used in such applications as catalytic membranes with true molecular selectivity or in the controlled access of molecules of preselected size to a sensor surface.

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21. This research was supported by the National Science Foundation and the Purdue Research Foundation.

24 May 1994; accepted 3 August 1994

Greenland Ice Evidence of Hemispheric Lead Pollution Two Millennia Ago by Greek and Roman Civilizations

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Analysis of the Greenland ice core covering the period from 3000 to 500 years ago—the Greek, Roman, Medieval and Renaissance times—shows that lead is present at concentrations four times as great as natural values from about 2500 to 1700 years ago (500 B.C. to 300 A.D.). These results show that Greek and Roman lead and silver mining and smelting activities polluted the middle troposphere of the Northern Hemisphere on a hemispheric scale two millennia ago, long before the Industrial Revolution. Cumulative lead fallout to the Greenland Ice Sheet during these eight centuries was as high as 15 percent of that caused by the massive use of lead alkyl additives in gasoline since the 1930s. Pronounced lead pollution is also observed during Medieval and Renaissance times.

The history of human lead production began about six millennia ago (Fig. 1A) (*1–7*). Significant lead production started only about one millennium later with the discovery of new techniques for smelting lead-silver alloys from lead sulfide ores (galena) and cupeling silver from the alloys (*1–7*). Lead production then rose continuously during the Copper, Bronze, and Iron ages (*5, 6, 8*), stimulated by the introduction of silver coinage (during those times, lead was as much as a 300-to-1 by-product of silver production) and the development of Greek civilization. A pronounced maximum of about 80,000 metric tons per year (approximately the rate at the time of the Industrial Revolution) was reached during the flourishing of Roman power and influence around two millennia ago (Fig. 1A). The use of lead was ubiquitous, and most districts that were suitable for mining in the Old World were known and worked, especially those in Spain, the Balkans, Greece, and Asia Minor (*5, 7*). Lead production then decreased sharply during the decline of the Roman Empire, down to a minimum of only a few thousand tons per year during medieval times, before increasing again from A.D. 1000 with the discovery of the lead and silver mines of Central Europe.

Lead poisoning from extensive lead production and use during Roman times has been suggested as one of the causes of the fall of Rome (*5, 9, 10*). Smelter emissions from these sources have also been documented as resulting in significant local or even regional lead pollution in Europe, as evidenced, for instance, by studies of peat deposits in Britain (*11, 12*) and lake sediments in southern Sweden (*13*). We show here that smelter emissions also resulted in significant contamination of the middle troposphere of the remote Arctic. This occurrence marks the oldest large-scale hemispheric pollution ever reported, long before the onset of the Industrial Revolution.

We analyzed 22 sections of the 3028.8-m European Greenland Ice-Core Project (GRIP) deep ice core electromechanically drilled in 1990 to 1992 at Summit (72°34'N, 37°37'W, elevation of 3238 m above sea level, annual mean air temperature of −32°C) in central Greenland (*14*). Fourteen sections were selected from the period between 2360 and 1775 years ago (depths of 511.0 to 349.3 m), which are the ~600 years corresponding to the flourishing of the Roman Republic and Empire. Two sections were selected from ice deposited 3000 to 2500 years ago (depths of 619.3 to 569.3 m, respectively), a period that includes the rise of Greek civilization. Five sections were selected from ice deposited 1520 to 470 years ago (depths of 349.3 to 129.3 m, respectively), during the Medieval and Renaissance periods. Finally, one section was chosen in ice from the pre-lead production period (7760 years ago, depth of 1286.5 m) to serve as a Holocene natural background sample. It was not possible to analyze samples deposited 3500 to 7000 years ago because this period corresponds to the brittle-zone depth interval in which the core quality is too poor to allow reliable measurements of heavy metals.

