly determined. Their measurements provided the first accurate values for atmospheric Pb/Si-dust ratios as a function of time which showed that enormous excesses of lead existed in present-day aerosols. Even though it should be easier to measure lead to silicate dust ratios directly on air filters, it has taken investigators considerable time to develop abilities to do this properly. Since early measurements, such as Zoller _et al_. (1974), and Chester _et al_. (1974) reported data that were in excessive positive error for lead, and present day measurements continue to be compromised by serious positive errors for lead (Feeley _et al_., 1978). However, a few investigators who have made significant contributions to scientific knowledge of this subject through extensive improvements in lead contamination control (Duce _et al_., 1981).

Cragin _et al_. (1975) reported an average concentration of 70 ng Pb/kg with no increase as a function of time in 12 cm-diameter ice cores collected from the center of the Greenland ice sheet at 65°N (Dye 3) from ice layers whose ages ranged from 1200 A.D. to 1910 A.D. Herron et al. (1977) reported an average concentration of 45 ng Pb/kg in cores of similar ages collected from the western interior of the ice sheet at 70°N (Milcent) with no increase as a function of time in these samples during the 1200 A.D. to 1910 A.D. period. These investigators reported an increase in lead concentrations with time after 1910, reaching 580 ng Pb/kg at the 65°N site for 1970-1971 and 140 ng Pb/kg at the 70°N site for 1971-1973. They found that lead at seawater and crustal concentration levels in dusts and salts in the firn could account for <1% of total lead in uppermost layers. Because they observed no increase in lead concentrations with time before 1910, they believed that their measured excesses of lead in ice before 1910 (about 100-fold above those provided by silicate dusts of crustal compositions) originated from natural sources. They claimed that the Murozumi et al. (1969) value of 11 ng Pb/kg ice at 1753 A.D. was spuriously low in light of the scatter of data caused by seasonal effects and that the <1 ng Pb/kg ice at 800 B.C. was anomalously low and of no significance because the sample was taken from an ablation zone near the edge of the glacier. They ascribed about two-thirds of the present excess lead in surface snow of Greenland to industrial sources and the remaining one-third of the excess to natural sources, citing volcanic gas emissions as a probable source.

Boutron and Lorius (1979) measured lead in snow strata at 74°S in East Antarctica (Dome C) for the period 1914 to 1974. They reported no change in lead concentrations with time with an average concentration of

26 ng Pb/kg ice. Their reported concentrations of salts and dusts would account for <1% of this lead. Since they observed no significant increase of lead with time while there has been a very large relative increase of emissions of industrial lead to the atmosphere, they claimed that the influence of industrial lead was negligible in the Southern Hemisphere and all of the excess lead above crustal values in Antarctic snow originates from natural sources such as volcanoes, enriched micro-layers in the oceans, and gaseous emissions from rocks and plants, and has been present since ancient times.

After 1969 a number of investigators measured ratios of lead to silicates in atmospheric dusts (summarized by Nriagu, 1978), and widespread observations of both erroneous and actual excess values of Pb/Si-dust ratios above silicate crust compositions. This generated the idea that such astonishingly large world-wide effects were beyond the capabilities of mere human industrialists, and it was proposed that natural causes, such as volcanoes and seasalts must be responsible. Recent accurate determinations of emission fluxes of lead to the atmosphere from volcanoes and seaspray (Buat-Menard and Arnold 1978, Buat-Menard et al. 1981, Ng and Patterson 1981, and Patterson and Settle 1981) have shown that these natural sources cannot provide the correctly measured excess amounts of lead which exist in the atmosphere.

Upon being confronted with published conflicting studies of lead in polar snows, we measured concentrations of lead and potassium in ice cores analogous to those studied by Cragin et al. (1975) and Herron et al. (1977). Improvements have been made in the technique formerly used at the CIT laboratory in 1967 to determine lead in glacial ice which now permit analyses of 500 gm samples to be made with greater absolute accuracy and sensitivity at the 1 ng Pb/kg level than had been attained in the analysis of 50 000 gm samples in 1967. This ability allowed us to accurately analyze lead and potassium in four millimeter thick concentric veneers of ice chiseled in sequence from the outsides toward the centers of 10 cm ice cores. These analytical results are interpreted and discussed in the light of new findings concerning the emissions of lead to the atmosphere from volcanoes and oceans.

2. METHODS

2.1 Sample Description

Ice core sections used for analyses were selected from archives at the State University of New York, Buffalo, New York. These cores has been stored at -30° for approximately 15 years. C. Langway, chairman of the Geology Department and director of the archives, assisted us in selecting samples. Core sections were chosen to be older than 3000 years to avoid possible effects from Roman smelting (Patterson *et al*. 1970, Settle and Patterson 1980). The cores were carefully inspected to exhibit no visible cracks on the light table and no show evidence of surface melting. Core sections were packed in dry ice, shipped to the CIT laboratory, and stored at -20° until analyzed.

The Greenland ice core sections came from the third hole at Camp Century, Greenland (77° 10'N, 61° 08'W, elevation 1885 m), and were obtained by electromechanical drilling in 1965 (Hansen and Langway, 1966), from a hole filled with a stabilizing fluid composed of 88% diesel fuel and 12% trichloroethylene. For comparitive purposes, we should use core sections similar to those that had been analyzed by Langway's group for lead; they were thermally drilled cores taken from non-fluid filled holes. However, they are not suitable for our study because they extended only down to medieval times where it is estimated (Patterson *et al*. 1970, Settle and Patterson 1980) that smelting operations in Germany may have added measurable amounts of lead to Greenland ice. To go back in time in Greenland ice beyond Roman smelting activities, which were far more intense than the medieval operations in Germany, we were forced to use electromechanically drilled cores taken from fluid-filled holes. We did analyse thermally drilled cores taken from Antarctica, we found those cores were less contaminated on the surface, but about same levels of lead contamination were found to have penetrated to the centers. Core samples from Greenland were not perfectly round in cross-section because an outer segment bounded by the surface and a chord and amounting to 15-20% of the volume had been sawn off each section for oxygen isotope studies. The core was originally drilled for a 10 cm diameter; however, in 1979, the core sections measured only 8-8.5 cm in diameter, the probable result of sublimation losses during storage. Approximate ages of the Greenland core sections were available to us from studies by Dansgaard et al. (1969), from oxygen isotope data which defined the Holocene boundary, and from accumulation-compaction data at the Camp Century site.

The Antarctic core sections came from New Byrd Station, Antarctica (80° 01'S, 119° 31'W, elevation 1530 m), where the core was obtained by thermal drilling in a hole not filled with fluid as part of the NSF U.S. Antarctic Research Program. Radial contamination characteristics of these cores provided criteria for evaluating the accuracy of the lead data obtained by Langway's group who used this type of core in their studies, as well as establishing the historic increase of lead concentrations in Antarctic ice. These core samples possessed complete cross-sections approximately 12 cm in in diameter. Ages were estimated from accumulation rates and compaction (Gow et al., 1968).

2.2 Sampling Core Sections

The cleaning procedure used by Herron *et al.* (1974) on dirty archived core sections involved washing the outer surface of core sections with acetone and distilled water. Boutron did not use dirty core sections, but attempted to collect snow samples under clean conditions in the field. He forced acid-cleaned lucite tubes into the snow in the field, placed caps over the ends, sealed the tubes in plastic bags, opened the bags and tubes in the laboratory, and melted the firn directly for analyses.

After some initial attempts to clean the dirty archived core sections by washing, we abandoned this approach and instead mechanically chiseled 4 to 6 successive veneers of ice, each about 3 to 5 mm thick, in progression from the outside toward the interior of each section, and determined lead and potassium concentrations in each separate ice veneer and in the remaining inner ice core itself. Ultra-clean procedures were used primarily to prevent transfer by entrainment and handling of lead and potassium contamination existing at high levels within ice chiseled from outer positions along the radii of the sections to cleaner portions of the solid ice core during the process of removing the veneer samples, and to exclude lead and potassium contamination from laboratory reagents, containers, air, and personnel to the ice samples during their analysis. We modified our sampling techniques a number of times as successive analyses disclosed the magnitudes of the problems of contamination transfer by entrainment that had to be solved at various positions along the radii of the core sections.

The method used which gave the most accurate lead and potassium concentrations in core sections at different radial positions (which was applied to one Camp Century and one Byrd Station core section out of the five core sections analyzed and reported in Table 1) was as follows. Sublimation crystals and core markings were scraped off and discarded in a first complete sampling-type operation. After a complete change of equipment as described below, the core section was laid flat and the first shaving cut was made along a side, throwing the shavings out and away from the core section in a pile alongside it. This cut was rotated upward, and the next adjacent cut was made along its lower edge. This cutting and rotation was repeated until the first shaving cut had been rotated nearly 250°. At this time the core section was lifted up and moved a short distance to a clean part of the cutting table so that the freshly shaved surface rested on a clean surface, while the shaving of sides was completed. The ends of the core section were shaved so that they were oriented toward the shavings pile.

A rectangular stainless steel chisel, 2 mm thick, 3 cm wide, and 10 cm long, sharpened to a single acute bevel across the leading edge and fastened to a 10 cm plastic-covered handle, was used in a series of rapid, forceful thrusting motions parallel with the core axis to make a continuous, shallow-chord shaving of the surface from one end of the core section to the other. The bevel was oriented so as to drive the chisel down into the ice and throw the ice chips up and away from the blade. These end-to-end shaving-cuts were repeated alongside each other in parallel directions so that the edges of each slightly overlapped the edges of its adjacent neighbor. The end surfaces of the core sections were shaved in the same manner. Each individual sample consisted of a single veneer of the entire core section surface with a thickness of about 4 mm.

The pile of ice shavings from one veneer was scooped with a flat quartz blade from the cutting table into a wide-mouthed polyethylene sample bottle and weighed. After the first veneer of ice was removed from a core section taken from a fluid filled hole (the first sample of such a core section), the core was held by stainless steel tongs over a polyethylene funnel and rinsed with ultra-pure $CHCl_3$ (<1 pg Pb/g) chilled to 0°C to remove traces of dirty oil and trichloroethylene and placed in a freshly cleaned polyethylene bag, sealed, and returned to the freezer. Rinsing was not repeated after later veneer samples were taken from the core. We do not do a first rinsing for the core section from a drill hole not filled with fluid. The weights of $CHCl_3$ and the rinse solution collected were carefully recorded. The weight of ice melted by the $CHCl_3$ was determined by difference. After the last veneer sample of ice had been removed (the next to last sample of the core section), the remaining core was held by stainless steel tongs over a polyethylene funnel and rinsed with 0.1% ultra-pure HNO_3 (<1 pg Pb/g) chilled to the freezing point and this ice was not bagged and returned to the freezer, but was analyzed without further handling. The weight of ice melted by the acid was also determined.

Two operators worked together. For the collection of each veneer sample, the core section remaining from the previous trimming step was removed from the freezer, and its bag seal was opened by one person with ordinary clean gloves, while the second person removed the core section from the bag and placed it on the cutting table using acid cleaned gloves. The first person then put on acid cleaned gloves. During the shaving process the second person held the ends and side, touching only surfaces not freshly shaven with an acid cleaned polyethylene glove and thrusting the chisel with the other hand, while the first person held and lifted the section, touching only the freshly shaved surfaces with acid cleaned gloves. That first person placed the shaved, cleaned core section into a fresh acid cleaned bag, sealed it, and returned the core to the freezer.

The cutting table consisted of a 50 × 30 × 8 cm polyethylene tray half-filled with crushed dry-ice. A 4 mm thick sheet of polyethylene was laid on top of the dry-ice. A larger, 0.2 mm thick polyethylene sheet was laid over this so that the edges of this sheet extended up, over, and down the outsides of the tray. The tray was shielded on the top, back and one end by transparent sheets of 3 mm plastic welded together so as to be self supporting and providing an opening 30 cm high along the front and one end. The operators worked under this shield, looking down through it at their work.

Cleaning procedures were as follows. The cutting table tray, thick sheet, and shield were cleaned with $CHCl_4$ then soaked 1 day with 4 N HNO_3 and rinsed with ultra-pure water (<1 pg Pb/g). The large, flexible conventional polyethylene sheet upon which the core section rested and its shavings collected was cleaned with a $CHCl_3$ rinse; 1 day at 55°C in 4 N HNO_3 (reagent grade in ultra-pure water); 2 days at 55°C in 1% N HNO_3 (~ 1 pg Pb/g); 2 days at 55°C in 0.1% ultra-pure HNO_3 (<1 pg Pb/g); and rinsed 3 times with ultra-pure water (<1 pg Pb/g). This sheet was held during the final rinsing and transfer to the tray by a person wearing acid cleaned polyethylene gloves. A new freshly cleaned sheet of this type was used for each veneer sample. The polyethylene bag in which the core section was placed after shaving had been cleaned in the same manner as the polyethylene sheet described above, and rinsed 3 times with ultra-pure water before use. A new bag was used for each core remaining after the veneer sample had been removed. The stainless steel chisel, tongs, and quartz scoop, after soaking for 1 day in concentrated HNO_3 and rinsing with ultra-pure water, were kept soaking in 0.05 N HNO_3 (<1 pg Pb/g) in a covered container, and were shaken moist-dry just before use, and the working parts allowed to touch no surface but the ice or the cutting table. These tools were recleaned for each veneer sample. The operators wore clean, lint-free gowns and caps. Over these they each wore a large, acid-cleaned polyethylene bag placed over the body, open side down, with slits cut for the arms and a small rectangular opening for the face. The edges of this opening were held tight against the forehead and cheeks by a strip of polyethylene film tied around the neck. The arms and hands of each operator were enclosed in shoulder-length polyethylene gloves. Over these gloves they wore wrist-length polyethylene gloves that had each been cleaned in the same manner as the flexible sheet on the cutting table tray. These gloves were kept soaking in batches in the final dilute acid bath, and were rinsed with ultra-pure water after they had been put on. These gloves were only used once, and were replaced once by a fresh pair during the collection of each veneer sample. Duties and motions were so arranged between operators that they touched no other surfaces with these gloves than the surfaces of the core section. These gloves were discarded after they had touched a tool, plastic bag, or any other surface but ice, and several pairs were used for each sample. All these operations were carried out in an ultra-clean laboratory, pressurized with filtered air (<10 ng Pb/m^3) (Patterson and Settle, 1976).

This entire cleaning and glove change procedure described above was repeated in detail before each succeeding veneer of an ice core section was collected. The ice core sections were kept in a freezer during this lengthy cleaning processes between sampling operations. This freezer faced into the ultra-clean laboratory, and was sealed into an opening in a wall, with the dirty motor and circulating air confined to a corridor outside the laboratory. One sample could be collected every day if required, because fresh plastic sheets and gloves were continuously cycled through the various acid baths.

The installation of the plastic dust shield, the use of a final acid rinse, and the changing of acid-cleaned gloves during a sampling process were late modifications of sampling procedures used only for the last two core sections (950 m Camp Century and 256 m Byrd Station). These samples gave the lowest lead concentration curves plotted in Figures 1 and 2. The other core sections were sampled in less satisfactory ways during earlier sampling trials. The cleaning method used by Herron _et al_. (1974) was tried at first on one core section, but was abandoned when the melt water were analyzed and found to contain 108 ng Pb/kg ice. Later cleaning steps involved rinsing the core with chilled CH_3OH and chilled water in addition to $CHCl_3$ between veneer sample collections. The CH_3OH rinse was discontinued because it caused visible cracks to form in core sections (even though chilled to the same temperature as the ice) which undoubtedly transferred contamination inward, and probably caused some of the scatter in data shown in Figures 1 and 2. The water rinses were discontinued for fear that the same process occurred from its use. Preliminary data from veneer samples obtained by early trial combinations of such rinsing treatments are plotted as the higher and more erratic lead concentration curves in Figures 1 and 2, while the lower curve in each figure was obtained by the collection method described above. We believe that the visible cracks produced (sometimes with audible noise) by the methanol were re-openings of pre-existing fractures instituted during the drilling process, which had subsequently been partially but incompletely annealed. We believe that contamination was introduced during the drilling process to the insides of the cores along these fractures. We believe that the final acid rinse caused more good than harm because there probably were fewer partially annealed fractures within the inner region of the core section.

2.3 Analytical Techniques

2.3.1 IDMS METHOD. The ice samples were analyzed by thermal ionization isotope dilution mass spectrometry (IDMS) using ultra-clean laboratory methods. The major problem associated with lead analyses at concentration levels of 1 ng Pb/kg is contamination. The simple use of accurate and sophisticated metal detection instruments will not, by itself, provide correct lead analyses at low lead concentrations. The reliability of trace lead analyses depends primarily on exclusion of artifact contamination during sample collection and on the control and accurate determination of lead contamination in the analytical laboratory.

2.3.2 CHEMICAL TREATMENT. Frozen cuttings, which had been contained in conventional polyethylene bottles and pure SiO_2 beakers, were thawed at room temperature. HNO_3 (10 pg Pb/g, NBS 2 × quartz distilled) was added to make a 1% HNO_3 solution. The solution was allowed to sit for 4 hours. Aliquots of this solution were removed for analyses of potassium, total lead and extractable lead.

For potassium concentration measurements, ^{41}K spike was added to 5-10 ml aliquots and HNO_3 and HF (10 pg Pb/g) were added to make up a 1% HF, 3% HNO_3 solution. The solution was allowed to stand for 30 minutes, then evaporated to dryness at ≈80°C in a filtered nitrogen flushed teflon oven, then 0.1 ml HNO_3 was added and evaporated twice with the residue, and the dried residue was dissolved in 2 μl of water and transferred to an oxidized tantalum filament and inserted into the mass spectrometer.

Total lead concentrations determined by rigorous HNO_3-HF decomposition were similar to those for potassium, except a larger aliquot was used and ^{208}Pb spike was added instead. After evaporation to dryness the residue was dissolved in 10 ml ultra-pure water and subjected to a chemical separation described below.

For measurement of dilute acid soluble lead concentrations, ^{208}Pb spike was added to a weighed aliquot of sample in a polyethylene bottle. Inner core samples were placed in quartz beakers and melted in them and HNO_3 added to make a 1% solution. Aliquots for potassium analysis were removed from these beakers. Solutions were allowed to equilibrate for two hours, and then transferred to a conditioned FEP teflon separatory funnel. The pH of the solution was adjusted to 8-9 with purified ammonium hydroxide (<1 pg Pb/g), and lead was extracted into 10-15 ml of purified dithiozone-chloroform (3 pg Pb/g) solution. This chloroform solution was washed with 20 ml dilute NH_4OH (<1 pg Pb/g) (pH 9-10) and the lead was then back extracted into 5 ml of 5% HNO_3 (<1 pg Pb/g). This aqueous solution was washed with 5 ml chloroform (<1 pg Pb/g), and then evaporated to dryness. The residue was transferred to a rhenium filament, treated with H_3PO_4 and silica gel (total Pb in these reagents and filaments 20 pg), and inserted into the mass spectrometer.

2.3.3 MASS SPECTROMETRY. Both lead and potassium were analyzed using a 12" radius, single focusing, solid sources, thermal ionization mass spectrometer. The $^{208}Pb/^{207}Pb$ ratio was measured to determine lead concentrations (^{208}Pb tracer was 99.94% ^{208}Pb).

The $^{39}K/^{41}K$ ratio was measured to determine potassium concentrations (^{41}K tracer was 86.16% ^{41}K), and an enriched $^{40}K/^{41}K$ in the tracer whose value was known beforehand was measured to determine a correction factor for mass fractionation during each analysis.

2.3.4 CONTAMINATION CORRECTIONS. Ultra-pure water, whose lead content was known (0.2 to 0.4 pg Pb/g) was substituted for ice and used to determine separately the lead contamination introduced by the extraction funnel, the sample bottle, and the beakers. Reagents were analyzed individually for lead.

