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Article

Lead in Archeological Human Bones Reflecting Historical Changes in Lead Production

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ABSTRACT: Forty years ago, in a seminal paper published in *Science*, Settle and Patterson used archeological and historical data to estimate the rates of worldwide lead production since the discovery of cupellation, approximately 5000 years ago. Here, we record actual lead exposure of a human population by direct measurements of the concentrations of lead in petrous bones of individuals representing approximately 12 000 years of inhabitation in Italy. This documentation of lead pollution throughout human history indicates that, remarkably, much of the estimated dynamics in lead production is replicated in human exposure. Thus, lead pollution in humans has closely followed anthropogenic lead production. This observation raises concerns that the forecasted increase in the production of lead and other metals might affect human health in the near future.

Pb production → Pb exposure → Pb accumulation in humans → health effects

This happened in the past – we should prevent it in the future

KEYWORDS: *lead pollution, petrous bones, diagenetic addition of metals*

INTRODUCTION

During the last few decades numerous geochemical and archaeo-metallurgical studies have documented the production of lead and other metals over millennia. Following Settle and Patterson[1] in 1980, many studies have confirmed the general pattern of lead production outlined in Figure 1.[2−9] The imperative features in this diagram include an abrupt increase in lead production incited by the discovery of cupellation approximately 5000 years ago,[10−14] followed by a slow increase in production until the introduction of coins in the middle of the first millennium BCE. Subsequently, the production rate accelerated until reaching a peak during the Roman Period, and then declined during the Middle Ages. Starting roughly 1000 years ago, the growth in lead production resumed, prompted by silver mining in Germany, then in the New World, and finally by the Industrial Revolution and the introduction of alkyl-lead at the beginning of the 20th century. Throughout most of human history lead production was mainly a byproduct of silver mining, and only during the last 250 years was lead mined significantly for its own uses.[2,15]

The increase in lead production rates was revealed in environmental archives such as terrestrial ice and sediments from lakes and peat-bogs.[3−9,16−24] In parallel, lead concentrations in human bones and teeth have been shown to reflect this increase, albeit, in specific sites and periods, and very seldom as a transect in human history.[8,25−37] Lead concentrations and ratios of lead to calcium (the major element in tooth and bone apatite—Pb/Ca) have been used to provide information regarding the extent of lead pollution and, by corollary, lead production and use.[26−37] Nevertheless, the in vivo accumulation of lead (and other metals) in bones and teeth is often hampered by post-mortem, diagenetic processes.[26,29,38,39] Such processes differentially affect different types of bones and teeth, as it has been shown that lead and other metals in tooth enamel are less affected by diagenetic processes relative to bones and tooth dentin.[26,29,38,39] In some instances, lead isotopes have been used in addition to Pb/Ca ratios to identify the source of in vivo lead contamination.[36,40,41] Alternatively, comparing Pb/Ca with barium-to-calcium (Ba/Ca) ratios is a well-established method that is commonly applied to correct for diagenetic alteration of in vivo Pb/Ca ratio.[26,28,29,36,41] This approach is based on the premise that Ba and Pb have similar tendencies to be incorporated into the bone or tooth apatite and that anthropogenic Ba emissions are insignificant relative to natural, rock-derived background levels.[26,28,29] Hence, elevated Ba concentrations exceeding the in vivo threshold of Ba/Ca in tooth enamel (5×10^{-6} mol/mol;[26,28,29,41]), suggest that at least some Ba, and probably also Pb, were added to the tooth after burial.

A recent time transect study sequenced ancient DNA from more than a hundred human individuals that occupied Rome and its surroundings during the past 12 000 years.[42] The ancient DNA was extracted from petrous bones, which house the internal segment of the ear and are among the hardest and densest bones in the body.[43] The use of petrous bones is standard in ancient DNA, as its DNA yield is orders of magnitude higher than from other bone types (https://

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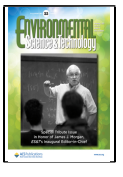