We mechanically decontaminated each core section (length of 55 cm) using an ultraclean procedure (*17*) derived from those of Patterson and his co-workers (*15, 16*). It involved the chiseling of successive veneers of ice from the outside to the central part of each section inside a laminar-flow clean bench in a cold room while the core was held horizontally in an all-polyeth-

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ylene lathe (*17*). Each veneer layer was analyzed separately in a clean laboratory (*18*). Lead contents were determined with a precision of about ±10% by graphite furnace atomic absorption spectrometry (GFAAS) after preconcentration by nonboiling evaporation (*19*). We also determined Al and Na contents by direct GFAAS and SO_4^{2-} contents by ion chromatography. Blank determinations were performed for each step of the analytical procedure. They included an evaluation of the blank contributed by the chiseling procedure, which was determined (*17*) by processing an artificial ice core made by freezing ultrapure water (*18*) whose Pb content was known beforehand. This last blank contribution was found to be 0.11 pg per gram of ice (pg/g) for the innermost veneer layer and 0.17 pg/g for the other layers (*17*).

To check the cleanliness of the most central part of the cores obtained after the chiseling was completed, we studied changes of Pb concentrations from the outside to the center of each of the 22 sections. Significant contamination was observed on the outside (first) layer of the sections, which confirms that they were significantly contaminated on their outside during drilling operations. On the other hand, excellent plateaus of concentrations were obtained from the second or third layers (Table 1). These plateaus serve as evidence that Pb concentrations measured in the most central part of the core sections do represent the original concentrations in Greenland ice.

The results (Fig. 1B) show that Pb concentration was low (0.55 pg/g, 7760 years ago) before the beginning of lead production, when atmospheric Pb still entirely originated from natural sources (*24*). The corresponding lead crustal enrichment factor (EF_{crust}) (*19*) of 0.8, which is close to unity, shows that virtually all this natural Pb was from soil and rock dust [sea-salt spray and volcanic contributions are minor as calculated (*16*) from the measured Na and SO_4^{2-} concentrations]. The Pb concentration at 2960 years ago, about 5000 years later, was essentially identical to that at the beginning of Pb production, showing that anthropogenic emissions of Pb to the atmosphere 3000 years ago were still negligible on a hemispheric scale compared with Pb originating from soil and rock dust [about 4000 metric tons per year for both hemispheres (*24*)]. Then, at 2500 years ago our record shows that Pb concentration started to increase markedly above this natural background up to about 2 pg/g (EF_{crust} ~3), which is an increase by a factor of ~4, and Pb concentration remained high from ~2500 to ~1700 years ago. This 800-year period corresponds to the flourishing of the Greco-Roman civilizations (Fig. 1A). Lead concentration declined to low values (0.7 pg/g) around 1500 years ago (that is, after the fall of the Roman Empire) and then increased continuously from 1500 to 500 years ago, during the Medieval and Renaissance times.