Ultra-pure water was put into ultra-cleaned conventional polyethylene containers, sealed, and frozen into a configuration similar to the ice cores. The exterior surfaces of these artificial ice cores were removed by the ultra-clean chiseling process described above and discarded, then additional veneer samples were removed from these cores and analyzed to determine the amount of lead contamination introduced by the chiseling and washing procedure, knowing beforehand how much lead was in the ice and was introduced by chemical analysis. Collecting a 150 gm ice veneer sample by chiseling according to the method described above introduced about 250 pg of lead. Handling and acid rinsing a 300 gm inner core introduced about 10 pg of lead contamination from air and containers during acid digestion of about 50 gm of ice in order to determine total lead concentrations introduced about 30 pg of lead. For dilute acid analyses of large samples, reagents added from 40 to 80 pg of lead. Solvent extraction and exposure to laboratory containers and air of these large samples introduced about 50 pg of lead. The analytical blank for large samples which varied from sample to sample, was therefore the sum of six to eight separately measured contamination contributions from reagents and ware, modified appropriately for yields determined by double isotope spiking. This total ranged from about 160 pg of lead per analysis for center core samples to 360 to 400 pg of lead for veneer samples. The latter usually contained more than 1000 pg of lead, so that laboratory lead contamination corrections for sampling and analysis usually amounted to less than 30% of the total. The cleanest center core samples contained about 400 pg of total lead, so that laboratory lead contamination corrections for sampling and analysis (about 160 pg lead) amounted to about 30% of the total in these types of samples.

The total potassium blank was about 2.4 ng potassium for an analysis of an ice veneer sample and 1.2 ng potassium for an analysis of an inner core sample, the difference being due to potassium contamination added during chiseling. Since all potassium determinations involved more than 10 ng of sample potassium, blank corrections were less than 20% of the sample potassium.

3. RESULTS AND DISCUSSION

3.1 Significance of data obtained in this study

Analyses listed in Table 1 of successive veneers of ice from core sections show that enormous amounts of artifact contamination of both lead and potassium reside on the surfaces of these cores, and that lead contamination intrudes in decreasing but significant amounts to the centers of these cores.

Figure 1 shows that the overall decrease in concentrations of lead was about 10^6-fold in Camp Century, Greenland cores, changing from exterior values of 10^6 ng Pb/kg to interior values of 1.4 ng Pb/kg ice. Figure 2 shows that the overall decrease of lead concentration in the Byrd Station, Antarctica ice cores was 10^4-fold, changing from exterior values of 10^4 ng Pb/kg to interior values of 1.2 ng Pb/kg ice. Contamination was added during coring operations and subsequently by sample handling during transportation and storage. The speciation of the contamination is not known, but it is readily soluble in cold 1% nitric acid, which indicates that it is capable of ionic diffusion. The main transfer of surface contamination into the interior probably occurred along cracks, since calculations based on diffusion coefficients within intact ice permit only infinitesimal transfer of foreign ions/molecules into the interior within a decade over a distance of <0.5 cm (Runnels 1969, Fletcher 1970). Contamination could have been forced into minute cracks formed during the drilling operations and these cracks could have annealed later to become invisible to the eye.

Continuous decreases in lead concentrations with no plateaus indicate that lead contamination from the exterior has penetrated to the centers of the cores, because lead concentrations along successive radial positions should have leveled off at fixed values if the interiors were not contaminated. This would be true if contamination was not transferred to the interior with sufficient rapidity during years the cores were stored so as to shallow out concentration gradients. The observed decline in lead concentrations cannot be attributed to a change in the fraction of sample lead accessible to the dilute acid method used to mix isotope tracer and sample leads. Total lead concentrations determined by destructive HF-HNO_3 dissolution at both high and low levels in some interior ice veneers did not exceed lead concentrations determined by dilute acid dissolution in parallel aliquots from the same samples. The concordance is shown in Table 2. Some of the lead concentrations measured in samples obtained by less satisfactory methods from the interiors of the ice core sections are high as a consequence of the transfer of contamination by entrainment during sampling, and the scatter in lead concentration data in the interior of the cores shown in Figures 1 and 2 is due in large part to improvements in cleaning procedures instituted between the sampling of the first and last core sections. The most refined sampling procedure involving the lowest contamination is associated with the data points showing the lowest lead concentrations. Concentrations measured at the centers of these core sections must represent upper limits of lead concentrations originally present in the ice. The most accurate value for this upper limit was determined by the best sampling method as 1.4 ng Pb/kg ice in 5000 year old Greenland ice. The most accurate value for this upper limit in 2000 year old Antarctic ice is less than 1.2 ng Pb/kg.

The overall decrease of potassium concentrations was about 100-fold in going from the exterior into the interior of both Greenland and Antarctic ice cores, changing from 500 to 2 μg K/ng ice in the Greenland core as shown in Figure 1, and from 80 to 0.9 μg K/kg ice in the Antarctic cores as shown in Figure 2. Potassium concentrations decrease slightly in the central portions of the Greenland cores but show no decline in the interior of the Antarctic cores. Some of the scatter of the potassium concentrations in the Greenland core shown in Figure 1 is associated with contamination transfer by unrefined sampling techniques as mentioned above. Concentrations of potassium measured at the centers of Greenland cores define an upper limit of 1.7 μg K/kg, which is probably not far from the original concentrations because there is little change of potassium concentration with radius near the center of the core section. Potassium concentrations at the centers of Antarctic cores probably represent original concentrations of 0.9 μg K/kg ice in 2000 year old ice.

Lead and potassium contamination are less on the exteriors of Antarctic cores compared to Greenland cores. The thermal drill coring method, in which the drill hole is not filled with fluid, is cleaner than the electro-mechanical drilling method, using fluid filled drill holes, since similar amounts of contamination should have been added to both types of cores during handling, shipping and storage. Higher concentrations of lead and potassium contamination at intermediate distances within the Greenland core sections shown in Figure 1, compared to those in Antarctic core sections shown in Figure 2, may have been caused by the removal of an outer segment of ice from each of the Greenland cores for $^{16}O/^{18}O$ studies, because this cross-sectional asymmetry made us mix inner and outer layers when we sampled concentric veneers of ice. Another cause of the difference may have been differences in magnitudes of surface contamination. Although the surfaces of Camp Century cores were more highly contaminated than were the Byrd Station cores, the contamination of the centers of the cores was about the same because melting associated with thermal drilling probably effectively transferred the smaller amount of contamination associated with that drilling method through microfractures produced in the ice core by temperature and pressure shocks during drilling.

Greenland and Antarctica have different meteorological regimes and relationships to proximities of the continents. The land area of the Northern Hemisphere is twice that of the Southern Hemisphere, and the atmospheric dust load in the Northern Hemisphere is correspondingly higher. Antarctica is protected by a more effective 50°S circumpolar atmospheric convergence from dust sources at lower latitudes than is Greenland by its circumpolar atmospheric convergence. Murozumi *et al.* (1969) observed that Byrd Station snow contained one-tenth of the silicate dust found in Greenland snow during the past two centuries. Cragin *et al.* (1976) observed that this proportion of dust concentrations has remained essentially constant during the past 10 000 years in Camp Century and Byrd Station snow. As stated in the INTRODUCTION, natural concentrations of lead in the atmosphere are determined for the most part by silicate dusts, so it would be expected that natural concentrations of lead in Greenland snow at Camp Century would be about 10-fold higher than in Antarctic snows at Byrd Station. Upper limits obtained from the interior of Greenland and Byrd Station cores are higher than true lead concentrations, so the 10-fold expected difference is obscured.

The lack of lead we found in ancient ice at Camp Century combined with the lack of lead found in ancient ice by Murozumi et al. (1969) at the western edge of the ice sheet shows that a lead concentration of less than 1 ng/kg is generally applicable on a broad geographic scale to Greenland ice strata older then 3000 years. Our upper limit for the concentration of lead in ancient Antarctic ice is much more accurate than the upper limit reported by Murozumi et al. (1969) due to our improved control of lead contamination in the laboratory. There can be no doubt but that the concentration of lead in ancient Antarctic ice is less than 1 ng Pb/kg.

Our 1.7 μg K/kg found in Camp Century ice is approximately the same as the 2.7 μg K/kg ice observed by Murozumi et al. (1969) and the 1.5 μg K/kg ice expected from 35 μg silicate dust and 67 μg sea salt per kg ice computed from their data. Our observed 0.9 μg K/kg ice at Byrd Station is approximately the same as the 1.5 μg K/kg ice observed earlier by Murozumi et al. (1969) and the 1.2 μg K/kg ice value expected from 110 μg sea salt determined by them. Differences among these values can result from different placement of core sections within the stratigraphic pattern of seasonal fluctuations in concentrations of sea salts and dusts.

3.2 Comparison with data of Langway and coworkers

The findings of Cragin *et al*. (1975) and Herron *et al*. (1977) regarding lead concentrations in Greenland firns and ices have been summarized in the INTRODUCTION. They interpreted their data to mean that there was an approximate 100-fold excess of lead in 800 year old Greenland ice above levels that could not be accounted for from silicate dust in the ice. The present study shows that Langway and coworkers were working with ice that had been contaminated in the field and that they further contaminated their samples during handling and analysis.

Langway and coworkers (Herron *et al.*, 1977) claimed that the 11 ng Pb/kg value for AD 1750 found by Murozumi *et al*. (1969) was spuriously low. It was shown in the latter paper that much of the sporadic variation in lead concentrations was due to the sporadic inclusion of either one summer layer plus one winter layer or two summer layers plus one winter layer in the various ice block samples, with winter layers containing more lead than summer layers. However this variation amounted only to about ±25% about a mean, and the lead concentration at AD 1750 was exceeded about 4-fold by lead concentrations in the next younger group of four samples from the period AD 1810 to 1880. The low lead concentration observed at AD 1750 is significant and indicates low concentrations of industrial lead in the atmosphere at that date compared to later times.

Langway and coworkers claimed that the <1 ng Pb/kg value obtained by Murozumi *et al*. (1969) in 2800 year old ice was anomalously low because the sample was taken from an ablation zone near the edge of the ice sheet. This is a valid concern, but data available at the time of the

Murozumi et al.(1969) study had already indicated that true metal concentrations in this ice probably had not been redistributed beyond stratigraphic distances of decimeters. The ^{14}C chronologies at different stratigraphic levels tens of meters apart within the stratigraphic section at this location appeared correct in both relative and absolute aspects. Both the salt and dust concentrations appeared correct in relative and absolute aspects in the old ice when compared to those in recent firn from the glacial interior, where the $^{16}O/^{18}O$ stratigraphy was preserved (less dust, more salt in the old ice formed nearer the sea). Although annual layers in this old ice sample had been thinned to a few centimeters by compression and horizontal flow, vertical stratigraphic integrity of trace chemical constituents in terms of centuries apparently had been maintained by a relatively simple ice-flow pattern which prevented extensive vertical solid mixing, especially with the bottom ice moving over bedrock, and a low enough ambient temperature regime which reduced vertical percolation and chemical alteration through stratigraphic horizons. Although our study shows that one 2800 year old ice sample from an ablation zone in Northern Greenland gave lead data that were significant with respect to atmospheric concentrations for that date, this does not mean that this should be the universal case, especially for temperate glaciers. The opposite is likely to be true at lower latitudes where ice-flow patterns are rapid and complex enough to contaminate the vertical section with portions of bedrock ice, and where ambient temperatures are high enough to allow percolation. Undisturbed $^{16}O/^{18}O$ and ^{14}C chronologies are rare in temperate glaciers while percolation and mixing is common in such cases.

3.3 Comparison with data of Boutron and coworkers

Findings reported by Boutron and Lorius (1979) concerning lead concentrations in Antarctic snow have been summarized in the INTRODUCTION. Like Cragin et al. (1975) and Herron et al. (1977), these investigators claim that their observed >100-fold excess of lead in Antarctic snow beyond that which could have been contributed by silicate dusts originated from natural sources such as volcanoes, sea spray and soil emissions. However, they differ from Langway's group in that they assert that this situation in Antarctica applies to snow accumulated during recent decades. Although the lead concentrations which Boutron and Lorius (1979) report for surface snows may be approximately correct, our study shows that they are unable to distinguish between true high lead concentrations in recent snows and true low lead concentrations in older snows because of artifact lead contamination they introduced into the samples. Their inability to measure lead concentrations less than about 26 ng/kg in permeable firn can result from either contamination during collection or during analytical procedures or both.

Boutron and Lorius (1979) and Boutron and Delmas (1980) attempted to prove that excess lead in Antarctic snow originated from volcanic emissions by correlating their reported increases in lead concentrations in these snows with increases of sulfate concentrations. The Pb/S ratio of 2×10^{-4} (wt) measured in volcanic gas from Mt. Etna (Buat-Menard 1978, Buat-Menard et al. 1981, Patterson et al. 1981) can be multiplied by the amount of excess sulfur in Antarctic snow, claimed by Boutron and Lorius (1979) to be perceived as originating from volcanic activities, to compute an expected increase of lead in that snow associated with the increase of sulfur. Provided the sulfate concentration did actually increase by the amount they claim it did, and provided the lead and sulfur originated from undiluted volcanic plumes which travelled through fortuitously favorable trajectories, the expected increase in lead concentration would be about 3.5 ng/kg snow. Since Boutron erroneously reported finding 26 ng/kg of lead, which didn't exist, he couldn't have correctly measured lead concentration differences of 3.5 ng/kg between different samples.

The 1.3 μg K/kg ice measured by Boutron and Lorius (1977) in snow at New Byrd Station agrees well with the 0.9 μg K/kg found by us and the average of 1.5 μg K/kg reported by Murozumi et al. (1969) at New Byrd Station. Seasonal variations could produce larger differences.

3.4 Differences between Pb/Si-dust ratios in air and in snow

The assumption was made in the Murozumi et al. (1969) study that chronological changes in Pb/Si-dust ratios in polar snows reflect parallel chronological changes of this ratio in the atmosphere. It has since been experimentally shown that Pb/Si-dust ratios are systematically about 10-fold smaller on air filters than in rain or snow collected at the same location and time. The most reliable available lead and Si-dust data for air, rain, and snow at remote geographic locations, listed in Table 3, show that this is the universal case at such wide spread remote locations as the Antarctic, the mid-Pacific and the remote High Sierra of North America. Most industrially produced lead-rich particles are very small compared to natural dust particles coexisting in the same air in remote regions (Duce et al. 1976a, Duce et al. 1980). These tiny lead-rich particles may be gathered by diffusion collection mechanisms onto surfaces of cloud-forming droplets and growing snowflakes so that their ratios to dusts within the droplets and flakes is much greater than their ratios to dusts in air that is sampled by passing through filters (Settle et al., 1981). There is no longer any doubt but that snows on the surface of the Greenland sheet display about a 10-fold greater excess of industrial lead above crustal silicate concentrations than exists in the air above the snows. It is important to recognize that this present-day relationship is probably anomalous compared to prehistoric natural conditions. During those earlier times silicate particles and lead-rich volcanic sulfur particles greater than a few micrometers in size contained most of the natural lead aerosols, so that there probably was little or no difference between Pb/Si-dust ratios in air and in precipitation. Our lead data, combined with the silicate dust data of Murozumi et al. (1969), show that the Pb/Si-dust ratio certainly increased by a minimum factor of 100-fold and probably increased by 300-fold in Greenland snow during the past 3000 years, while the present-day Pb/Si-dust ratio in the atmosphere of remote areas of the North Pacific and North Atlantic is about 50-fold above levels expected from natural silicate dust contributions (Duce et al. 1976-b, Chow et al. 1969, Ng et al. 1981, Settle and Patterson 1981).

It would be improper to infer that the prehistoric Pb/Si-dust ratio in the atmosphere of the Northern Hemisphere was much more than 1/50th of the present value simply because polar snows record on a more sensitive scale the extent of industrial lead pollution of the atmosphere. There are three reasons for this. (1) Mass inventories suggest an historical increase in the atmospheric Pb/Si-dust ratio of about 100-fold. (2) The prehistoric natural output flux of soluble lead from the eastern North Pacific ocean to its pelagic sediments was about 3 ng Pb/cm^{2}yr (Chow and Patterson, 1962) which was probably mainly fluvial in origin, while the present eolian input flux of soluble lead to the eastern North Pacific is about 60 ng Pb/cm^{2}yr (Schaule and Patterson, 1981), and the present Pb/Si-dust ratio in Pacific air is about 50-fold greater than the Pb/Silicate ratio in average crustal rocks (Settle and Patterson, 1981). (3) Increases of Pb/Si-dust ratios with time in air in remote regions of the Northern Hemisphere are bracketed between documented 300-fold values for increases of this ratio in precipitation on the high side and documented 4-fold values for increases of this ratio on the low side by industrial lead in water laid sediments. Just as there are plausible explanations for the greater present-day industrial Pb/Si-dust ratio in precipitation compared to that in air, there are valid reasons for expecting the present-day industrial Pb/Si-dust ratio in air to be greater than the industrial Pb/Si-dust ratio in water laid sediments. It is not generally understood that increases of industrial lead concentrations in sediments are caused by much larger increases of lead concentrations in the atmosphere with time. Atmospheric inputs of industrial lead to watersheds of ponds and lakes must increase by large factors before they can overtake and effectively exceed natural fluvial inputs of lead to ponds and lakes. According to the sedimentary record in a remote watershed pond, the atmospheric input of lead to that ecosystem was only about 1/5th of the input from rock weathering during prehistoric times, but today the atmospheric input of industrial lead by precipitation and dry deposition to the same ecosystem is about 20 times greater than the input from rock weathering (Shirahata *et al*. 1979, Elias *et al*. 1981). The extra input results from an approximate 100-fold increase in the atmospheric Pb/Si-dust ratio. Thus, explanatory models require that the Pb/Si-dust ratio in Northern Hemisphere air today should lie between a 300-fold excess of industrial lead in precipitation and a 4-fold excess of industrial lead in sediments.

In contrast to general hemispheric relationships, Pb/Si-dust ratios in urban precipitation are not 10-fold greater than those in air, but are much less. The enormous excesses of industrial lead, localized in air at low altitudes in regions which serve as primary sources of lead emissions to the atmosphere, far exceed enrichments of lead-rich fine particles occurring on larger aerosols during cloud-forming processes in less contaminated air at high altitudes. Data for lead in air and rain at Los Angeles, shown in Table 3, illustrate this point, which is that Pb/Si-dust ratios in air and precipitation are not related at locations near towns or traffic arteries in open country.

3.5 Natural sources of excess lead in polar snow

Silicate dusts contribute about 2000 tons Pb/yr to the atmosphere and constitute the largest natural source of lead (Settle and Patterson, 1980). Proponents of natural origins for the excess lead observed in polar snows have relied heavily on volcanoes as sources, but our coworkers and others (Buat-Menard and Arnold 1978, Patterson et al. 1981, Buat-Menard et al. 1981) have recently demonstrated experimentally from measurements of Pb/S ratios in volcano eruption plumes normalized to world-wide volcanic sulfur fluxes to the atmosphere that the average world-wide contribution of lead from volcanoes to the atmosphere (⩽ 1500 tons/yr) in the form of highly lead (and other metals) enriched micron-sized sulfur aerosols (Patterson et al., 1981) cannot be more than, and is probably less than, contributions of atmospheric natural lead from silicate dusts. The major bulk of volcanic silicate ash contains crustal abundances of lead. Since excess lead in polar snows is by definition that above the silicate dust level, and the present-day mass inventory flux of industrial lead to the atmosphere is about 400,000 tons/yr on a world-wide scale and about 40 000 tons/yr in the southern hemisphere (Settle and Patterson, 1980), it is clear that volcanoes make no significant contribution to the excess lead either on a world-wide scale or in the southern hemisphere.

Emissions of natural lead from surface lead-enriched micro-layers of the oceans to the atmosphere in the form of sea spray aerosols have been shown by means of measurements of enrichment of lead in aerosols produced by artificial bubblers, and in marine air under natural conditions (Ng and Patterson 1980, Settle and Patterson 1981) to account for smaller atmospheric lead concentrations in the marine atmosphere than those contributed by silicate dusts. Lead in marine aerosol salts formed by bursting bubbles in the ocean is enriched ⩽500-fold above lead/sea salt ratios in surface seawater, which is contaminated about 10-fold by industrial lead at present. Contributions of natural lead from the oceans to marine atmospheres in the North Pacific amount to only about 1/500th of the total lead present in such air today while silicate dusts can account for 1/10th to 1/100th of the total lead in marine air.

Other proposed natural sources for excess lead in the atmosphere such as direct volatilization from rock (Goldberg, 1976) are unworthy of quantitative consideration at this time because of there is no data base. Some of the experimental data (Beauford et al., 1977) used to support alleged natural lead emissions from plant leaves are seriously compromised by positive errors due to improperly controlled lead contamination.