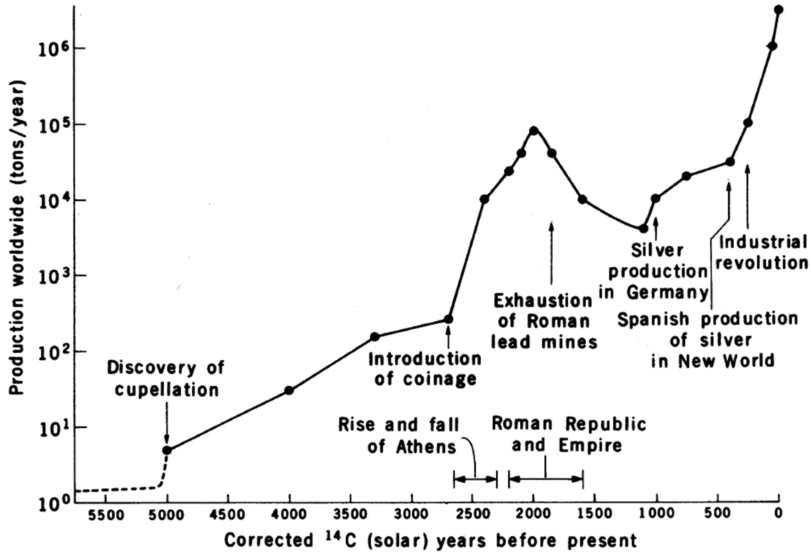

Figure 1. World lead production during the past 5500 years.[1] From Settle and Patterson.[1] Reprinted with permission from AAAS.

Table 1. Summary Statistics of the Elemental Concentrations (in ppm) of the Studied Petrous Bone Samples[a]

	all samples								samples with Ba/Ca < 5 × 10^{-5}							
	avg	SD	RSD (%)	med	avg/med	max	min	max/min	avg	SD	RSD (%)	med	avg/med	max	min	max/min
Li	0.93	1.02	110	0.62	1.5	9.5	0.05	204	0.66	0.40	62	0.53	1.2	2.1	0.17	12
Na	2750	1441	52	2609	1.1	16815	1311	13	2936	778	27	2874	1.0	5348	1556	3.4
Mg	935	540	58	807	1.2	5991	436	14	972	379	39	885	1.1	2170	506	4.3
Al	837	2175	260	362	2.3	23391	54	437	454	413	91	338	1.3	1698	58	29
K	125	104	83	95	1.3	917	29	32	105	59	56	93	1.1	255	35	7.3
V	27	20	74	24	1.2	108	2.2	48	35	24	70	31	1.1	108	3.5	31
Cr	6.0	6.7	112	3.4	1.8	43	0.25	172	6.2	8.5	137	2.9	2.1	43	0.25	172
Mn	124	236	190	31	4.0	1132	0.82	1374	110	196	179	21	5.3	830	3.6	232
Fe	681	1297	190	323	2.1	10151	18	566	420	587	140	291	1.4	3586	36	99
Co	0.69	1.4	201	0.28	2.5	10	0.01	1290	0.49	0.81	165	0.21	2.4	4.2	0.05	80
Ni	2.4	2.8	119	1.3	1.8	15	0.06	241	1.7	1.4	83	1.0	1.7	5.6	0.17	33
Cu	24	35	149	13	1.7	215	0.62	346	16	12	77	13	1.2	46	0.62	74
Zn	103	50	49	90	1.1	414	41	10	97	29	30	90	1.1	161	44	3.6
As	11	35	315	2.9	3.8	267	0.40	663	4.3	5.2	122	2.6	1.6	30	0.50	59
Se	1.5	3.6	245	0.59	2.5	30	0.16	184	0.90	1.0	111	0.60	1.5	4.0	0.16	24
Rb	1.3	3.4	256	0.49	2.7	32	0.06	588	0.63	0.7	111	0.30	2.1	3.4	0.08	41
Sr	427	237	55	396	1.1	1209	86	14	353	205	58	329	1.1	770	86	9.0
Mo	1.6	3.2	194	1.00	1.6	29	0.05	558	1.1	1.6	148	0.58	1.9	8.2	0.11	75
Ag	0.29	0.95	327	0.10	3.0	10	0.01	1714	0.19	0.26	133	0.09	2.1	1.2	0.01	101
Cd	0.34	0.44	131	0.19	1.8	2.7	0.01	401	0.31	0.40	132	0.17	1.8	2.0	0.03	71
Sn	0.19	0.74	387	0.06	3.4	7.1	0.002	3628	0.10	0.20	196	0.05	1.9	1.0	0.003	292
Ba	144	216	150	75	1.9	1874	14	133	36	12	33	36	1.0	59	14	4.2
Pb	94	476	507	23	4.0	5379	0.11	50275	173	857	497	24	7.2	5379	0.11	50275

[a]avg, SD, RSD, med, max, and min denote the average, standard deviation, relative standard deviation, median, maximum, and minimum values, respectively.

pubmed.ncbi.nlm.nih.gov/26086078/). In the current study, we traced pollution through time in these same individuals, by measuring the elemental composition (Ca, Pb, Ba, and an additional 21 elements) of their petrous bones. We demonstrate the use of elemental composition measurements in petrous bones, and show how to modify the use of Ba/Ca ratios to account for diagenetic processes in this bone type. Using our method, we directly compute the level of lead pollution over time, and show that it closely follows the rate of worldwide lead production.