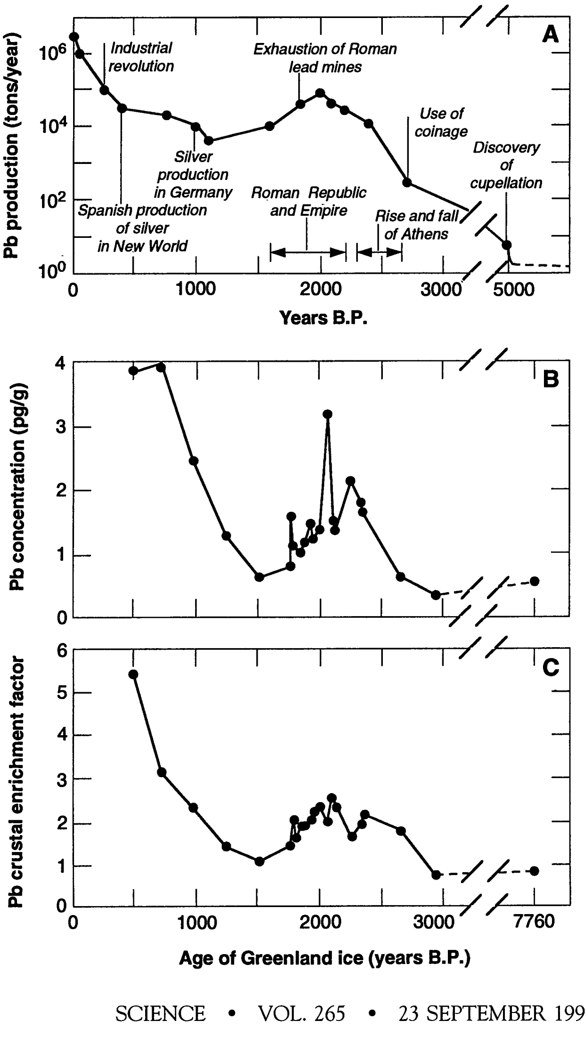

Fig. 1. (**A**) Changes in worldwide Pb production over the past 5500 years [redrawn from (*3*, *4*)]. (**B** and **C**) Changes in Pb concentration and Pb crustal enrichment factor (*19*) in central Greenland ice from 2960 to 470 years ago. Each data point was obtained from the analysis of a core length corresponding to exactly 2 years of ice accumulation (except one for which it was only 1 year because of poor core quality) to eliminate the influence of possible short-term (seasonal) changes in Pb deposition.

The high (about fourfold the natural level) Pb concentration and EF_{crust} observed in Greenland ice from ~2500 to ~1700 years ago cannot be explained by an increase in natural Pb emissions to the atmosphere: The measured Al, Na, and SO_4^{2-} concentrations in the ice do not change significantly during the whole period covered by our samples. We interpret the increase as a result of anthropogenic Pb emissions to the atmosphere from the large lead-silver production by Greeks and Romans [production in the other parts of the world such as Asia was minor and is unlikely to have made a significant contribution (*5*, *6*)]. This production peaked at about 80,000 metric tons per year around 2000 years ago, and it is estimated that ~5% of the mined and smelted Pb was emitted to the atmosphere (*25*), which would have given a peak value of ~4000 metric tons per year to the atmosphere. The data show that the resulting pollution was not only local (*5*, *6*, *9*–*10*) or regional (*11*–*13*) in scale but reached the middle troposphere (Summit is located at a high elevation of 3238 m above sea level) of the remote Arctic region. It represents the oldest hemispheric-scale atmospheric pollution ever reported, well before the Industrial Revolution.

The fourfold increase during the Greco-Roman period for a middle troposphere location in central Greenland is in excellent

Table 1. Lead concentrations measured in the second and third layers and in the final inner core for five typical GRIP ice-core sections. For three of these sections (129.25, 399.3, and 1286.45 m), the concentrations are virtually the same in all three subsamples: Contamination was only present in the outside (first) layer. For the 349.25- and 510.95-m sections, the outside contamination reached the second layer but the third layer and the inner core remained free of contamination.

Depth (m)	Age (years ago)	Measured Pb concentration (pg/g)		
		2nd layer	3rd layer	Inner core
129.25	470	4.77	3.99	3.90
349.25	1520	1.79	0.65	0.66
399.3	1775	1.06	1.07	1.17
510.95	2360	43	1.64	1.64
1286.45	7760	0.57	0.56	0.55

agreement with that (about fivefold) hypothesized by Shirahata and colleagues. (*25*); it is lower than the increase (about tenfold) speculated by Patterson earlier (*26*). During the Greco-Roman times, most Pb emitted to the atmosphere would have been due to lead-silver mining and smelting in Spain (which represented ~40% of the worldwide Pb production during the Roman Empire), Central Europe, Britain, the Balkans, Greece, and Asia Minor (*5*, *6*). The Pb was produced in open-air furnaces with no control on emission rates. Small Pb aerosol particles emitted during these activities could easily be transported from these regions to the Arctic through well-known pathways (*27*, *28*). However, differences in transport efficiencies between the different source regions and central Greenland cannot be ruled out. Such differences could, for instance, help to explain why Pb levels in the ice during the Greek and Roman periods are similar, although Pb production was severalfold lower during Greek times. An alternative explanation could be the differences in Pb emission rates for mining and smelting activities between the Greek and Roman times or uncertainties in the historical data shown in Fig. 1A.