In summary, prehistoric natural lead inputs to the world atmosphere from silicate dusts were about 2000 tons Pb/yr, about 1500 tons Pb/yr from volcanoes, and 500 tons Pb/yr from sea spray, while today industrial lead emissions to the world atmosphere from gasoline exhausts, smelter emissions, and reintrained lead contaminated soil dusts, pollens, and forest fire smokes total about 400 000 tons/yr.

This knowledge, combined with that concerning fractionation in precipitation outlined in the section above, allows the silicate dust level in Holocene Greenland snow to be used as a normalization factor. An estimated natural level of lead in that snow can be computed with an assurance which warrants the value receiving serious attention. 35 μg dust/kg ice (Murozumi et al., 1969) containing 12 ng Pb/g dust (Chow and Patterson, 1962) would provide 0.4 ng Pg/kg ice. This value would be approximately doubled to account for volcanic lead emissions plus natural lead in sea spray salts. It is assumed, with justification, that little fractionation occurs between lead and silicate dust in going from air to snow under natural conditions. The present best estimate of the total natural level in Greenland snow is, therefore, about 0.8 ng Pb/kg ice, with a natural Pb/Si-dust ratio about 2-fold above the average crustal value.

4. CONCLUSIONS

No controversy exists regarding the occurrence of lead in ancient Greenland ice. This study shows that some investigators made erroneous measurements. This is not a controversial matter. Our findings strengthen the foundation for the view that industrial lead pollution is global in extent and is serious. Upper limit constraints were imposed upon Murozumi *et al.* (1969) by errors in the determination of lead contamination in the laboratory. Although we used greatly improved analytical techniques to eliminate such constraints, contamination of our ice samples in the field during drilling imposed a different type of constraint, which again limited analyses for lead in ancient polar ice to upper limits so that actual concentration values could still not be measured.

This study shows that a proper experimental extension of the pioneering experiments of Murozumi *et al.* (1969), which would utilize the more sensitive and accurate analytical techniques that are now available, cannot be based on small diameter drill core samples but must utilize samples which have have large cross-sections and which have been collected (probably manually: Patterson *et al.*, 1970) with great care to exclude contamination.

It is important to determine with accuracy the true excess of lead above silicate dust values by carefully studying the record in polar ice, not only to correctly assess the extent of industrial lead pollution, but to properly understand the global geochemical cycles of lead in natural states. There certainly is some extra natural lead in the atmosphere not provided by silicate dusts, and perhaps not provided only by volcanoes and sea spray. Gaseous emissions by methylation, although seeming doubtful at present, haven't been conclusively eliminated. The origin of the natural easily soluble authigenic lead in pelagic sediments which occurs in about 2-fold excess beyond that which is provided for by silicates in pelagic sediments (Chow and Patterson, 1962) may have come from leachings of fluvial material deposited mainly on continental shelves, but this is not conclusive (Schaule and Patterson, 1981). Geographic patterns of lead isotopic data in pelagic sediments on a broad scale (Chow and Patterson 1962, Chow et al. 1980) show that such non-silicate lead over most of the basin areas didn't originate from hot spreading centers, except locally near the centers (Unruh and Tatsumoto, 1976), but the isotopic data would still permit eolian sources under certain meteorological conditions.

5. ACKNOWLEDGEMENTS

I am grateful to C. Langway for help in obtaining the ice core sections used in this study and for advice and information relating to them. This study was supported by NSF Contract Nos. DPP77-07803 and DEB79-11548.

6. REFERENCES

Beauford W., Barber J., and Barringer A. R. (1977) Release of particles containing metals from vegetation into the atmosphere. Science, 195: 128-129.

Boutron C. and Delmas R. (1980) Historical record of global atmospheric pollution revealed in polar ice sheets. Ambio, 9: 210-215.

Boutron C. and Lorius C. (1979) Trace metals in Antarctic snows since 1914. Nature, 277: 551-554.

Buat-Menard P. and Arnold M. (1978) The heavy metal chemistry of atmospheric particulate matter emitted by Mount Etna volcano. Geophys. Res. Lett., 5: 245-248.

Buat-Menard and coworkers (1981) Studies of lead and other metals in plume and fumarolic gases from Mt. Etna and Vulcano. To be published in J. Geophys. Res.

Chester R., Aston S. R., Stoner J. H., and Bruty D. (1974) Trace metals in soil-sized particles from the lower troposphere over the world ocean. Journal De Recherches Atmosphêriques, 8: 777-789.

Chow T. J. and Patterson C. C. (1962) The occurrence and significance of lead isotopes in pelagic sediments. Geochimica et Cosmochimica Acta, 26: 263-293.

Chow T. J., Earl J. L., and Bennett C. F. (1969) Lead aerosols in the marine atmosphere. Environ. Sci. Tech., 3: 737-740.

Chow T. J., Earl J. L., and Snyder C. B. (1980) Lead isotopes in Atlantic DSDP sediment cores. In: Isotope Marine Chemistry, E.D. Goldberg, Y. Horibe, K. Saruhashi, eds.: 399-412, Uchida Rokakuho Publishing Co., Tokyo.

Cragin J. H., Herron M. M., and Langway C. C. (1975) The chemistry of 700 years of precipitation at Dye 3, Greenland. U.S. Army Cold Regions Research and Engineering Lab Res. Rep.: 341.

Cragin J. H., Herron M. M., Langway C. C., and Klonda G. (1976) Interhemispheric comparison of changes in the composition of atmospheric precipitation during the late Cenozoic Era. Proceedings of ZUGG Symposium, Grenoble, IASN Publ.: 118.

Dansgaard W., Johnson S. J., Moller J., and Langway C.C. (1969) One thousand centuries of climactic record from Camp Century on the Greenland Ice Sheet. Science: 166, 377-381.

Duce R. A., Ray B. J., Hoffman G. L., and Walsh P.R. (1976-a) Trace metal concentration as a function of particle size in marine aerosols from Bermuda. Geophys. Res. Lett., 3: 339-342.

Duce R. A., Hoffman G. L., Ray B. J., Fletcher I. S., Wallace G. T., Fasching J. L., Piotrowicz S. R., Walsh P. R., Hoffman E. J., Miller J. M., and Heffter J. L. (1976-b) Trace metals in the marine atmosphere: sources and fluxes. In: Marine Pollutant Transfer, 77-119, H. Windom and R. Duce, eds., Lexington Books, Lexington, Mass.

Duce R. A., Unni C. K., Ray B. J., Harder P., and Pazenny A. (1980) Trace element studies at Enewetak. In: SEAREX Newsletter: 3, July, 31-34, Graduate School of Oceanography, University of Rhode Island, Kingston, RI 02881.

Duce R. A., Unni C. K., Ray B. J., Prospero J. M., Merrill J. T. (1980) Long-range atmospheric transport of soil dust from Asia to the tropical north Pacific: temporal variations. Science: 209, 1522-1524.

Duce R. A. and coworkers (1981) Anomalously enriched elements in the marine atmosphere: sources, fluxes, and oceanic exchange mechanisms. Research Renewal Proposal, NSF Office for the International Decade of Ocean Exploration.

Elias R. W. and Patterson C.C. (1980) The toxicological implications of biogeochemical studies of atmospheric lead. In: Polluted Rain, T. Toribara, M. Miller, P. Morrow, eds., Plenum Publishing Co., Newton: 391-403.

Elias R., Hirao Y., and Patterson C.C. (1981) The input, output, and distribution of lead and six other metals among biomass reservoirs in Thompson Canyon. To be submitted to Geochim. Cosmochim. Acta.

Ericson J. E., Shirahata H., and Patterson C. C. (1979) Skeletal concentrations of lead in ancient Peruvians. New England Journal of Medicine, 300: 946-951.

Feeley H. W., Toonkel L. E., and Larsen R.J. (1978) Radionuclides and trace metals in surface air. Environ. Quart., Environmental Measurements Laboratory EML-356 Appendix B: 173-185.

Fletcher N. H. (1970) The Chemical Physics of Ice. Cambridge Monographs on Physics, Cambridge University Press.

Goldberg E. (1976) Rock volatility and aerosol composition. Nature: 260, 128-129.

Gow A. J., Ueda H. T., and Garfield D. E. (1968) Antarctic ice sheet: preliminary results of first core to bed rock. Science: 161, 1011-1012.

Hansen B. L. and Langway C. C. (1966) Deep core drilling in ice and core analysis at Camp Century, Greenland, 1961-1966. Antarctic J. U.S., 1: 207-208.

Hanappe F., Vorsters M., Picciotto E., and Deutsch S. (1968) Chemistry of Antarctic snow and the rate of deposition of extraterrestrial material. II. Earth Planet. Sci. Lett., 4: 487-495.

Herron M. M., Cragin J. H., and Langway C. C. (1974) Improved procedures for the removal of surface contaminants from ice cores for chemical analysis. U.S. Army Cold Regions Res. Engineering Lab. Tech. Note, April.

Herron M. M., Langway C. C., Weiss H. V., and Cragin J.H. (1977) Atmospheric trace metals and sulfate in the Greenland ice sheet. Geochimica et Cosmochimica Acta, 41: 915-920.

Langway C.C. (1967) Stratigraphic analysis of a deep ice core from Greenland U.S. Army Cold Regions Research and Engineering Lab. Res. Rep.: 77

Liljestrand H. M. and Morgan J. M. (1981) Spatial variations of acid precipitation in Southern California. Enrivon. Sci. Tech.: 15 333-339.

Maenhaut W., Zoller W. N., Duce R. A., and Hoffman G. L. (1979) Concentrations and size distributions of particulate trace elements in the South Pole atmosphere. J. Geophys. Res.: 84, 2421-2431.

Mueller P. K., Cahill T. A., and Alcocer A. E. (1972) Chemical composition of Pasadena aerosol by particle size and time of day. In: Aerosols and Atmospheric Chemistry, G. Hidy, ed.: 306, Academic Press, New York.

Murozumi M., Chow T. J., and Patterson C. C. (1969) Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata. Geochimica et Cosmochimica Acta: 33, 1247-1294.

Ng A. and Patterson C. C. (1981) An upper limit for the enrichment of lead in seaspray compared to seawater determined in seaspray generated by a bubble interfacial microlayer sampler. Submitted to Earth Planet. Sci. Lett.

Ng A., Schaule B., Bruland K., and Patterson C. C. (1981) The relationship between Pb and ^{210}Pb in air, rain, and surface seawater. To be submitted to Earth Planet. Sci. Lett.

Nriagu J. O. (1978) Lead in the atmosphere. In: The Biochemistry of Lead in the Environment, J. O. Nriagu, ed., Vol. 1A: 137-184, Elsevier, Amsterdam.

Patterson C. C. and Settle D. M. (1974) Contribution of lead via aerosol impact to the Southern California Bight. J. de Recherches Atmos., 8: 957-960.

Patterson C. C. and Settle D. M. (1976) The reduction of orders of magnitude error in lead analyses of biological materials and natural waters by evaluating and controlling the extent and sources of industrial lead contamination introduced during sample collecting and analysis. In: Accuracy in Trace Analysis: Sampling, Sample Handling, Analysis, P. LaFleu , ed., NBS Special Publication 422, 1: 321-351.

Patterson C. C., Settle D. M., Unni C. K., and Duce R. A. (1981) Magnitude of lead flux to the atmosphere from volcanoes. Submitted to J. Geophys. Res.

Patterson C. C., Chow T. S., and Murozumi M. (1970) The possibility of measuring variations in the intensity of world wide lead smelting during medieval and ancient times using lead aerosol deposits in polar snow strata. In: Scientific Methods in Medieval Archaeology, R. Berger, ed.: 339-350, University of California Press, Berkeley.

Runnels H. K. (1969) Diffusion and relaxation phenomena in ice. In: Physics of Ice - Proceedings of the International Symposium on Physics of Ice, Munich, Germany, Sept. 9-14, 1968, N. Riehl, B. Bullemer, and H. Engelhardt, eds., Plenum Press, NY.

Schaule B. K. and Patterson C. C. (1981) Lead concentrations in the Northeast Pacific Ocean: evidence for global anthropogenic perturbations. Accepted for publication by Earth Planet. Sci. Lett.

Settle D. M. and Patterson C. C. (1980) Lead in albacore: guide to lead pollution in Americans. Science: 207, 1167-1176.

Settle D. M. and Patterson C. C. (1981) Magnitudes and sources of precipitation and dry deposition fluxes of industrial and natural leads to the North Pacific at Enewetak. Submitted to Earth Planet. Sci. Lett.

Settle D. M., Duce R. A., and Patterson C. C. (1981) Importance of transfer in the atmosphere of metal-rich sub-micrometer particles to large particles in determining magnitudes of dry deposition fluxes of metals. Presented at the IAMAP Third Scientific Assembly, Symposium on the Role of Oceans in Atmospheric Chemistry, Hamburg, Fed. Rep. Germany, August 1981.

Shirahata H., Elias R. W., Patterson C. C., and Koide M. (1980) Chronological variations in concentrations and isotopic compositions of anthropogenic atmospheric lead in sediments of a remote subalpine pond. Geochimica et Cosmochimica Acta: 44, 149-162.

Turekian K. K., Settle D. M., Patterson C. C., and Cochran J. K. (1981) Common lead precipitation fluxes from ^{210}Pb measurements in rain at tropical oceanic sites. Submitted to J. Geophys. Res.

Unni C. K. (1978) Analyses of Pigeon Key rain and dry deposition samples. SEAREX Newsletter: 1, No. 4, 13. Available from Graduate School of Oceanography, University of Rhode Island, Kingston, Rhode Island 02881.

Unruh D. M. and Tatsumoto M. (1976) Lead isotope composition and uranium, thorium, and lead concentrations in sediments and basalts from the Nazca Plate. Initial Reports of the Deep Sea Drilling Project, 34: 341-347.

Wilson A. T. and House D. A. (1965) Chemical composition of south polar snow. J. Geophys. Res., 70: 5515-5523.

Zoller W. H., Gladney E. S., and Duce R. A. (1974) Atmospheric concentrations and sources of trace metals at the South Pole. Science, 183: 198-200.

Table 1. Concentrations of lead and potassium measured in veneer samples from Greenland and Antarctic ice core sections.

Sample Identification	Radial Interval of Sample (cm)	% of Core Analyzed	Pb Conc. ng/kg	K Conc. µg/kg
Camp Century 2700 yrs bp	4.2 - 4.0	11	2.7 x 10^5	3.7 x 10^2
676 m depth	4.0 - 3.9	16	2.2 x 10^5	2.1 x 10^2
	3.9 - 3.7	10	1.7 x 10^4	3.4 x 10^1
Ultra-acid cleaned sheet, plastic dust shield, 2nd replacement of acid cleaned gloves, dilute acid soak of tools not used.	3.7 - 3.5	10	1.1 x 10^4	8.2
	3.5 - 3.3	11	1.1 x 10^3	3.7
	3.3 - 3.0	9	7.1 x 10^1	2.8
*Wash with $CHCl_3$, CH_3OH and 1% HNO_3 before analysing this sample.	3.0 - 2.7	8	1.3 x 10^1	6.0
	2.7 - 2.2	14	1.4 x 10^1	2.6
	*2.2 - 0	21	4.9	2.0
Camp Century 4500 yrs bp	4.3 - 3.9	21	3.1 x 10^6	6.0 x 10^2
874 m depth	3.8 - 3.6	8	1.4 x 10^3	3.0 x 10^1
Wash between intervals with $CHCl_3$, CH_3OH and 1% HNO_3, cracks developed, discard loose pieces.	3.3 - 3.1	10	5.7 x 10^1	9.5
	2.4 - 2.2	5	3.5 x 10^1	6.6
	2.1 - 0	19	4.2	1.8
Camp Century 5500 yrs bp	4.3 - 3.9	21	8.0 x 10^5	3.7 x 10^2
949 m depth	*3.9 - 3.5	15	9.5 x 10^3	3.0 x 10^1
*Wash with $CHCl_3$.	3.5 - 3.4	7	5.4 x 10^2	1.3 x 10^1
	3.4 - 3.0	13	1.6 x 10^1	5
**Wash with $CHCl_3$ and 1% HNO_3 before proceeding.	3.0 - 2.7	11	8.7	2.9
	2.7 - 2.2	12	5.3	2.6
	**2.2 - 0	21	1.6	1.7
Byrd Station 2010 yrs bp	5.9 - 5.6	11	3.2 x 10^4	8.9 x 10^1
342 m depth	*5.5 - 5.3	11	1.5 x 10^2	3.6
	5.3 - 5.1	8	9.3	1.2
Plastic dust shield, 2nd replacement of acid cleaned gloves, dilute acid soak of tools not used.	5.1 - 4.6	11	7.7	0.9
	4.6 - 4.4	8	8.8	0.8
	4.4 - 3.5	19	4.6	1.0
*Wash with $CHCl_3$, CH_3OH and 1% HNO_3 before proceeding.	*3.5 - 0	27	2.2	0.9
Byrd Station 1490 yrs bp	5.8 - 5.4	19	2.1 x 10^4	5.4 x 10^1
256 m depth	5.4 - 5.0	14	1.1 x 10^2	2.6
*Wash with $CHCl_3$ and 1% HNO_3 before proceeding.	5.0 - 4.6	14	5.7	1.1
	4.6 - 4.1	13	3.9	1.2
	4.1 - 3.4	14	3.7	1.0
	3.4 - 2.9	10	3.3	1.0
	*2.8 - 0	16	1.4	0.9

Table 2. Analyses of lead in samples dissolved in 1%HNO_3 compared with analyses of samples taken to dryness with HF and HNO_3.

Sample Identification	Lead Concentration ng/kg Dissolved in 1% HNO_3	Lead Concentration ng/kg Evap. to Dryness with HNO_3 + HF
Camp Century 2700 yrs bp fifth veneer	1.1×10^3	1.1×10^3
Camp Century 4500 yrs bp third veneer	5.7×10^1	5.9×10^1
Byrd Station 2010 yrs bp third veneer	9	10

Table 3. Pb/Si-dust ratios in precipitation compared to air at remote locations. (Units used in table are pg Pb/ng Si-dust which yields a crustal value for the Pb/Si-dust ratio of 0.01.)

	Air			Precipitation			
Location	Pb (pg/m^3)	Si-dust (ng/m^3)	Pb/Si-dust (R_A)	Pb (pg/g)	Si-dust (ng/g)	Pb/(Si-dust) (R_P)	R_P/R_A
South Pole & Byrd Station (Antarctica)	30(a)	10(a)	3	15(b)	2(b)	8 (snow)	3
Enewetak (wet season)	100(c)	60(c,d)	2	28(e)	7(c)	4 (rain)	2
Enewetak (dry season)	230(c)	2600(c,d)	0.09	110(e)	88(c)	1 (rain)	11
Pigeon Key (Florida)	590(c)	5700(f)	0.1	900(e)	290(f)	3 (rain)	30
Thompson Canyon (Yosemite High-Sierra)	15000(g)	14000(g)	1	5000(g)	600(g)	8 (snow)	8
						remote location mean	11
Los Angeles (California)	2000000(h)	20000(h)	100	10000(i)	70000(j)	0.1 (rain)	0.001
						typical urban location	0.001

(a) Maenhaut *et al.* (1979) blank corrections are very large and uncertain. (b) Murozumi *et al.* (1969). (c) Settle and Patterson (1981). (d) Similar values for times within 1 or 2 weeks were obtained by Duce *et al.* (1981). (e) Turekian *et al.* (1981). (f) Unni (1978). (g) Elias *et al.* (1981). (h) Mueller *et al.* (1972). (i) Patterson and Settle (1974). (j) Liljestrand and Morgan (1981) in this case lead and dust were determined in different rains.