MATERIALS AND METHODS

The 132 individuals analyzed in this study and their burial sites are described in the "Supplementary Site and Archaeological Details" section, pp 30−41, of a recent paper published by two of the authors.[42] Petrous samples were shipped to the Hebrew University of Jerusalem. There, they were dissolved following the protocol outlined by Patterson and co-workers.[26,28−30] It involved crushing the samples and then washing them with ultrapure water, hydrogen peroxide, alcohol, and dilute HCl and HNO_3. After this, the samples were dissolved in

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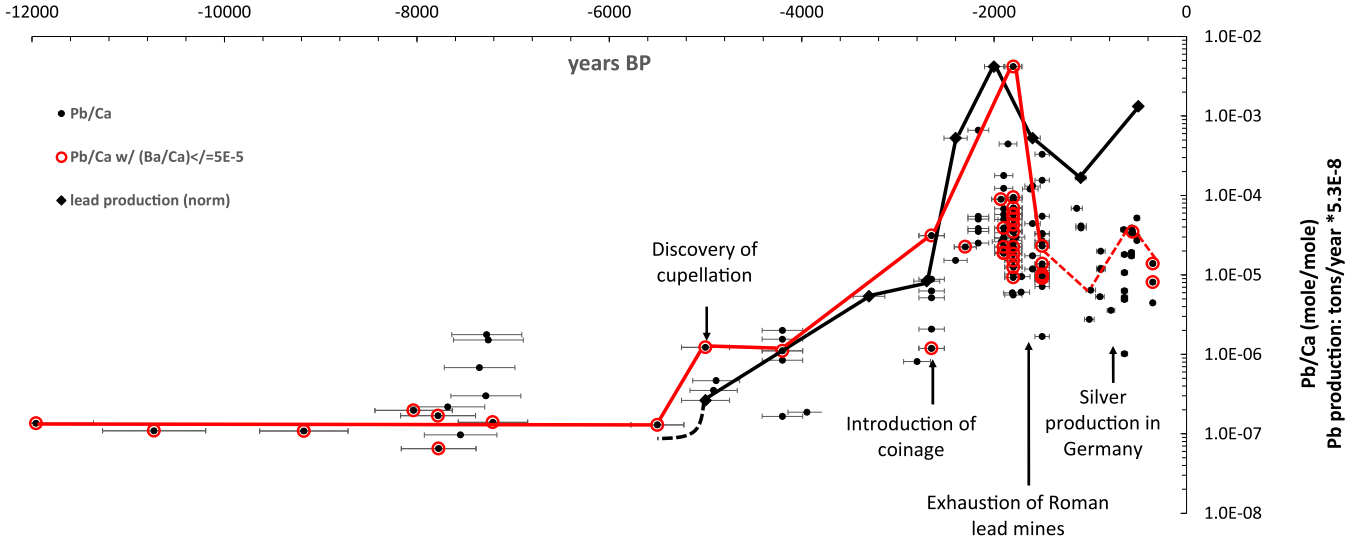

Figure 2. Lead/Ca (mol/mol) in petrous bones of individuals from the vicinity of Rome and Sardinia ranging in age from approximately 12 000 BCE to ca. 1650 CE and Pb production (tones/year * 5.3×10^{-8}), taken from Figure 1. The red line connects the highest Pb/Ca values of same-age samples with Ba/Ca (M/M) $\leq 5 \times 10^{-5}$.

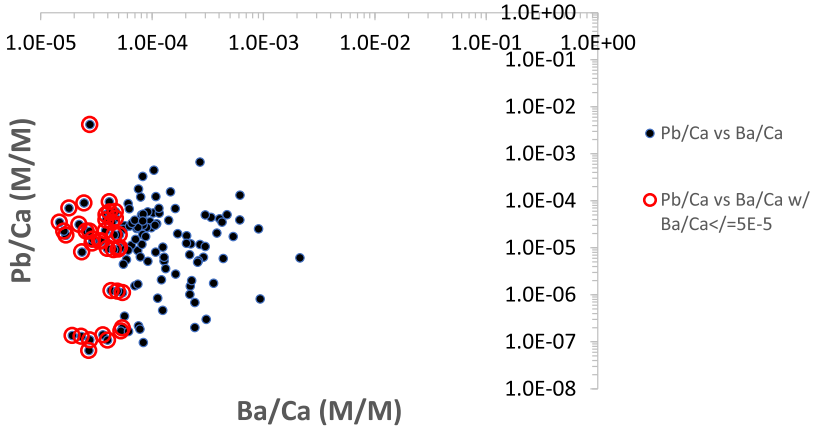

Figure 3. Ba/Ca versus Pb/Ca of the studied petrous bones.