The cumulative anthropogenic Pb fallout over Greenland from ~2500 to 1700 years ago, estimated by combining a Pb excess value of ~1 pg/g over the value during the pre-Pb time with a mean ice accumulation rate of 23 g of H_2O cm^{-2} $year^{-1}$, is 23×10^{-12} g of Pb cm^{-2} $year^{-1}$. Over 800 years, this rate represents 1.84×10^{-8} g of Pb cm^{-2}. For the whole Greenland ice cap (surface of 1.4×10^6 km^2, mean annual accumulation rate of 34 g of H_2O cm^{-2} $year^{-1}$), the net deposition is about 400 tons during these 800 years. This estimate is as much as ~15% of the cumulative fallout of Pb to Greenland during the past 60 years that is linked to the massive use of Pb alkyl additives in gasoline, calculated from a mean concentration of 100 pg of Pb per gram in 1930 to 1990 Greenland snow (*29*). Further evidence of this hemispheric-scale pollution by Greco-Roman civilization might be found in other archives, such as sea sediments in the North Atlantic Ocean and in the Mediterranean Sea. Analyses of lead isotopes could fingerprint the relative contributions of the different ancient mining districts to this pollution.

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$$EF_{crust}(Pb) = (Pb_{ice}/Al_{ice})/(Pb/Al)_{mean\ crust}$$

where Pb_{ice} and Al_{ice} are the measured concentrations of Pb and Al in the ice, respectively, and $(Pb/Al)_{mean\ crust}$ is the Pb/Al ratio in mean crustal material given by Taylor and McLennan (*22*). Such crustal reference material is appropriate to characterize the composition of soil- and rock-derived dust (*23*).
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30. This work is a contribution of GRIP organized by the European Science Foundation. We thank B. Stauffer and J. P. Steffensen for their very kind assistance in core selection, M. Legrand for the ion chromatography measurements, and R. J. Delmas for his continuous interest and helpful discussions. We thank the national funding agencies and organizations in Belgium, Denmark, France, Germany, Iceland, Italy, Switzerland, and the United Kingdom as well as the XII Directorate of the Commission of European Communities for financial support. Supported by the French Ministry of the Environment (grant 92295), the Institut National des Sciences de l'Univers, and the University of Grenoble.

20 May 1994; accepted 5 August 1994

Nitrogen Uptake, Dissolved Organic Nitrogen Release, and New Production

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In oceanic, coastal, and estuarine environments, an average of 25 to 41 percent of the dissolved inorganic nitrogen (NH_4^+ and NO_3^-) taken up by phytoplankton is released as dissolved organic nitrogen (DON). Release rates for DON in oceanic systems range from 4 to 26 nanogram-atoms of nitrogen per liter per hour. Failure to account for the production of DON during nitrogen-15 uptake experiments results in an underestimate of gross nitrogen uptake rates and thus an underestimate of new and regenerated production. In these studies, traditional nitrogen-15 techniques were found to underestimate new and regenerated production by up to 74 and 50 percent, respectively. Total DON turnover times, estimated from DON release resulting from both NH_4^+ and NO_3^- uptake, were 10 ± 1, 18 ± 14, and 4 days for oceanic, coastal, and estuarine sites, respectively.

A paradigm of modern oceanography is that the production of biomass within the surface ocean is nitrogen-limited and that primary production is supported in part by nitrogen supplied from outside the system (new production) and in part by nitrogen supplied within the system [regenerated production (*1*)]. Researchers have assumed that new and regenerated production could be traced independently by using ^{15}N tracer techniques; new production is estimated by measuring NO_3^- uptake, and regenerated production is estimated by measuring NH_4^+ uptake (*1*). Furthermore, uptake of new nitrogen (that is, NO_3^-) by phytoplankton is thought to be equal to the upward flux of NO_3^- into surface waters, and this flux is approximately balanced by the flux of particulate nitrogen (PN) out of surface waters over appropriate space and time scales (*2*) (Fig. 1A).

This paradigm for new production has been used to guide our thinking about the interaction between inorganic nitrogen (NH_4^+ and NO_3^-), primary production, and particle flux for the past two decades.

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