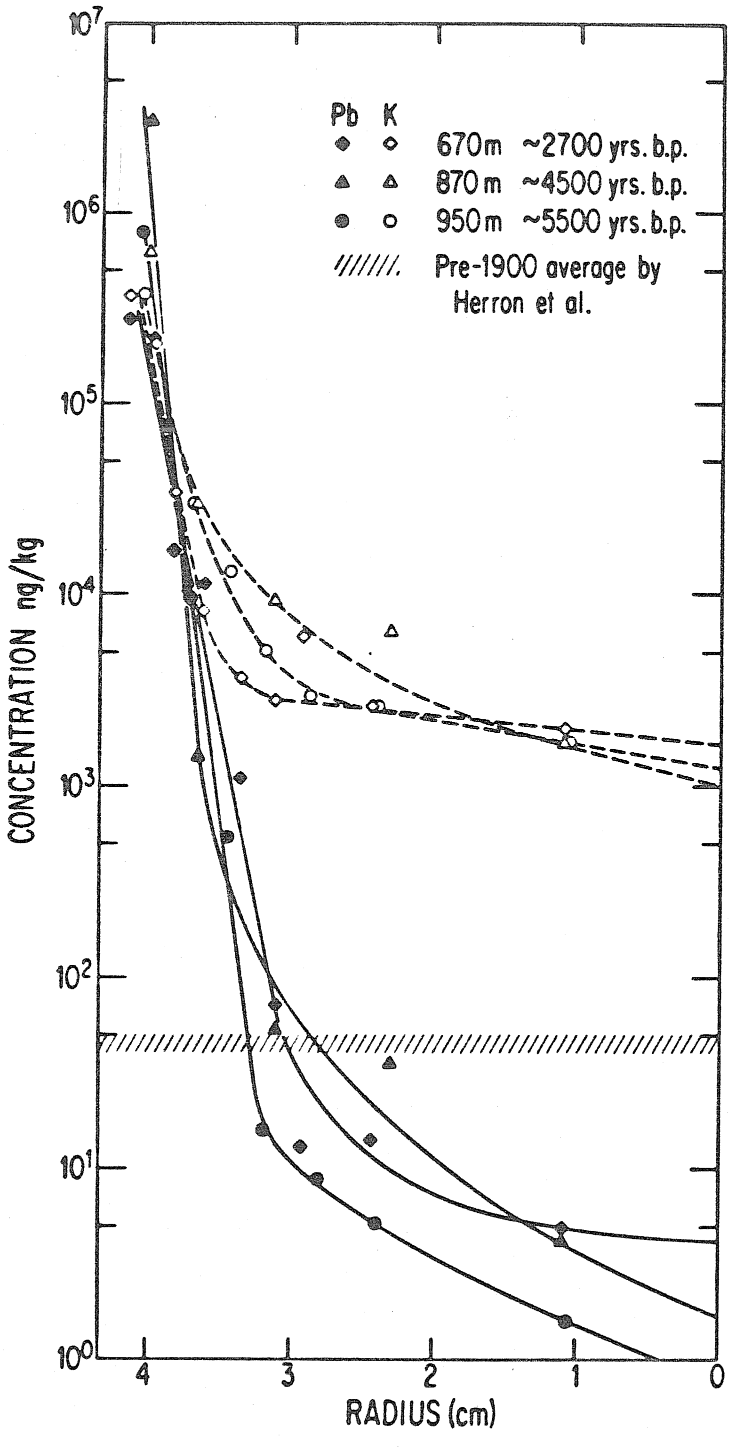

Figure 1. Pb and K concentrations as a function of radius in >3000 year old ice sections of a core obtained by electromechanical drilling in a fluid-filled hole at Camp Century, Greenland. The erroneous average lead concentration level reported by Herron *et al.* (1977) in ice of medieval age from less contaminated thermally drilled core sections in Greenland is indicated by the hashed zone. Contamination characteristics of the core sections studied by them are illustrated in Figure 2. The present day concentration level of lead in snow near Camp Century is about 200 ng/kg (Murozumi *et al.*, 1969).

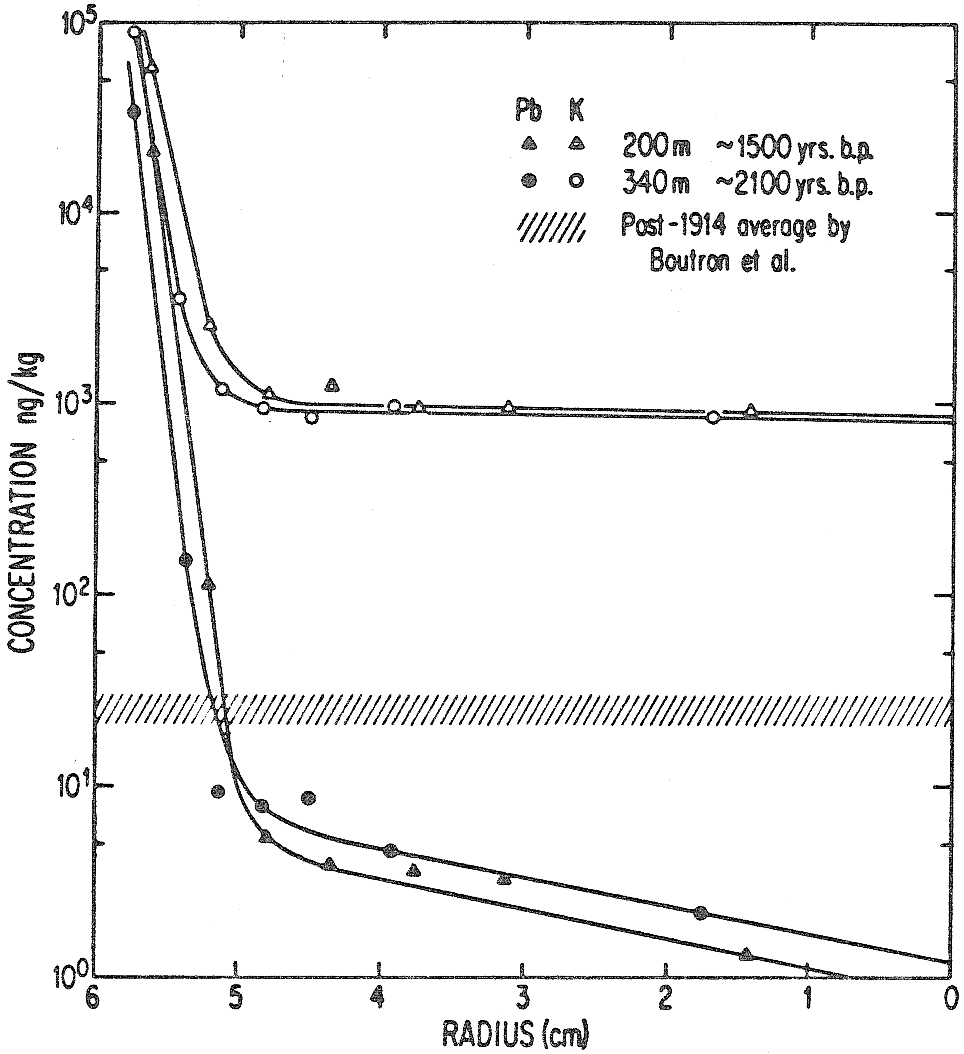

Figure 2. Pb and K concentrations as a function of radius in ~ 2 000 year old ice sections of a core obtained by thermal drilling in a non-fluid filled hole at Byrd Station, Antarctica. The erroneous average lead concentration level reported by Boutron (1979) in hand collected permeable firn in the age range of zero to 60 years from the Antarctic is indicated by the hashed zone. The contamination characteristics of the cylindrical samples collected and studied by them are not known. The present-day concentration level of lead in snow east of Byrd Station is about 15 ng/kg (Murozumi *et al.*, 1969).

PART II

CHRONOLOGICAL VARIATIONS IN LEAD AND BARIUM CONCENTRATIONS AND LEAD ISOTOPIC COMPOSITIONS IN SEDIMENTS OF FOUR SOUTHERN CALIFORNIA OFF-SHORE BASINS

1. INTRODUCTION

During the past century industrial lead emissions have overwhelmed natural reservoirs and perturbed natural geochemical cycling pathways. World lead production increased from about five tons per year 5000 years ago to about one million tons per year a century ago (Settle and Patterson, 1980). Today, about four million tons are produced annually world-wide (U.S. Bureau of Mines, 1976). The natural flux of soluble lead (excluding silicate mineral lead) to the world oceans may have been only a few tens of thousands of tons per year (Patterson, 1971). Lead pollution is world-wide as a result of the dispersal of industrial lead aerosols originating mainly from smelter fumes before the mid-1920's and from automobile exhaust fumes thereafter. A >200-fold increase of atmospheric lead pollution during the past 3000 years is recorded in Greenland ice strata (Murozumi et al. 1969, Ng and Patterson 1981). Surface mixed waters of oceans in the northern hemisphere contain about 10-fold more lead than they did in in prehistoric times (Schaule and Patterson, 1980, 1981). The estimated natural concentration of lead in air over land in prehistoric times is estimated to have been about 0.04 ng Pb/m^3 (Settle and Patterson, 1980). Today, lead in the atmosphere of regions remote from cities and towns is about 10 ng Pb/m^3 (Elias et al. 1977, Elias and Patterson 1980, Chow et al. 1972). Through the study of sedimentary record, a pollution history of lead can be reconstructed. The Los Angles-Southern California Bight system was chosen for our study.

The Southern California Bight includes the 30,000 km^2 of ocean extending from Point Conception to Cabo Colnett, and lying between the mainland shoreline and the eastern edge of the California Current. A larger area of the sea floor, the Southern California Continental Borderland, occupies 78,580 km^2. The bottom topography consists of thirteen closed basins, seven open troughs and associated highlands. The basins and troughs have general elongation trends approximately parallel to the topography of the adjacent land areas, and can be grouped into parallel belts progressing further seaward. Although the floors of these basins and troughs comprise only 17% of the borderland, they are the chief areas of sediment accumulation (Emery, 1960). Figure 1 is a location map of the Southern California Borderland.

Three inner basins, Santa Barbara, Santa Monica and San Pedro basins, are located 30 km offshore. San Pedro basin (33°34.9'N, 118°26.1'W 890 m deep, 700 km^2 floor area) is located southwest of Palos Verdes Peninsula. Santa Monica basin (33°45.5'N, 118°50'W 930 m deep, 2000 km^2 floor area) is located directly northwest of San Pedro basin off Point Dume. These two basins are connected above a sill depth of 740 m which controls both basins. Their floors have a gentle (0.3°) seaward slope. The Santa Barbara basin (34°15.9'N, 120°1.7'W 580 m deep, 1100 km^2 floor area) lies about 100 km northwest of Los Angeles, directly off Santa Barbara. This basin has a more or less symmetrical cross section. All three of the inner basins have sills at depths within the range of oxygen minimum in the open sea, and their waters have oxygen contents of only 0.2-0.3 ml/l in contrast to about 2.0 ml/l for waters in deeper outer basins, or about 6 ml/l in oxygen saturated surface seawater; consequently these basin floors are barren, with few living organisms, and bioturbation in the sediments is usually not evident.

The San Nicolas basin (33°1.1'N, 119°1.8'W 1800 m deep, 960 km^2 floor area) is located 125 km offshore, directly east of San Clemente Island and southeast of San Nicolas Island. Islands between the mainland and the basin protect it from direct sewage discharge. The basin sill is well below the oxygen minimum, so the oxygen content of the basin water is high enough to populate the basin floor with organisms which, through bioturbation, have biased ^{210}Pb dates for sediments within the basin.

The Southern California Counter Current, a near-coastal countercurrent swirl from the outer main southerly-flowing California Current, is the major current system operating within the Bight. It flows in a northwesterly direction along the coast throughout the year. The deep current below 100 m flows with a steady velocity of about 25 cm/sec, while the surface current, which is better developed in late summer and fall than in the spring, has an average velocity of 5-10 cm/sec (Jones, 1971).

Sediments reaching the borderland basins are derived ultimately from coastal ranges via storm runoffs, turbidity currents, river and eolian input. River input is of minor importance, since most Southern California streams are active only during and shortly after occasional rainstorms. Transport via turbidity currents is important for only the inner basins, while the outer basins are filled mainly by suspended particle transport. San Pedro and Santa Monica basins receive larger fluxes of turbidity current sediments than does Santa Barbara basin (Emery, 1960). Lead in basin sediments is incorporated in mineral lattices (leached residue fraction) or chelated in organic substances (acid soluble fraction).

Patterson et al. (1974) estimated the ancient natural lead flux into the Bight to be about 41 tons/yr, and that industrial lead amounting to about 680 tons/yr is delivered into the Bight through three major pathways: dry aerosol deposition on the water; storm runoff from roofed and paved areas; and sewage outfall. Atmospheric lead has been maintained at about 3000 ng Pb/m^3 throughout the 5000 km^2 area of the Los Angeles urban complex for more than a decade (Mueller et al. 1972, Patterson and Settle 1974). Huntzicker et al. (1975) estimated that about 6500 tons/yr of lead from gasoline exhausts and other industrial sources were injected as aerosols into the atmosphere of the Los Angeles urban basin on land during the late 1960's and early 1970's. The major fraction of this aerosol lead was locally deposited and retained in soil humus, but about 310 tons/yr was deposited in the Bight waters as dry deposition and precipitation. There are 200 to 300 surface runoff discharge locations along the Southern California coast, but about 70% of the average annual flow is carried by only fifteen major streams that are evenly spread along the coast. Storm runoff plus dry season flow from storm drains added approximately 170 tons of industrial lead/yr (Patterson et al. 1974, Burnett et al. 1980). Approximately 200 tons/yr of industrial lead were introduced into the Bight water via wastewater discharge. 84% of the waste discharge was delivered through three major sewage outfalls (Joint Water Pollution Control Plant, Santa Monica Bay; Hyperion Sewage Treatment Plant; and Orange County Sanitation District) located within about 30 km of Palos Verdes Peninsula (Young et al., 1973). About 80% of the sewage lead comes from industrial sources, so that although residential sources contribute a major portion of sewage solids, they contribute only a minor fraction of lead. Almost all of the sewage lead is in the solid phase of the effluent (Patterson _et al_., 1976). 89% of the lead is introduced to the Bight as particulates (Young _et al_., 1973). It is believed that a significant fraction of the industrial lead becomes solubilized. Studies show that 50% of the eolian input is converted to a soluble form of lead within a brief period (Hodge _et al_., 1978) and that 11% of the sewage (and storm runoff) particle lead is also solubilized within a day upon entry into saline waters (Patterson _et al_. 1976, Galloway 1979). Morel's (1975) model calculation predicts even a greater portion of sewage lead to have been solubilized by dilution and oxidation. Lead is also transported out of the immediate area of outfall as particles. Hendrick and Young (1974) estimated about 50% of the effluent particles is deposited within 8 km of the outfall, Galloway (1978) estimated only about 5% of the effluent metals is found in the adjacent sediment, Morel _et al_. (1975) calculated only 0.5% of the total wastewater particulates is deposited in the affected area. Variations among these calculations result from various assigned depositional rates in the area. The effluent particles would be spread northwestward by deep water currents, with deposition fluxes of these particles decreasing away from the outfalls. The Joint Water Pollution Control Plant outfall system of the Los Angeles Country Sanitation District, the largest of the municipal wastewater plants, discharges into the Bight off the Palos Verdes Peninsula, and this effluent enters the San Pedro basin. The effluent and sludge outfalls of the Hyperion Sewage Treatment Plant of the City of Los Angeles discharges into Santa Monica Bay and the Santa Monica basin. These outfalls are among the largest in the world.

A number of investigators have reported increased concentrations of lead in the upper sediment layers from lake and marine basins (Crecelius and Piper 1973, Crecelius 1975, Edgington and Robbins 1976, Förstner 1976, Goldberg et al. 1976, 1977, Hamilton and Clifton 1979, Murray and Ku 1977, Erlenkeuser et al. 1974, Helz 1976, Bertine et al. 1978, Nriagu et al. 1979). However, dating of sediments in many of these studies was not satisfactory, and lead analyses were usually performed on totally digested sediments, so that changes in concentrations of anthropogenic lead were obscured by lead contained in mineral lattices. Furthermore, some investigators believed it was possible that natural diagenetic processes could have produced the observed increases of lead concentrations near sediment surfaces.

Natural and anthropogenic components of lead in sediments can be distinguished by means of isotopic tracers because isotope ratios of natural lead are usually different from those of industrial lead. Chronological increases of lead concentrations in the sediments, when combined with chronological changes of isotopic ratios of lead, constitute a powerful tool for determining with assurance the magnitude of industrial lead pollution at any given time in sediments. Isotopic compositions of lead were determined in pioneering studies of Goldberg and associates (Chow et al. 1973, Bruland et al. 1974) and by Hamilton and Clifton (1979). In both of these studies, only a few isotopic determinations of lead were made, but these data indicated that the isotopic composition of the excess lead at the surface of the sediments not only was unlike that of natural lead in deeper layers, but was similar to that of industrial lead in the atmosphere. Our work extends and refines these earlier studies.

In our study, organically complexed lead was separated by dilute acid leaching from natural lead in silicate minerals in the sediments. Since industrial lead is confined to this leached phase, changes in its concentrations are more clearly perceived in this phase than in the total sediment, where it is diluted with natural mineral lead. Sediment layers, carefully collect and dated, going back several centuries, were sampled under ultra-clean conditions, the isotopic compositions of the various leads were determined, various possible mechanisms for the transport of soluble lead into sediments were considered, and particle interceptor traps were used to collected samples of sedimenting materials from the water column. Our analyses of these materials and interpretations of the data prove conclusively that the original view of Chow et al. (1973) regarding the industrial origin of the excess lead in these sediments is correct, and that natural diagenesis cannot account for the observed increases of lead concentrations near sediment surfaces.

2. METHODS

2.1 Sample Collection and Age Determination

A sediment core was collected by A. Soutar of Scripps Institute of Oceanography (Soutar, 1978) from each of the four basins by means of a minimum displacement box coring device in which the sediments are frozen in the field. Results from a single core probably represent the basin well, since horizontal water currents have effectively dispersed and homogenized sediment over the basin floor (Soutar and Crill, 1977). Frozen slabs of sediment 2 cm thick, 10 cm wide, and 25 to 35 cm deep from each of the four basins were delivered to the CIT laboratory, along with templates, obtained from x-ray radiography, depicting the internal stratigraphic structure and ages of layers within each slab. The slabs were kept frozen until they were subsampled. The Santa Barbara Basin core showed a succession of annual varves virtually unbroken back to 1850 with no signs of bioturbation. The Santa Monica Basin and San Pedro Basin cores had well defined layer structures with no major bioturbation in the Santa Monica Basin core, but some burrowing displacement (avoidable by selective sampling) in the older section of the San Pedro Basin core. The San Nicolas Basin core showed major burrowing activity througout. Ages at various depths within the cores and accumulation rates were determined by both annual varve stratigraphy and ^{210}Pb radiometric analysis (Bruland et al., 1978). Bias of age assignments due to bioturbation was disclosed, when present, by crosschecking ^{210}Pb ages with ^{228}Th ages. Sediment fluxes between ~ 1700 to 1979 were 92, 19, 30 mg/cm^2/yr for the Santa Barbara, Santa Monica and San Pedro basins, respectively. Since 1970, slightly higher deposition values of 96, 34, and 47 mg/cm^2/yr are calculated. Because of bioturbation in the San Nicolas Basin core, there are no reliable age estimates, and the accumulation rate ranges from 12 to 28 mg/cm^2/yr (Bruland et al., 1978).

Suspended sediment samples were also collected by A. Soutar et al. using particle interceptor traps (PIT). Particle trap units were deployed between September 5-6, and October 31, 1977 in each of the four basins, but only the units from Santa Barbara basin and Santa Monica basin were recovered. Sedimentation rates calculated for the inorganic PITS units, assuming 100% efficiency, were 72.6 mg/cm^{2}yr for Santa Barbara and 16.9 mg/cm^2/yr for Santa Monica (Soutar et al., 1979).

Sediment-trap particles contained slightly higher percentages of sand and lower percentages of total and organic carbon than in surface benthic sediments from the same area (Anderhalt and Reed, 1978). Clay-lithics dominate over the organically-derived particles (Soutar and Baxter, 1978), and the principal minerals were illite, feldspar, quartz and calcite (Crisp et al., 1979). Frozen portions of suspended sediment PITS samples from Santa Barbara and Santa Monica basins were delivered to CIT.

2.2 Subsampling

Subsampling was performed in a clean laboratory within a clean air bench, where barium and lead contamination was strictly controlled.

Sampling zones in dated sediment layers were first selected from templates which had been previously prepared from x-radiographs of the sediment slabs. Areas showing disturbances of layering caused by freezing displacement or burrowing animals or the presence of macro-organisms were avoided. Each sediment slab was kept frozen on a tray of dry ice during subsampling. The slab was worked from the oldest to youngest sections at periodic intervals, cleaning and removing only several samples at any one time from a small section at the oldest part of the slab, with the slab being re-frozen between intervals. Surface contamination was removed from a vertical 2-4 cm oldest section of the slab by chiseling away outside surfaces in three successive stages. Each section was left attached to the slab during cleaning and sample removal. A relatively thick outside layer was chiseled away first from the top, sides and end of the slab section to expose fresh surfaces, then two thin veneers approximately 1 mm thick were peeled away in succession. A sample was then removed in segments from this freshly exposed clean section of the slab with a chisel, leaving behind the lower 3 mm of the section resting against the dry ice tray untouched, which was not sampled to avoid contamination. It was removed when the next younger section was sampled. Layer contours defined the tops and bottoms of samples. These contours had been dated by annual varves or ^{210}Pb, and labeled on the template. Index points were transferred from the template to the cleaned slab by measurements, using a cleaned plastic rule to place them with a sharp, clean stainless steel tool on the cleaned slab. A small stainless steel chisel and hammer and a sharp spatula were used to peel away discarded material and to collect sample material. The chisel and spatula were used in such a manner that the side facing the discarded material never contacted the freshly exposed sample surface, and that the side of the tool near the clean surface never touched discarded cuttings. Usually the chisel and spatula were rinsed with dilute HNO_3 and then with ultra-pure water after each insertion into the sediment slab followed by removal of material, which entailed numerous, repetitive cleanings.

An acid cleaned rectangular shallow plastic tray containing crushed dry ice was covered with an acid cleaned polyethylene sheet 3 mm thick, and this was placed within a clean air bench. The frozen slab was placed directly on the sheet and blocked against the edge of the tray. Two operators worked together, each wearing clean polyethylene gloves that were discarded for fresh ones at appropriate times. One operator worked with the chisel and spatula, discarding material and collecting samples, while the other operator transferred measurements from the template, cleaned the tools, took away the cuttings, and held the sample vials.

Collected samples were transferred to polyethylene vials, weighed and frozen. Frozen samples were vacuum dried for) 48 hours to constant weight. PITS sediment samples were thawed, excess liquid decanted, and the residues were freeze dried. Aliquots of dried samples were taken for barium and lead analysis.

2.3 Analytical Procedures

All analytical steps were performed in a clean laboratory where industrial lead and barium artifact contamination is controlled and at a minimum. Elaborate cleaning procedures were used on containers and labware, which reduced contamination to a minimum and permitted quantitative evaluation of contributions by that contamination to the samples. Only high purity quartz, FEP-teflon lab-ware were used for dissolution and chemical separation (Patterson and Settle, 1976).

2.3.1 TOTAL DISSOLUTION. Approximately 100 mg of sample was used for each analysis. For concentration measurements, ^{208}Pb and ^{136}Ba spikes were added. No isotope spike was used when lead was isolated for isotopic composition determinations. 1 ml HNO_3, 1 ml $HClO_4$, and 1 ml HF were added to digest both silicate and organic fractions, and the covered beaker was allowed to stand overnight (10-12 hours). The mixture was then heated uncovered at 55°C for two hours in a nitrogen flushed teflon oven, evaporated to dryness at 80°C, and then baked at 150°C until $HClO_4$ fuming stopped. The residue was converted to chlorides by evaporating to dryness twice with 1 ml HCl and let stand covered overnight with another 1 ml HCl. The solution was taken to dryness and residue redissolved in 5 ml 6N HCl. A 0.3 ml aliquot was removed, dried, and converted back to nitrates by being taking to dryness twice with 0.1 ml HNO_3. The residue was analyzed in the mass spectrometer for barium without further chemical treatment. The other aliquot was dried and ready for chemical separation of lead as described below.

2.3.2 LEACHING PROCEDURE FOR LEAD. Dilute acid was used to leach lead sorbed on clay particle surfaces or in organic debris without removing lead in igneous or clay mineral lattices. Dilute acids are the most effective leaching agents (Loring 1976, Luoma and Bryan 1978, Agemian and Chau 1977, Malo 1977, Chester et al. 1976, Gupta and Chen 1975), and it was found that 1 N hydrochloric acid removed more lead from oxidized sediments than other acids (Luoma and Bryan, 1981). Other investigators have ignited sediments and then leached them with cold 1 N HNO_3. Experiments on pond sediments (Shirahata et al., 1980) showed that a 12 hour leach with cold dilute acid achieved the same result as a 10 minute leach with dilute acid after ignition at 450°C. In this study we used a 10 hour cold leach with 1 N HNO_3 which entailed less contamination and loss of sample. Aliquots of one dried sediment (SB 1969) were leached with different strengths of acids and the concentrations, and isotopic compositions of lead in the leachates and in the solid residues were measured. Results in Table 1 show that acid concentrations greater than 1 N all release about equal quantities of sorbed lead. The constancy of the isotopic composition of the leached leads indicates that it was released from only one type of reservoir.

10 ml 1N HNO_3 was added to 150 mg of dry sample in an FEP beaker and allowed to stand covered for 10 hours, with periodic swirling. The solution was then pipetted into a quartz centrifuge tube sealed with acid cleaned polyethylene film and centrifuged. A weighed aliquot of this supernate ($\simeq$ 25% was transferred to another FEP beaker containing a weighed amount of ^{208}Pb spike, the mixture was dried and used for concentration measurements. The remaining supernate, used for lead isotopic composition analysis, was dried in a second FEP beaker. Residues for both lead concentration and lead isotopic composition were subsequently treated identically prior to chemical separation. 0.1 ml HNO_3 and 0.03 ml

$HClO_4$ was added to each beaker, and taken to dryness. 5 ml 6 N HCl was added to each residue, dried, and subjected to chemical separation described later.

2.3.3 PREPARATION OF LEACHED RESIDUE FOR LEAD ISOTOPIC COMPOSITION DETERMINATIONS. Some sediment residues remaining in the beaker after leaching were analyzed for lead concentrations and lead isotopic composition. The excess liquid was pipetted away and the residue was transferred to a quartz centrifuge tube and rinsed twice with ultra-pure water. The residue was then transferred back to a clean FEP beaker with a 10 ml QDW. The excess liquid was removed with a pipette, and the residue was dissolved as described above in the TOTAL DISSOLUTION section.

2.3.4 CHEMICAL SEPARATION. Each lead aliquot was dissolved in 5 ml 1 N HCl and put through 5 ml of purified 100-200 mesh Dowex AG-1-X8 ion exchange resin pretreated with two 10 ml portions of 6 N HCl, and three 5 ml portions of 1 N HCl. The column was washed with two 5 ml portions of 1 N HCl and the lead was eluted into a FEP beaker with 15 ml 6 N HCl. The eluate was evaporated to dryness, dissolved in 1 ml 25% purified ammonium citrate and transferred with 10 ml QDW to a FEP separatory funnel. The pH was adjusted to 8-9 with purified ammonium hydroxide, 2 ml 1% purified potassium cyanide were added, and lead was extracted into 10 ml of purified dithizone-chloroform solution. This chloroform solution was washed with 20 ml QDW containing 0.03 ml NH_4OH and the lead was then back extracted into 5 ml QDW containing 0.3 ml HNO_3. This aqueous solution was washed with 5 ml chloroform, and then evaporated to dryness. The residue was used for mass spectrometry. The yield of each step was checked intermittently by adding ^{206}Pb tracer right after the appropriate step.

2.3.5 MASS SPECTROMETRY. Samples were analyzed by thermal ionization isotope dilution mass spectrometry using clean laboratory methods. It is an absolute method because it incorporates an internal standard (^{208}Pb tracer [99.74% ^{208}Pb] to measure lead concentrations and ^{136}Ba tracer [95.3% ^{136}Ba] for measurement of barium concentrations), and uses no working curves for comparative purposes. A single measurement is sufficient for each determination.

Both lead and barium were analyzed using a 12" radius, single focusing, solid source, thermal ionization mass spectrometer. The lead aliquot was loaded onto an outgassed rhenium filament using the silica gel method (Patterson and Settle, 1976). The $^{208}Pb/^{207}Pb$ ratio was measured to determine the lead concentration and $^{207}Pb/^{206}Pb$ was used to determine chemical yield. Any decrease in the $^{208}Pb/^{207}Pb$ ratio from 1750 in the ^{208}Pb tracer is caused by the addition of ^{207}Pb from the sample and blanks of common lead whose $^{208}Pb/^{207}Pb$ ratio is 2.3. In a similar way, the deviation of the $^{208}Pb/^{206}Pb$ ratio from that expected from known additions of ^{206}Pb tracers is used to determine the chemical yield.

The aliquot for barium analysis was dissolved in a drop of QDW, and 1 microliter of the solution was transferred to an oxidized tantalum filament. Barium was determined from the $^{138}Ba/^{136}Ba$ ratio, and the increase of the ratio from 0.0492 in the ^{136}Ba tracer is caused by the presence of common barium whose 138/136 ratio is 9.175.

Since the tracer and sample weights and the ratio of tracer to sample metal isotopes are all measured reliably to 0.1%, low lead concentrations can be determined with great accuracy, providing blanks have been properly measured and isotopic equilibration has been achieved. This analytical technique, although somewhat time-consuming and expensive, provides reliable metal concentrations at levels that are a hundred to a thousand times below the useful analytical limits of commonly used techniques, as shown by interlaboratory comparison studies (Lead in Seawater Workshop, 1974).

2.3.6 BLANKS, YIELDS, AND ERRORS. Both blanks and yields for successive analytical steps were determined so that reliable corrections for contamination could be made. Overall lead blanks amounted to about 3 ng per analysis. Resin column yields were about 70%, while extraction yields were about 95% (determined by double spiking with ^{206}Pb). The barium blank was about 1 ng per analysis. Blanks were insignificant relative to quantities of sample lead and barium, but they were accounted for in the case of barium as follows:

$$(\mathrm{Ba})_{\mathrm{total}} = \left[(\mathrm{Ba})_{\mathrm{sample}} + (\mathrm{Ba})\begin{matrix}{}^{136}\mathrm{Ba}\\ \mathrm{tracer}\\ \mathrm{blank}\end{matrix} + (\mathrm{Ba})\begin{matrix}\mathrm{dissolution}\\ \mathrm{blank}\end{matrix}\right] \times \begin{pmatrix}\mathrm{sample}\\ \mathrm{fraction}\end{pmatrix} + (\mathrm{Ba})\begin{matrix}\mathrm{mass\ spec.}\\ \mathrm{loading}\\ \mathrm{blank}\end{matrix}$$

The expression for lead is as follows:

$$
\begin{aligned}
(\mathrm{Pb})_{\mathrm{total}} = \Bigg[\Bigg\{ \Big[(\mathrm{Pb})_{\mathrm{sample}} + (\mathrm{Pb})^{\substack{{}^{208}\mathrm{Pb} \\ \mathrm{tracer}}}_{\mathrm{blank}} + (\mathrm{Pb})^{\mathrm{dissolution}}_{\mathrm{blank}} \Big] \\
\times \begin{pmatrix} \text{sample} \\ \text{fraction} \end{pmatrix} + (\mathrm{Pb})^{\mathrm{column}}_{\mathrm{blank}} \Bigg\} \times \begin{pmatrix} \text{column} \\ \text{yield} \end{pmatrix} + (\mathrm{Pb})^{\substack{\mathrm{solvent} \\ \mathrm{extraction}}}_{\mathrm{blank}} \Bigg] \\
\times \begin{pmatrix} \text{solvent} \\ \text{extraction} \\ \text{yield} \end{pmatrix} + (\mathrm{Pb})^{\substack{{}^{206}\mathrm{Pb} \\ \mathrm{tracer}}}_{\mathrm{blank}} + (\mathrm{Pb})^{\substack{\text{mass spec.} \\ \text{loading}}}_{\mathrm{blank}}
\end{aligned}
$$

Some blanks listed singly above were actually sums of individually and separately evaluated contributions of lead contamination from a number of different sources involved in that particular step of the analysis.

Errors associated with isotope ratio measurements were 1 to 3 parts per thousand, being least for $^{206}\mathrm{Pb}/^{207}\mathrm{Pb}$ and largest for $^{206}\mathrm{Pb}/^{204}\mathrm{Pb}$. However, errors originating from other factors such as incomplete isotopic equilibration, weighing, and improper contamination control are the main determinants for overall error, which may vary among different analyses. The absolute error, estimated from experience over the years, is probably about ±5% for lead and barium concentrations.

2.3.7 SEA SALT CORRECTION. Sea salts were not removed by rinsing because some evidence indicated that portions of bound lead may be released into solution because of the sudden change in ionic strength of the rinse (Patterson _et al._, 1976). All dried sediment weights were reduced by an amount of sea salt in them, calculated from the water lost during drying, assuming it was normal sea water.

The contribution of lead and barium from the seasalt is negligible, so it is not corrected. The concentrations of both lead and barium sediment are expressed in ppm units on a salt-free dry weight basis.

3. RESULTS

Lead and barium concentrations and lead isotopic compositions are listed in Table 2 for total sediments, leached sediments and leachates, together with corresponding sediment depths and ages, from San Nicolas, Santa Barbara, Santa Monica, and San Pedro basins. Sediments in San Nicolas basin contain anomalous ^{210}Pb activities (Bruland et al., 1978) due to bioturbation, and data only for sediment layers down to 95 mm depths with no asigned ages are reported in Table 2 for this basin.

Concentrations of lead in the leached residues are rather similar and constant in all basins, while leached lead concentrations increase near sediment surfaces of all basins. It is supposed that there is a natural component in the leached leads whose concentrations are relatively constant and whose magnitudes are indicated by concentrations of lead leached from the oldest non-polluted sediment layers in each basin. When these concentrations are converted to deposition fluxes of natural leached lead (listed in Table 4) the largest is found in the Santa Barbara basin, and the smallest is found in the Santa Monica basin.

Concentrations of leachable industrial lead in sediment layers, obtained after subtracting the natural leachable component from total amounts leached, increase in sediments of all three basins after 1900, as shown in Figure 2. Concentration values are given in Table 3 (values for San Nicolas basin cannot be computed since ages are unknown). Concentrations of this anthropogenic lead component are highest in uppermost layers of sediments in the San Pedro basin and lowest in the

Santa Barbara basin. When these data are recomputed into deposition fluxes of leached industrial lead (listed in Table 4), the greatest is found in the San Pedro basin, and the smallest is found in the Santa Monica basin.

Even though the anthropogenic component in leached lead cannot be computed for sediments from the San Nicolas basin, lead concentrations in Table 2 show an increase with time despite extensive dilution with older sedimentary material through bioturbation. The apparent deposition flux of leachable anthropogenic lead in the San Nicolas basin, estimated from lead concentrations in top sediment layers and an apparent ^{210}Pb derived sediment accumulation rate, is comparable to that for the Santa Monica Basin. It should be recognized, therefore, that lead contamination effects from industrial sources in the Los Angeles urban basin on land extend seaward well beyond the inner basins.

Concentrations and isotopic compositions of leads in leached sediment mineral residues from old layers (pre 1910) are similar among all three basins, ranging mostly from about 5 to 6 ppm dw, and showing $^{206}Pb/^{207}Pb$ ratios of 1.209 to 1.212. In younger layers the variation in this ratio is somewhat larger, ranging systematically on a geographic basis from a mean of 1.200 in the eastern San Pedro basin, to 1.204 in the Santa Monica basin, to 1.210 in the western Santa Barbara basin.

Although the concentration of natural leached lead is about the same in old sediments in the three basins, 6 to 8 ppm dw, the $^{206}Pb/^{207}Pb$ ratios are significantly different, ranging systematically on a geographic basis from 1.206 in the San Pedro basin to 1.212 in Santa Monica basin, to 1.216 in the Santa Barbara basin. The geographic pattern of $^{206}Pb/^{207}Pb$

ratios in sediments among the three basins is therefore clear, becoming distinctly more radiogenic in going from east to west, with lead in the leached lead fraction being more radiogenic than lead in the mineral fraction in every instance.

In order to use the isotopic composition of the supposed industrial component in the leached lead as a tracer to identify sources of this lead, it is necessary to compute it from the observed isotopic composition of the total amount of leached lead, because the latter is a mixture of a natural component with the industrial component. To simplify the computation, it is assumed that the isotopic composition of the natural component in each basin is constant throughout all layers. The amount of natural lead component leached per gram of sediment must be assumed, and it was estimated for each basin from a mean of values obtained for sediment layers older than 1910. Values of the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the industrial component, were approximated as follows,

$$[6/7]_{\text{Industrial}} = \frac{[6/7]_{\text{total}} \;]\; [\text{ppm Pb}]_{\text{total}} - [6/7]_{\text{natural}} \;]\; [\text{ppm Pb}]_{\text{natural}}}{[\text{ppm Pb}]_{\text{Industrial}}}$$

are sensitive to assumed values chosen for the concentrations of the natural lead component in the leached leads, which may vary. To get an estimate of the change in $^{206}\text{Pb}/^{207}\text{Pb}$ values calculated for industrial lead caused by this factor, we calculated two values for this ratio in lead leached from each sediment layer younger than 1910, using a high and a low mean concentration for the natural lead component for each basin. High means were obtained by excluding a lowest value in each case, while low means were obtained by excluding a highest value. In most instances ranges in values for $^{206}Pb/^{207}Pb$ ratios calculated from these two different parameters are relatively small in each of the basins, as shown in Table 3. In those few cases when measured concentrations of lead in residues from acid leached young layers were considerably smaller than from pre 1910 layers, it was believed that the above assumptions no longer applied, so concentrations of the natural lead components in leachates from these residues were estimated on a different basis. It was assumed that in these instances greater than usual amounts of natural lead could have been leached from minerals. Upper limit concentrations of the natural lead components, C_n^{upper}, were calculated as K_n^{max} + $(X_n^{residue} - X_m^{residue})$, where K_n^{max} was the high mean concentration of the natural component, $X_n^{residue}$ was the concentration of lead in the natural residue, and $X_m^{residue}$ was the concentration of lead in the residue of that year. On the other hand, lower limit concentrations, C_n^{lower} were calculated as $(F_n^{leach}/F_n^{residue})\ X_m^{residue}$, where F_n^{leach} and and $F_n^{residue}$ were mean fractions of total natural lead in pre-1910 sediment layers that were leached and left in residues respectively. Two values for the $^{206}Pb/^{207}Pb$ ratio were calculated on this basis from these two greatly different values for the concentration of the natural component of leached lead for each sediment layer, where the lead concentration in the leached residue was unusually low. In this case the range in calculated values for $^{206}Pb/^{207}Pb$ ratios was still small when the component of industrial lead was large compared to the natural component, but when these components were more equal, then great changes in the concentration of natural leached lead produced corresponding large changes in the calculated $^{206}Pb/^{207}Pb$ ratio for the industrial component. As shown in Table 3, this latter effect was significant only in the older and lower parts of the anthropogenically perturbed stratigraphic sections of the basin sediments, so that in the recent upper parts of the sediment section the calculated $^{206}Pb/^{207}Pb$ ratio of the industrial components of the leached leads are known to within about ± 0.25% of actual values.

The major features of these data (shown in Figures 3 and 4) are: (1) $^{206}Pb/^{207}Pb$ ratios in the excess leached industrial lead component in sediments from all three basins are nearly the same at any given time between 1963 and 1977, varying from about 1.160 ± .010 at the beginning to about 1.182 ± .005 at the end of this period; (2) these ratios are quite distinct from those of about 1.212 ± .005 in leached natural leads; and (3) the change in the leached industrial lead $^{206}Pb/^{207}Pb$ ratios with time follows the trend of the change of atmospheric industrial lead $^{206}Pb/^{207}Pb$ ratios (Chow et al. 1975, Elias et al. 1981) measured during this same period in southern California.

Total barium concentrations of the basin sediments listed in Table 2 show highest concentrations in the San Pedro basin and lowest in the Santa Barbara basin, but when these are converted to deposition fluxes, Santa Barbara basin has the highest flux and Santa Monica basin the lowest (Table 4). There is a large maximum in barium concentrations in San Pedro basin sediments during the mid 1960's, which shows on a reduced scale in the Santa Monica, but not in the Santa Barbara basin. On the other hand, barium concentrations increase steadily in the Santa Barbara basin after 1965.

Total organic carbon, carbonate, and barium concentrations, and lead concentrations and isotopic compositions in leached residues and leachates of particle interceptor collected samples from the Santa Barbara and Santa Monica basin waters are listed in Table 5. Also tabulated in Table 5 are mass deposition fluxes calculated from these data compared to mass deposition fluxes calculated directly from ^{210}Pb chronometries in stratigraphic columns for each basin. PIT mass deposition fluxes are less than sediment mass deposition fluxes.

4. DISCUSSION

4.1 Deposition Mechanisms for Natural Soluble Lead

Dilute acid leaching procedures will, for the most part, solublize biogenic and inorganically sorbed lead contained in biological debris and ferro-manganese films, and will leave behind in the leached residue most of the lead contained within clay lattices and igneous minerals. Lead leached from basin sediments originates from soluble lead in overlying waters. The mechanism by which soluble lead was transported to the sediments is disclosed by looking at differences between various kinds of sediment deposition fluxes among the three basins.

Burnett *et al*. (1980) and Burnett and Patterson (1980) have shown that the primary route for the entry of soluble lead in sea water to the marine biomass probably occurs by sorption through passive chelation on the surfaces of primary producers. Primary consumers then transform some of this material into fecal pellets and degraded organism particles. This process is crucial to the interpretive model that follows. In shelf waters where biological productivity is excessive, large amounts of ultra-fine organic debris may be formed directly from decomposition of primary producers and primary consumers, and this material containing lead originally soluble but sorbed by living plants from sea water, may then become attached to settling clay particles which probably act as mechanical substrates that carry attached organic colloids and or ferro-manganese oxide films containing lead down to the sediments (Krauskopf 1956, Craig 1974, Jenne 1968, 1977). In Table 4 various kinds of deposition fluxes are compared among the three basins. The first two lines show that large differences in sediment mass fluxes among these basins are faithfully adhered to on a relative basis by corresponding deposition fluxes of natural soluble lead. It would appear that this type of mechanism might account for most of the deposition flux of natural organic in these basin sediments. In contrast, if deposition fluxes of organic lead by direct sedimentation of organic debris independent of clay transport were the dominant mechanism, fluxes would be expected to be uniform among the three basins, since biological productivity is relatively uniform among the waters of all three basins. Instead, it has been found (Crisp et al., 1979) that the deposition flux of organic carbon parallels both the sediment mass flux and the leachable lead deposition flux, which suggests that most of the organic debris containing lead may indeed be sedimented by settling clay particles.

The relative importance of the above mechanism of clay-sorption of organic films followed by settling depends on the relative abundances and reactivities of the other transporting substrates, distribution coefficients and depositional environments. In some sedimentary environments, hydrated iron and magnangese oxide films may also provide important transporting substrates for lead. Extraction experiments by Malo (1977) suggest that occurrences of trace metals in sediments are more closely approximated by the sequestering of trace metals by iron and manganese oxides than by silica or alumina. Luoma and Bryan (1978) have shown that the biological availability of lead in sediments is controlled mainly by level of readily extractable iron. Another of their studies (Luoma and Bryan, 1981) showed that concentrations of lead in oxidized sediments correlated strongly with concentrations of amorphous iron and manganese. Correlations of lead with amorphous iron were generally stronger than correlations of lead with amorphous manganese. Lead is sequestered by organic material to a major extent in sediments only when they are deficient in hydrous iron and manganese oxides. Gupta and Chen (1975) worked with San Pedro Bay sediments and found that 76% of the leachable lead is associated with leachable hydrogenous iron, although the percentage of leachable lead associated with sulfide and organic material increased with increasing sulfide content. Other studies (Pickering *et al*. 1966, Gibbs 1973, 1977) have shown that iron precipitates as coatings on clay surfaces. Follett (1965) demonstrated experimentally that colloidal iron hydroxides are readily sorbed on clay mineral surfaces, and Berg (1960) showed that the amount of iron sequestered as a coating on clay particles was related to the surface area rather than the cation exchange capacity of the clay. The heavy metal absorption capability was also related to the surface area rather than the cation exchange capability (Tiller *et al*., 1963). Anderson and Jenne (1970) found that iron oxides in clays existed both as separate particles and as films on clay particles, and that most trace metals were sorbed on the easily dissolved iron oxide films rather than being contained in the more difficultly dissolved iron oxide particles. It seems likely that the lead sorption by iron-manganese oxide films on clays followed by settling mechanism might account for a significant portion of the depositional flux of leachable lead in these basins. Our data suggest that lead-containing organic detritus or iron oxide films attached to clay particles operate to provide deposition fluxes of dilute acid leachable lead to basin sediments, and that this lead originally existed as soluble lead or stable colloidal dispersion in sea water.

Concentrations of lead leached from ancient layers of these basin sediments are approximately the same as lead concentrations in the leached sediment residues, so the magnitudes of the deposition fluxes of these two kinds of lead in the basins were about the same in ancient times. This situation cannot have prevailed throughout all areas of the continental shelves and trenches because there is no known fluvial source for such an excessive flux of soluble lead on a world-wide scale, so it must be more or less unique to the basins.

4.2 Historic Increase in Leachable Lead Deposition Flux

Concentrations of leachable lead increase sharply in sediments deposited after 1910 in all three basins, as shown in Figure 2. Excesses of leachable lead above natural amounts that can be leached from sediments younger than 1910 will be shown in the next section to be industrial by means of isotopic tracers, and deposition fluxes of this industrial lead are different among the basins. If all industrial lead introduced to Southern California Bight waters were soluble, the clay transport mechanism discussed in the previous section should operate to produce relative differences in deposition fluxes of industrial lead similar to those for natural lead during ancient times. The fourth line in Table 4 shows that this did not happen. The present deposition flux of leachable industrial lead in the San Pedro basin is 10% greater than that in the Santa Barbara basin, although the natural deposition flux of leachable lead used to be 73% less during ancient times. For the Santa Monica basin, the present flux is only 38% less than that in the Santa Barbara basin while it was 80% less in ancient times. It is clear that some leachable industrial lead comes from sewage or soil particles large enough to settle directly in areas adjacent to sewage outfalls. Lead concentrations in organic industrial sewage particles range from 500 to 1200 ppm dry wt (Patterson et al., 1976). The largest industrial wastewater treatment plant and sewage outfall in Los Angeles County was installed in 1950, and it discharges into the San Pedro basin, causing the greatest rate of deposition of sewage particles to occur there. This agrees with observations showing higher total organic carbon in San Pedro basin sediments compared to Santa Barbara basin sediments (Anderhalt and Reed 1978, Bruland et al. 1974).

Assuming that most of the industrial lead in the Santa Barbara basin is deposited by the clay transport mechanism, the fraction of the total fluxes of industrial lead in the other two basins associated with clay transport can be estimated by normalization from flux ratios that prevailed during ancient times. On this basis all of the Santa Barbara, 1/3 of the Santa Monica, and 1/4 of the San Pedro basin industrial lead deposition fluxes originate from soluble lead sedimented by clay transport, while the rest originates from directly deposited large lead-rich sewage or soil particles. Total increases of leachable lead deposition fluxes in the three basins during the past 130 years due to industrial lead pollution and resulting from combined clay transport of soluble lead plus directly sedimented sewage particles are: Santa Barbara 3-fold; Santa Monica 8-fold, and San Pedro 10-fold.

4.3 Sources of Natural and Industrial Leads

The $^{206}Pb/^{207}Pb$ ratios of leached natural lead increase from 1.206 in the eastern San Pedro basin to 1.212 in the Santa Monica basin to 1.216 in the western Santa Barbara basin. These leads are distinctly more radiogenic than the mean of 1.196 found for $^{206}Pb/^{207}Pb$ ratios in pelagic sediments off the shelf of southern California (Chow and Patterson, 1962). These local radiogenic leads originate in part from local soils weathered from old (1.2 to 1.8 by) rocks outcropping in the transverse ranges north of Los Angeles and Santa Barbara (Silver, 1971). The east-west variation in radiogenic character of these leached basin sediment leads is due to differences in accessibility to Pre-Cambrian rock soils by major drainages along eastern to western sections of the shore, such as the Los Angeles and Santa Clara rivers. The abnormally high $^{206}Pb/^{207}Pb$ ratio of 1.217 in sediment lead from the Gulf of California which originated from very old rocks in the Colorado river drainage (Chow and Patterson, 1962) is an example of this effect. The geographic trend in isotopic compositions of leached natural lead exists, and in addition is congruent with that in the mineral residues of the basin sediments. This shows that the residence time of soluble lead in these basin waters is extremely short, and probably similar to that of sedimenting clay particles.

It has been argued that the increased concentrations of lead observed at the surfaces of lake and marine sediments may result from interstitial upward transport of lead within the sediments during diagenesis, and that they were not produced by increased inputs of anthropogenic lead in recent times (Fairhall, 1978). Other investigators have also suggested the mobility of manganese and iron (Turekian, 1977), and uranium (Aller and Cochran, 1976) within the sedimentary column. Goldberg (1977), however, suggested the diffusional movement of metals is not possible in anoxic sediments, but may take place in aerated ones. There is no similarity between the computed $^{206}Pb/^{207}Pb$ ratios of industrial lead, listed in Table 3 and plotted in Figures 3 and 4, and natural $^{206}Pb/^{207}Pb$ ratios in the sediments. This disproves a natural origin for the excess concentrations of lead found near the surfaces of the basin sediments. Changes with time in the isotopic composition of industrial lead in the sediments are indeterminate before the 1960's, but after that time it is clear that $^{206}Pb/^{207}Pb$ ratios in this type of lead increase with time uniformly in all three basins. The preservation of isotopic variations in this lead with depth shows that isotopic homogenization, which would have occurred during transfer in pore fluids, did not take place.

The increase in the values for $^{206}Pb/^{207}Pb$ ratios in industrial lead with time during the late 1960's and early 1970's is due to a shift in ore sources of U.S. lead during this period. Major sources of industrial lead used in the United States before 1960 were mines in Australia, Canada, Mexico and Peru, where the $^{206}Pb/^{207}Pb$ ratios in the ores are about 1.037, 1.064, 1.192 and 1.200 respectively. After that time production of lead from ore deposits in Missouri increased from 9% of the total primary lead used in the U.S. in 1962 to 27% of such lead in 1968, to 57% in 1971, and to 82% in 1976 (U.S. Bureau of Mines, 1962-1976). $^{206}Pb/^{207}Pb$ ratios in Missouri ore deposits range from 1.28 to 1.33 (Doe, 1970), so increasing use of this lead increased the values of $^{206}Pb/^{207}Pb$ ratios in U.S. industrial lead. Isotopic changes in urban atmospheric leads closely follow isotopic changes in stocks of industrial lead because they originate mainly from gasoline exhausts, and residence times of both industrial stocks of lead alkyls and lead in the atmosphere are short. As shown in Figure 3 and 4, the $^{206}Pb/^{207}Pb$ ratio of atmospheric lead in southern California increased from a low of about 1.145 in 1963 to a high of about 1.225 in 1978 (Chow *et al*. 1975, Shirahata *et al*. 1980) as a direct consequence of the increased use in the U.S. of lead from mines in Missouri. As mentioned earlier, a major portion of the industrial lead in Southern California Bight waters appears to have come, after 1960, from gasoline exhaust lead introduced via rain, dry deposition on water, and storm runoff from roofs and paved surfaces. $^{206}Pb/^{207}Pb$ ratios in this fraction of industrial lead in the basin sediments would therefore be expected to change rapidly with time in accordance with changes of $^{206}Pb/^{207}Pb$ ratios in urban atmospheric lead. However, industrial leads from sewage and soils, which are also present in the sediments, came from more long-lived lead reservoirs where changes of over-all $^{206}Pb/^{207}Pb$ ratios were more sluggish in response to annual isotopic changes in each new year's supply of industrial lead. As a result, the $^{206}Pb/^{207}Pb$ ratios of total industrial leads in successively younger basin sediment layers would be expected to follow the trend of, but lag quantitatively behind, changes in values of $^{206}Pb/^{207}Pb$ ratios with time in atmospheric industrial leads. This effect is observed in Figure 3 and 4.

4.4 Comparison of PIT with Sediment Data

The PIT samples were collected during late summer, which is the dry season, and a time when inputs of industrial lead to the basins via precipitation and storm runoff are minimal. Sewage lead dominates inputs during this season, and the difference between the PIT sample data and surface sediment data in the Santa Monica basin, shown in Table 5, conforms with this situation: the PIT mass flux, projected for a year, is less than that for the sediment surface because there is less clay associated with sewage in summer waters; the concentration of carbonate is less in the PIT sample; the $^{206}Pb/^{207}Pb$ ratio in the PIT sample is lower than in the surface sediment because it comes mainly from older industrial lead reservoirs in sewage; and lead and barium concentrations are higher in the PIT sample because they are more concentrated in sewage than in storm runoff solids. Except for an isotopic difference in lead, there is little difference between the PIT sample data and surface sediment data in the Santa Barbara basin, possibly because the impact by sewage is less for this basin.

4.5 Historic Increases of Barium

The annual production of barium is approximately the same as that for lead on a mass basis. About 80% of the barium produced is used in oil and gas well drilling muds. In the Santa Barbara Channel region, about 10% of the muds are lost during drilling operations, and there are periodic discharges of drilling wastes in the form of cuttings and muds into the ocean. At present, most industrial barium is introduced in solid forms which do not become widely dispersed. The increased use of barium in offshore drilling operations and as smoke depressants in diesel fuels may lead to increased barium pollution, and one aim of this study is to delineate the main features of the natural occurrences of barium in coastal sediments.

Relations of barium concentrations with time in the basin sediments are shown in Figure 5. The large peak in barium concentrations which occurs in the San Pedro basin sediments during the period 1963-1973 is probably due to the waxing and waning of an input from industrial sewage. It is doubtful that it originated from a climatic erosion event from proximal gypsum beds along the coast (which contain barite) because the concentration peak coincides with a concentration peak of industrial lead in the same sediment. This lead could not have originated from the gypsum bed because the isotopic compositions varies, and follow the atmosphic composition. Barium flux data also indicate a sewage origin for the barium concentration peak in the San Pedro sediment. As shown in Table 4, barium deposition fluxes among the three basins were proportional to mass depositional fluxes before 1950. The large barium deposition flux in the San Pedro basin after 1950 is about 5-fold greater than would be expected on a mass flux basis, which indicates an industrial sewage rather than an erosional source. The small maximum of barium concentrations in Santa Monica basin sediments in the 1960's may be associated with the larger sewage event in the San Pedro basin. It is doubtful that the increase of barium in the Santa Barbara basin in recent layers is due to increased input from sewage. Rather, it may reflect dispersal of barium-rich drilling muds from local drilling operations.

6. REFERENCES

Agemian H. and Chan A. S. Y. (1977) A study of different analytical extraction methods for non-detrital heavy metals in aquatic sediments. Arch. Environ. Contamination and Toxicology, 6: 69-81.

Aller R. C. and Cochran J. K. (1976) $^{234}Th/^{238}U$ disequilibrium in nearshore sediment: particle reworking and diagenetic time scales. Earth and Planetary Science Letters, 29: 37-50.

Anderhalt R. and Reed W. E. (1978) Sediment characterization and TOC analysis. In Annual Report to Bureau of Land Management, Southern California Outer Continental Shelf Benthic and Water Column Program Year 2, Vol. II, Report 15. NTIS, BLM contract to SAI, Contract No. AA550-CT6-40.

Anderson B. J. and Jenne E. A. (1970) Free-iron and -manganese oxide content of reference clays. Soil Science, 100: 163-169.

Berg W. A. (1960) A theory of an exchange behavior in iron oxide-kaolinite systems, Ph.D. Thesis, North Carolina State University, Raleigh.

Bertine K. K., Walawender J. J., and Koide M. (1978) Chronological strategies and metal fluxes in semi-arid lake sediments. Geochimica et Cosmochimica Acta, 42: 1559-1571.

Bruland K. W., Bertine K. K., Koide M., and Goldberg E. D. (1974) History of metal pollution in Southern California coastal zone. Environmental Science and Technology, 8: 425-432.

Bruland K. W., Franks R. P., Bellows J. D., and Soutar A. (1978) Age Dating of Box Cores. In Annual Report to Bureau of Land Management, Southern California Outer Continental Shelf Benthic and Water Column Program Year 2, Vol. II, Report 12. NTIS, BIM Contract to SAI, Contract No. AA550-CT6-40.

Burnett M., Ng A., Settle D., and Patterson C. C. (1980) Impact of man on coastal marine ecosystems. In: Lead in the Marine Environment, Proc. Int. Experts Discussion on lead: Occurrence, Fate, and Pollution in the Marine Environment, Rovinji, Yugoslavia, 1977, M. Branika and and Z. Konrad, eds., Pergamon Press, Oxford, England: 15-30.

Burnett M. W. and Patterson C. C. (1980) Perturbation of natural lead transport in nutrient calcium pathways of marine ecosystems by industrial lead. In: Isotope Marine Chemistry, E. D. Goldberg, Y. Horibe, and K. Saruhashi, eds., Uchida Rokakuho Publishing Co., Ltd., Japan: 413-438.

Chester R., Aston S. R., and Bruty D. (1976) The trace-element partition geochemistry in an ancient deep-sea sediment core from the Bermuda Rise. Marine Geology, 21: 249-292.

Chow T. J. and Patterson C. C. (1962) The occurrence and significance of lead isotopes in pelagic sediments. Geochimica et Cosmochimica Acta, 26: 263-308.

Chow T. J., Earl J. L., and Snyder C. B. (1972) Lead concentrations in air, White Mountains, California. Science, 178: 401-402.

Chow T. J., Bruland K. W., Bertine K. K., Soutar A., Koide M., and Goldberg E. D. (1973) Records in Southern California coastal sediments. Science, 181: 551-552.

Chow T. J., Snyder C. B., and Earl J.L. (1975) Isotopic ratios of lead as pollutant source indicator. United Nations FAO and International Atomic Energy Association Symposium, Vienna, Austria (IAEA-SM-191/4). Proceedings: pp. 95-108.

Craig H. (1974) A scavenging model for trace elements in the deep sea. Earth and Planetary Science Letters, 23: 149-159.

Crecelius E. A. and Piper D. Z. (1973) Particulate lead contamination recorded in sedimentary cores from Lake Washington. Environ. Sci. and Tech., 7: 1053-1055.

Crecelius E. A. (1975) The geochemical cycle of arsenic in Lake Washington and its relation to other elements. Limnol. Oceanogr., 20: 441-451.

Crisp P. T., Brenner S., Venkatesan M. I., Ruth E., and Kaplan I. R. (1979) Organic chemical characterization of sediment-trap particulates from San Nicolas, Santa Barbara, Santa Monica and San Pedro Basins, California. Geochimica et Cosmochimica Acta, 43: 1791-1801.

Doe B. R. (1970) Lead Isotopes: pp. 73. Springer-Verlag.

Edgington D. N. and Robbins J. A. (1976) Records of lead deposition in Lake Michigan sediments since 1800. Envir. Sci. Tech., 10: 266-274.

Elias R. W. and Patterson C. C. (1980) The toxicological implications of biogeochemical studies of atmospheric lead. In: Polluted Rain, T. Toribara, M. Miller, P. Morrow, eds., Plenum Publishing Co., Newton: 391-403.

Elias R. W., Hirao Y., and Patterson C. C. (1981) The input, output, and distribution of lead and six other metals among biomass reservoirs in Thompson Canyon, California. (To be submitted to Geochimica et Cosmochimica Acta.)

Elias R. W., Hirao Y., and Patterson C.C. (1978) The deposition of lead aerosols on plant surfaces in a remote, subalpine ecosystem. In: *Enrivonmental Chemistry and Cycling Processes*, D. C. Adriano and I. Lehr Brisbin, Jr., eds., DOE pub. no. CONF-260429: 691-699.

Emery K.O. (1960) *The Sea off Southern California: A Modern Habitat of Petroleum.* John Wiley & Sons, New York, N.Y: 366 pp.

Erlenkeuser H., Suess E., and Willkomm H. (1974) Industrialization effects of heavy metal and carbon isotope concentrations in recent Baltic Sea sediments. *Geochim. Cosmochim Acta*, **38**: 823-842.

Fairhall A. W. (1978) Heavy metal levels of past environments: can they be reconstructed. Monitoring and Assessment Research Center, London, (in press).

Follett E. A. C. (1965) The retention of amorphous, colloidal 'ferric hydroxide' by kaolinites. *Journal of Soil Science*, **16**, 1965: 334-341.

Förstner V. (1976) Lake sediments as indicators of heavy metal pollution. *Naturwissenschaften*, **63**: 465-470.

Galloway J. N. (1979) Alteration of trace metal geochemical cycles due to the marine discharge of wastewater. *Geochimica et Cosmochimica Acta*, **43**: 207-218.

Gibbs R. J. (1973) Mechanisms of trace metal transport in rivers. *Science*, **180**: 71-73.

Gibbs R. J. (1977) Transport phases of transition metals in the Amazon and Yukon Rivers. *Geological Society of America Bulletin*, **88**: 829-843.

Goldberg E. D., Hodge V., Koide M., and Griffin J. J. (1976) Metal pollution in Tokyo as recorded in sediments of the Palace Moat. *Geochemical Journal*, **10**: 165-174.

Goldberg E. D., Gamble E., Griffin J. J., and Koide M. (1977) Pollution history of Narragansett Bay as recorded in its sediments. *Estuarine and Coastal Marine Science*, **5**: 549-561.

Gupta S. K. and Chen K. P. (1975) Partitioning of trace metals in selective chemical fractions of nearshore sediments. *Environ. Letters*, **10**: 129.

Hamilton E. I. and Clifton R. J. (1979) Isotopic abundances of lead in estuarine sediments, Swansea Bay, Bristol Channel. *Estuarine and Coastal Marine Science*, **8**: 271-278.

Helz G. R. (1976) Trace element inventory for the northern Chesapeake Bay with emphasis on the influence of man. *Geochimica et Cosmochimica Acta*, **40**: 573-580.

Hendricks T. J. and Young D. R. (1974) Modeling the fates of metals in ocean-discharged wastewater. Technical Memorandum 208, Southern California Coastal Water Research Project, El Segundo, CA 94265.

Hirao Y., Elias R., and Patterson C. C. (1975) Impact of present levels of aerosol lead concentration on both natural ecosystems and humans. In: *Internationas Conference on Heavy Metals in the Environment*, Toronto, *2*: part 1,257-272

Hodge V., Johnson S. R., and Goldberg E. D. (1978) Influence of atmospherically transported aerosols on surface ocean water composition. *Geochemical Journal*, **12**: 7-20.

Huntzicker J. J., Friedlander S. K., and Davidson C. I. (1975) Material balance for automobile-emitted lead in Los Angeles Basin. *Environ. Sci. and Tech.*, **9**: 448-456.

Jenne E. A. (1968) Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. In: *Trace Inorganics in Water*, R. G. Gould, ed., American Chemical Society, Washington, D. C.: 337-387.

Jenne E. A. (1977) Trace elements sorption by sediments and soils--sites and processes. In: *Molybdenium in the Environment*, **2**, W. Chappell and K. Peterson, eds., M. Dekker, Inc., NY: 125-553.

Jones J. H. (1971) General circulation and water characteristics in the Southern California Bight. Southern California Coastal Water Research Project, TR 101: 37 pp.

Krauskopf K. B. (1956) Factors controlling the concentrations of thirteen rare metals in seawater. *Geochimica et Cosmochimica Acta*, **9**: 1-32B.

Loring W. H. (1976) The distribution and partitioning of zinc, copper and lead in the sediments of the Saguenay Fjord. *Canadian Journal of Earth Science* **13**: 960-971.

Luoma S. N. and Bryan G. W. (1978) Factors controlling the availability of sediment-bound lead to the estuarine bivalve *Scrobicularia plana*. *J. Mar. Biol. Ass. U.K.*, **58**: 793-802.

Luoma S. N. and Bryan G. W. (1981) Statistical assessments of the form of trace metals in oxidized sediments employing chemical extractants. *Science of the Total Environment*, **17**: 165-196.

Malo B. A. (1977) Partial extraction of metals from sediments. *Environ. Sci. and Tech.*, **1**: 277-282.

Morel F. M. M., Westall J. C., O'Melia C. R., and Morgan J. J. (1975) Fate of trace metals in Los Angeles County Wastewater Discharge. *Environ. Sci. and Tech.*, **9**: 756-761.

Mueller R. K., Cahill T. A., and Alcocer A. E. (1972) Chemical composition of Pasadena aerosol by particle size and time of day. In: *Aerosols and Atmospheric Chemistry*, G. Hidy, ed., Academic Press, New York.

Murozumi M., Chow T. J., and Patterson C.C. (1969) Chemical concentrations of pollutant lead aerosols, terrestrial dusts, and sea salts in Greenland and Antarctic snow strata. *Geochimica et Cosmochimica Acta*, **33**: 1247-2194.

Murray S.M. and Ku T.L. (1977) Recent deposition of lead off the coast of Southern California. In: *Chemistry of Marine Sediments*, T.F. Yen, ed., Ann Arbor Science Publisher, Inc.

Ng A. C. and Patterson C. C. (1981) Ancient Arctic ice does not contain large excess of natural lead. Accepted for publication by *Geochimica et Cosmochimica Acta*.

Nriagu J. O., Kemp A. L. W., Wong H. K. T., and Harper N. (1979) Sedimentary record of heavy metal pollution in Lake Erie. *Geochimica et Cosmochimica Acta*, **43**: 247-258.

Patterson C. C. (1971) Lead. In: *Impingement of Man on the Oceans*, P. W. Hood, ed., John Wiley and Sons, Inc., New York: 245-258.

Patterson C. C. and Settle D. (1974) Contribution of lead via aerosol impact to the Southern California Bight. *Journal de Recherches Atmosphériques*, juillet-decembre 1974. International Symposium on the Chemistry of Sea/Air Particulate Exchange Processes, Nice, France.

Patterson C. C. (1974) Lead in seawater workshop. Meeting report. *Science*, **183**: 553-554.

Patterson C. C. and Settle D. M. (1976) The reduction of orders of magnitude error in lead analyses of biological materials and natural waters by evaluating and controlling the extent and sources of industrial lead contamination introduced during sample collecting and analysis. In: *Accuracy in Trace Analysis: Sampling, Sample Handling, Analysis*, P. LaFleur, ed., NBS Special Publication 422, **1**: 321-351.

Patterson C. C., Settle W., Schaule B., and Burnett M. (1976) Standardization of reference samples for certain trace metals: the first step in a multistage program designed to insure the reliability and significance of baseline data for the trace metals. *Baseline Studies of Outer Continental Shelf, Southern California*, **3**, Report 44. Bureau of Land Management Contact #696-16.

Patterson C., Settle D., and Glover B. (1976) Analysis of lead in polluted coastal seawater. *Marine Chemistry* **4**: 305-319.

Pickering R. J., Carrigan P. H. Jr., Tamura T., Albee H. H., Berverage J. W., and Andrew R. W. Jr. (1966) Variation of oxidic iron and aluminum with clay silt content of core segments from the Clinch River, Tennessee. In: Disposal of Radioactive Wastes into Seas, Oceans, and Surface Waters, Proc. of a symposium, International Atomic Energy Agency, Vienna.

Schaule B. K. and Patterson C. C. (1980) The occurrence of lead in the Northeast Pacific and the effects of anthropogenic inputs. In: Lead in the Marine Environment, Proceedings of an International Experts Discussion on Lead: Occurence, Fate, and Pollution in the Marine Environment, Rovinji, Yugoslavia, 1977, M. Branica, ed., Pergamon Press, Oxford, England: 31-43.

Schaule B. K. and Patterson C. C. (1981) Lead concentrations in the Northeast Pacific Ocean: evidence for global antrhopogenic perturbations. Accepted for publication by Earth and Planetary Science Letters.

Settle D.M. and Patterson C.C. (1980) Lead in albacore: guide to lead pollution in Americans. Science 207: 1167-1176.

Shirahata H., Elias, R. W., Patterson C.C., and Koide K. (1980) Chronological variations in concentrations and isotopic compositions of anthropogenic atmospheric lead in sediments of a remote subalpine pond. Geochimica et Cosmochimica Acta 44: 149-162.

Silver L. T. (1971) Problems of crystalline rocks of the Transverse Ranges. Geological Society America Abstract of Programs, 3: 193-194.

Soutar A. and Crill P. A. (1977) Sedimentation and climatic patterns in the Santa Barbara Basin during the 19th and 20th Centuries. Geological Society of America Bulletin, 88: 1161-1172.

Soutar A. (1978) Collection of sediment cores for age date and geochemical analysis. In Annual Report to Bureau of Land Management, Southern California Outer Continental Shelf Benthic and Water Column Program Year 2, Vol. II, NTIS BLM Contract to SAI, Contract No. AA550-CT6-40.

Soutar A. and Baxter D. (1978) Particle characterization of PIT samples by SEM/XES analysis. In Annual Report to Bureau of Land Management, Southern California Outer Continental Shelf Benthic and Water Column Program, Year 2, Vol. II, Report 17. NTIS BLM Contract to SAI, Contract No. AA550-CT6-40.

Soutar A., Singleton J., Butler M., and Baxter D. (1978) Collection of pelagic sediment samples for geochemical analysis (PIT deployment). In Annual Report to Bureau of Land Management, Southern California Outer Continental Shelf Benthic and Water Column Program Year 2, Vol. II, NTIS BLM contract to SAI, Contract No. AA550-DT6-4.

Tiller K. G., Hodgson J. F., and Peech M. (1963) Specific sorption of cobalt by soil clays. Soil Science, 95: 392-399.

Turekian K. K. (1977) The fate of metals in the oceans. Geochimica et Cosmochimica Acta, 41: 1139-1144.

U.S. Bureau of Mines (1976). Minerals Yearbook 1923-1975.

Young D. R., Young C. S., and Hearka G. E. (1973) Sources of trace metals from highly-urbanized Southern California to the adjacent marine ecosystem. In Cycling and Controls of Metals, Proceedings of an Environmental Resources Conference, 31 October - 2 November, 1972, M. G. Curry and G. M. Giglioth, eds., National Environmental Research Center, Cincinnati.

Table 1. Comparison of leads leached from a dried sediment by different acids for 10 hours cold.

Acid Strength	Leached from Sediment				Leached Sediment Residue		
	Pb μg/g	Pb isotopic composition			Pb isotopic composition		
		206/207	206/208	206/204	206/207	206/208	206/204
0.2N HCl	19.6	1.1930	0.4925	18.989	1.2089	0.4867	18.841
1 N HCl	20.9	1.1949	0.4970	19.068	1.2109	0.4852	18.961
2.6N HCl	21.0	1.1946	0.4850	18.548	1.2106	0.4867	18.922
6 N HCl	20.5	1.1950	0.4840	18.726	1.2100	0.4858	18.898
1 N HNO_3	20.6	1.1925	0.4852	18.521	1.2105	0.4859	18.927

Table 2. Lead and barium concentrations, lead isotopic compositions, and wt.% water in different fractions of Particle Interceptor trapped sediments (PITS) and basin sediments of four Southern California offshore basins.

			Total Digested Sediment					Leached from Sediment				Leached Sediment Residue			
					Pb isotopic composition				Pb isotopic composition				Pb isotopic composition		
Depth (mm)	Age	Sea Water (wt.%)	Ba µg/g	Pb µg/g	206/207	206/208	206/204	Pb µg/g	206/207	206/208	206/204	Pbf µg/g	206/207	206/208	206/204
San Nicolas Basin															
0-2.5	1974-76	77.8	1540	13.9				9.5	1.1966	0.4835	18.613	4.41	1.2148	0.4882	18.904
13-14	1964-66	77.5						8.7	1.2003	0.4856	18.749				
45-49	1938-42	67.8	1400	11.9				6.7	1.2086	0.4865	18.804	5.14	1.2148	0.4894	18.855
76-80	1910	61.9						5.5	1.2115	0.4873	18.872				
127-131	1850	67.2	2160	13.3				9.3	1.2067	0.4863	18.750	4.05	1.2153	0.4880	18.910
Santa Barbara Basin															
	PITS	72.0	800	25.7	1.1949	0.4853	18.568	19.3	1.1914	0.4846	18.347	6.4			
0-3	1977	90.6	830	26.2				20.7	1.1988	0.4859	18.663	5.5			
4-11	1976	85.5	770	28.1				22.7	1.196	0.4854	18.617	5.4	1.2107	0.4880	18.864
41-55	1970-71	86.7	680	26.1				20.5	1.193	0.4851	18.553	5.6			
56-60	1969	79.9						20.6	1.1925	0.4852	18.521		1.2105	0.4859	18.927
72-75	1966	82.4	690	24.5				18.8	1.1847*	0.4827*	18.439*	5.7			
86-98	1962-63	84.5	570*	20.8*				16.6	1.1916	0.4836	18.519	3.4	1.2087	0.4859	18.867
118-121	1954-55	82.1	550	18.4				14.5	1.1992	0.4855	18.659	3.97			
176-185	1938-39	79.2	530	15.5	1.2059	0.4860	18.770	12.4	1.2056	0.4862	18.807	3.04			
215-220	1925-26	77.1	520	14.7				9.6	1.2118	0.4868	18.855	5.13	1.2083	0.4860	-
274-279	1908-09	77.3	540	14.7				9.5	1.2126	0.4872	18.941	5.23	1.2104	0.4851	18.905
455-466	1845-50	73.1	630*	13.9				9.3	1.2196	0.4881	19.031	4.65	1.2113	0.4847	18.881
715-720	~ 1745	62.2	530	12.8				7.2	1.2198	0.4863	18.978	5.65	1.2064	0.4848	18.968

Table 2. (continued)

Santa Monica Basin

	PITS	86.9	1210	41.7	1.1860	0.4847	18.402	36.0	1.1823	0.4831	18.506	5.63			
1-2	1976	85.9	650	37.0	1.1921	0.4858	18.557	30.7	1.1931	0.4875	18.432	6.3			
7-10	1973-74	91.6	790	40.8				34.3	1.1889	0.4862	18.545	6.48	1.2121	0.4909	18.856
11-13	1972	89.5	940	36.7				31.1	1.1855	0.4834	18.439	5.62	1.2049	0.4860	18.773
17-20	1965-69	85.9						39.2	1.1801	0.4839	18.332				
21-23	1962-64	84.4	1240	45.2				39.3	1.1760	0.4811	18.254	5.94	1.2008	0.4859	18.718
27-29	1955-58	82.2	860	37.9				32.2	1.1721	0.4800	18.184	5.71	1.1984	0.4843	18.703
36-39	1937-43	77.4	860	27.7				22.0	1.1815	0.4818	18.363	5.74	1.2047	0.4858	18.708
51-55	1911-19	75.3	790	15.6				10.6	1.1952	0.4835	18.580	5.07	1.2096	0.4866	18.757
83-88	1850-58	74.4	980	12.1	1.2100	0.4851	18.857	6.9	1.2116	0.4869	18.769	5.24			
191-196	1670-80	71.1	1060	12.4	1.2116	0.4863	18.928	6.9	1.2123	0.4857	18.838	5.51	1.2120	0.4856	18.859

San Pedro Basin

2-4	1975	89.1	910*	53.9	1.1913	0.4864	18.534	39.0	1.1867	0.4848	18.498	14.9			
6-9	1973	86.6	4000*	46.2				38.8	1.1815	0.4841	18.347	7.41	1.2027	0.4862	18.678
10-14	1972	85.9						76.0	1.1758*	0.4824*	18.257*				
15-17	1970	83.8	8160	60.6				53.2	1.1772	0.4824	18.296	7.4			
20-22	1966-67	83.4	12000*	69.8*				67.3*	1.1702*	0.4804*	18.386*	2.5	1.1984*	0.4843*	18.766*
26-28	1963-64	81.3	1580	49.0	1.1732	0.4804	18.230	46.5	1.1679	0.4802	18.139	2.47			
32-35	1958-60	80.0	820	42.4				35.4	1.1693	0.4798	18.193	6.99	1.1986	0.4837	18.646
45-49	1945-49	76.7						16.0	1.1838	0.4829	18.372				
64-69	1923-28	75.1	800	18.7				13.1	1.1889	0.4824	18.512	5.61	1.2093	0.4855	18.894
77-81	1910-14	73.9						8.6	1.1986	0.4846	18.589				
121-128	1850-59	68.2	960*	12.4	1.2098	0.4845	18.956	6.3	1.2093	0.4862	18.910	6.08			
194-200	~ 1700	69.3	930	11.6	1.2099	0.4854	18.863	5.7	1.2090	0.4859	19.004	5.94	1.2103	0.4852	18.863

†Calculated by difference of Pb in total sediment - Pb leached from sediment.

*Average of replicate determinations.

Table 3. Range of concentrations, isotopic compositions of industrial and natural component of lead in basin sediments.

Age	Industrial Component				Natural Component			Residue
	Pb µg/g dw		$^{206}Pb/^{207}Pb$		Pb µg/g dw		$^{206}Pb/^{207}Pb$	Pb
	upper	lower	upper	lower	upper	lower	average	µg/g dw
Santa Barbara Basin								
1977	12.4	11.3	1.186	1.183	9.4	8.3	1.2173	5.5
1976	14.4	13.3	1.184	1.181	9.4	8.3	↑	5.4
1970-71	12.2	11.1	1.177	1.172	9.4	8.3		5.6
1969	12.3	11.2	1.176	1.172	9.4	8.3		5.5*
1966	10.5	9.4	1.159	1.152	9.4	8.3		5.7
1962-63	10.9	5.4	1.178	1.138	11.2	5.7	↓	3.4
1954	7.8	3.9	1.184	1.150	10.6	6.7	1.2173	4.0
Santa Monica Basin								
1976	23.8		1.188		6.9	6.9	1.2120	6.3
1973-74	27.4		1.183		↑	↑	↑	6.5
1972	24.2		1.178					5.6
1965-69	32.3		1.173					5.3
1962-64	32.4		1.168					5.9
1955-58	25.3		1.161					5.7
1937-43	15.1		1.168		↓	↓	↓	5.7
1911-19	3.7		1.164		6.9	6.9	1.2120	5.1
San Pedro Basin								
1975	24.1	24.1	1.175	1.175	14.9	14.9	1.2056	14.9
1973	32.8	31.3	1.177	1.176	7.5	6.0	↑	7.4
1972	70.0	68.5	1.173	1.173	7.5	6.0		6*
1970	47.2	45.7	1.174	1.173	7.5	6.0		7.4
1966-67	64.8	56.3	1.169	1.163	11.0	2.5		2.5
1963-64	44.0	35.5	1.166	1.156	11.0	2.5		2.5
1958-60	29.4	27.9	1.162	1.16	7.5	6.0		7.0
1945-49	10.0	8.5	1.171	1.165	7.5	6.0	↓	6*
1923-28	7.5	5.2	1.176	1.164	7.9	5.6	1.2056	5.6

*Assumed value.

Table 4. Comparison of natural and anthropogenic lead deposition fluxes, barium deposition fluxes among Santa Barbara, Santa Monica and San Pedro Basin.

Fluxes	Santa Barbara Basin	Santa Monica Basin	San Pedro Basin
Sediment mass flux before 1970 mg/cm^{2}yr	92	19	30
Natural flux of acid leachable lead before 1750 ng/cm^{2}yr	662	131	180
Sediment mass flux after 1970 mg/cm^{2}yr	96	34	47
Excess flux of acid leachable lead after 1970 ng/cm^{2}yr	1397	867	1551
Average natural barium flux µg/cm^{2}yr	52	16	27
Average present barium flux µg/cm^{2}yr	77	34	240

Table 5. Comparison of depositional fluxes and compositions of Particle Interceptor trapped material with surface sediments in the Santa Barbara and Santa Monica basins.

	Sediment mass flux mg km^2/yr	Total digested sediment			Leach from sediment		Leached sediment residue
		organic carbon† %	carbonate† %	Ba ppm dw	Pb ppm dw	Pb isotope ratio 206/207	Pb ppm dw
Santa Barbara Basin							
Particle Interceptor Trap	72.6*	3.55	8.0	800	19.3	1.1914	6.4
Surface Sediment	92.0**	5.10	5.5	830	20.7	1.1988	5.5
Santa Monica Basin							
Particle Interceptor Trap	16.9*	6.15	12.4	1200	36.0	1.1823	5.6
Surface Sediment	34**	5.30	19.2	650	30.7	1.1931	6.3

† Anderhalt and Reed (1978); analysed in different PITS sample and sediment sections.

* Soutar *et al.* (1978).

** Bruland *et al.* (1978).

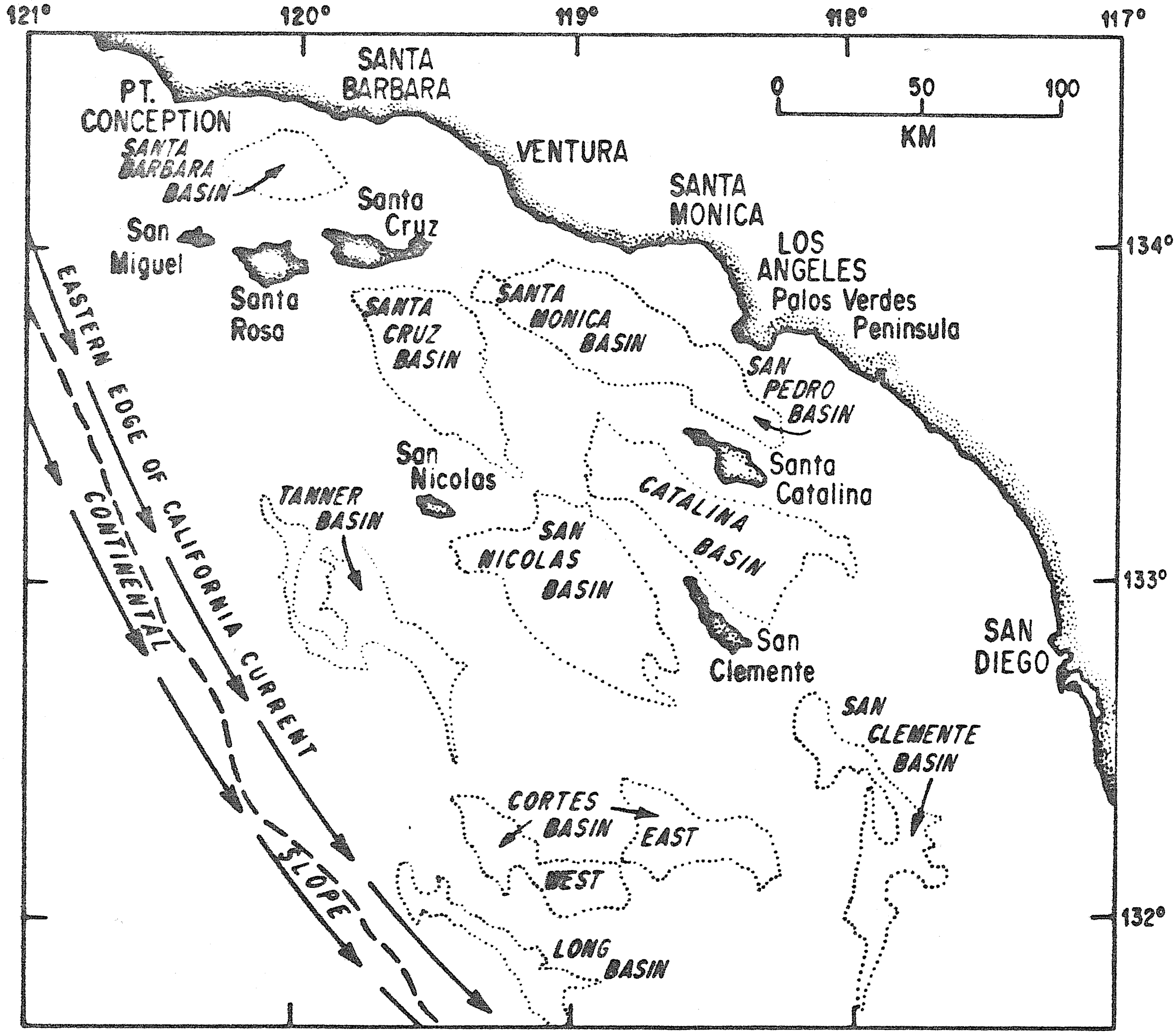

Figure 1. Location map of Southern California Borderland

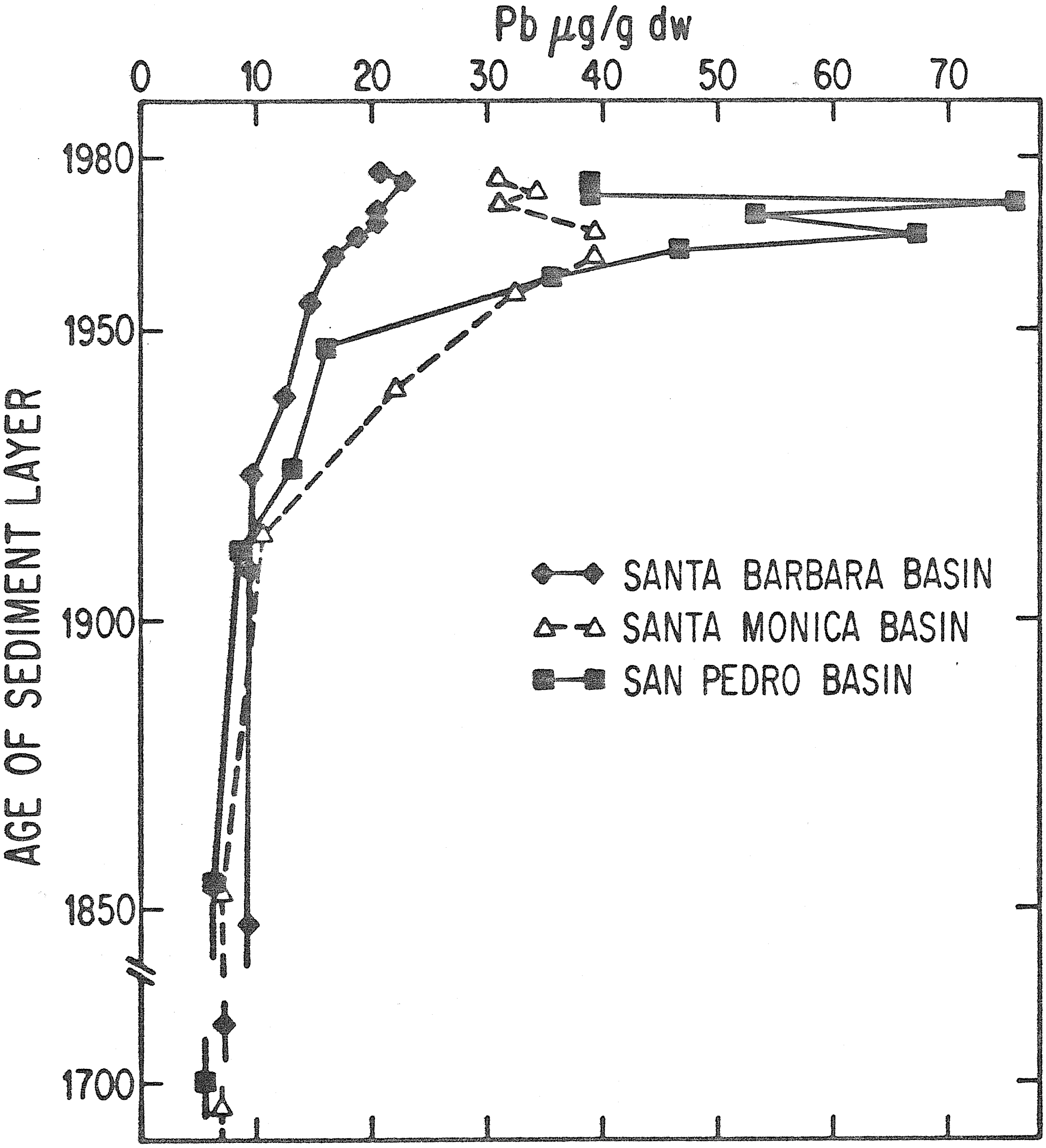

Figure 2. Historic change of concentrations of leachable lead in basin sediments

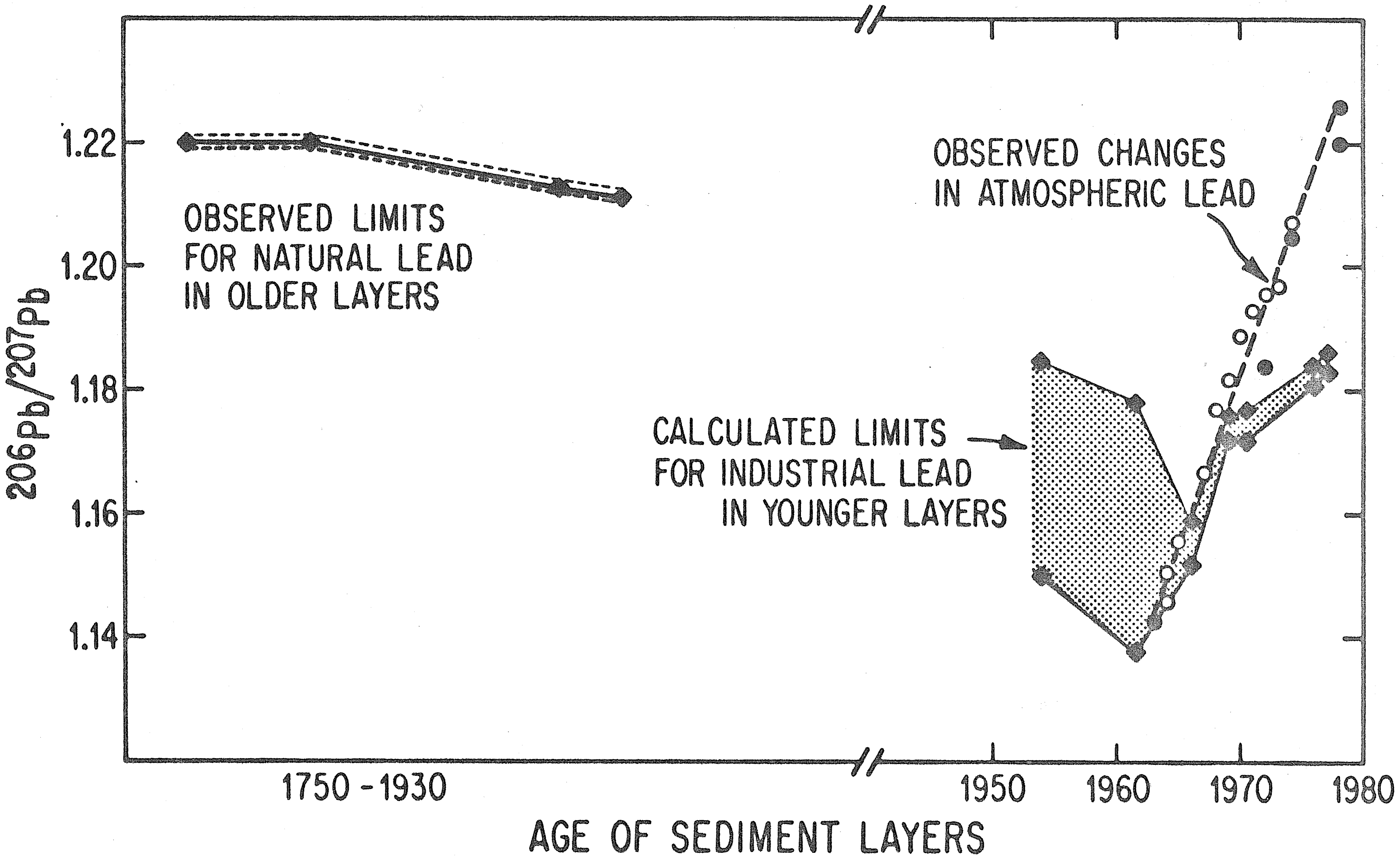

Figure 3. Comparison of $^{206}Pb/ ^{207}Pb$ ratios in natural leads with those in industrial lead in Santa Barbara basin sediments and in the atmosphere.
Dashed boundaries indicate measurement errors, while ▨ indicates calculation uncertainty ● data from Elias <u>et al</u>. (1981), ○ data from Chow <u>et al</u>. (1975)

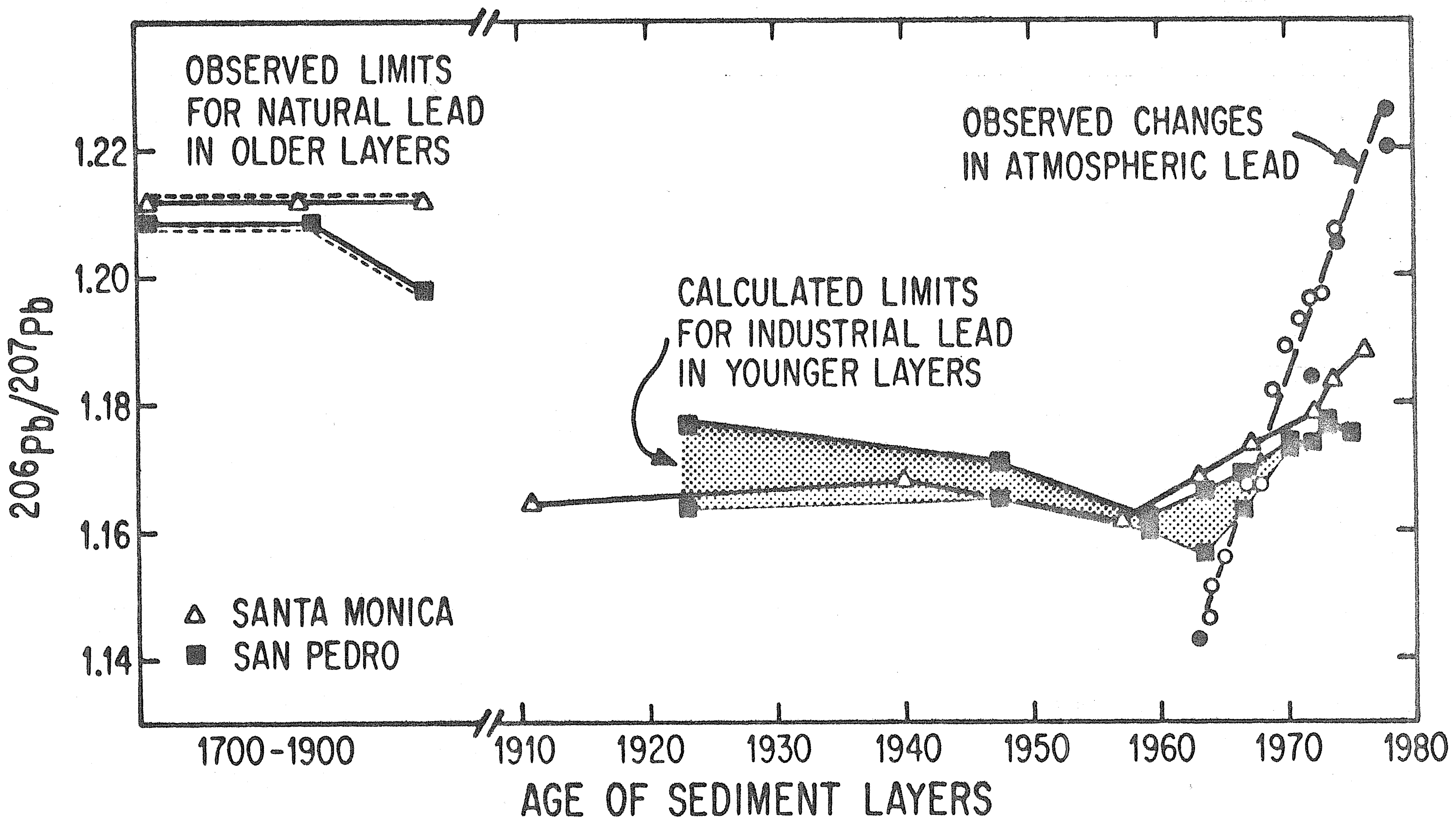

Figure 4. Comparison of $^{206}Pb/^{207}Pb$ ratios in natural leads with those in industrial lead in Santa Monica and San Pedro basins sediments and in the atmosphere. Dashed boundaries indicate measurement errors, while ░ indicates calculation uncertainties ● data from Elias et al. (1981), ○ data from Chow et al. (1975)

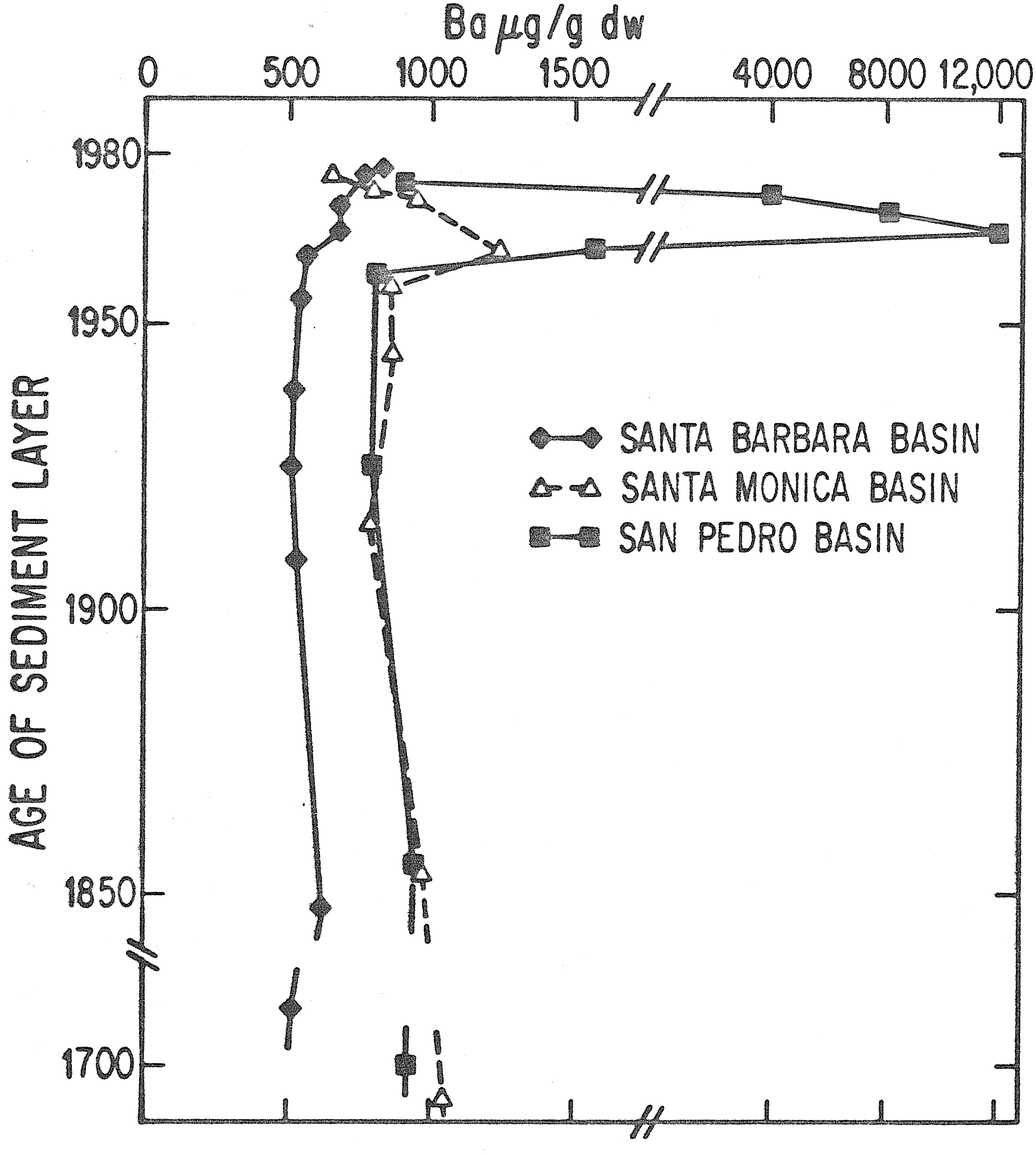

Figure 5. Historic change of concentrations of barium in basin sediments