concentrated, ultrapure HNO_3. The presence of dissolved organic matter was apparent in all samples, indicated by foam and nontransparent solutions. Hence, all samples were evaporated to dryness and redissolved in concentrated HNO_3 to fully oxidize the organic matter. The dissolved samples were analyzed for their Ca, Li, Na, Mg, Al, K, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Ag, Cd, Sn, Ba, and Pb concentrations using ICP-MS (Agilent 7500cx) after calibration with external multielement standards (Merck ME VI). An internal standard (50 ng/mL Sc, 5 ng/mL Re and Rh) was added to every standard and sample for drift correction. The contribution of metals from the acid used in the procedures was determined by measuring procedural blank samples. The blank and selected standards were re-examined every 30 samples and at the end of the analysis for precision and detection limit estimation. In addition, standard reference samples (USGS SRS T-183, T-175) were examined at the end of the calibration and at the end of the analysis for accuracy estimation. Blanks were always lower than 1%. The precision and accuracy of the ICP-MS were ±5% for most samples.

RESULTS AND DISCUSSION

We measured the concentrations of 24 elements in the petrous bones of 132 individuals (Tables 1 and S1 of the Supporting Information, SI). The samples include 127 individuals from the vicinity of Rome and five from Sardinia, ranging in age from the Mesolithic period (~12 000 BCE) to the 17th century CE. These individuals were sampled as part of an ancient DNA study conducted previously.[42] From all elements, we focus here on the temporal variation in lead, for two reasons. First, it shows the largest range of concentrations and the largest variability across samples (Table 1). Second, the normalized lead concentration (Pb/Ca) shows a clear temporal variation, which closely follows the worldwide trend of Pb production (Figures 1 and 2). In addition, Pb does not significantly correlate with any other element, including those that are indicative of diagenetic addition (e.g., V, Mn, Fe;[37] Table S1), suggesting that the temporal trend in the level of lead cannot be accounted for by diagenetic post-mortem processes only. In particular, normalized barium levels (Ba/Ca), known as proxies for levels of diagenetic processes,[26,28,29,41] show no correlation ($r = -0.04$, $P = 0.61$) with Pb/Ca levels (Table S1, Figure 3), corroborating the fact that the temporal trends of lead are not fully explained by diagenetic processes.

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Following Harkness and Darrah,[44] we paid special attention to zinc (Zn) concentrations, as it is known to be regulated by homeostatic processes. The values of Zn in our samples (average = 103 ppm, median = 90 ppm; Table 1, Table S1) lie within the range reported for modern humans (refs 37 and 44 average values of 215 and 128 ppm, respectively). Also, Zn concentrations have a very narrow range of values (maximum/minimum = 10) and do not display any trend with time (Tables 1 and S1). Other essential elements (e.g., K, Mg, Na) in our samples also have a narrow range of concentrations and do not display any trend with time (Tables 1 and S1). This suggests that Pb/Ca levels are not determined by homeostatic processes.

Metal content is known to depend on bone type. For example, there are large differences in the measured concentrations of certain metals in contemporary people between cortical bones and tooth enamel.[37,44] In addition, it was reported recently that variations in Pb and Ba concentrations are linked to bone microstructure.[45] Given the lack of known standards for post-mortem diagenesis-indicative elements in petrous bones of modern people, we decided to use Ba/Ca ratios as indicators for diagenetic alteration, following Patterson's and our own work.[26,28,29,41] Lead normalized concentrations (Pb/Ca) versus Ba/Ca values (Figure 3) show the same pattern of no correlation also reported by us in a recent study carried out on Iron Age individuals from the Levant, but with a different threshold for Ba/Ca addition by diagenetic processes.[41] As comparison between Pb/Ca and Ba/Ca has not been carried out in petrous bones, we first turned to investigate the relationship between Pb/Ca and Ba/Ca in this bone type. This was done by comparing Pb/Ca and Ba/Ca values in two individuals for which we analyzed both tooth enamel and petrous bones (Table 2). Indeed, Pb/Ca in the tooth enamel and in the petrous bones of both individuals are similar (within a factor of 3), but Ba/Ca are at least an order of magnitude higher in petrous bones relative to tooth enamels. Therefore, we set the Ba/Ca threshold for determining post-mortem diagenetic processes to be 5×10^{-5} (mol/mol), a factor of 10 higher than the established Ba/Ca threshold for tooth enamel (Figure 3[26,28,29,41]). In order to further corroborate this finding, we determined the average (2×10^{-5}) and the standard deviation (5×10^{-6}) of our lowest 10% Ba/Ca values (calculated from Table S1). The threshold, computed as the average + three standard deviations, gives the value of 4×10^{-5} (mol/mol), almost identical to the one estimated based on the comparison with tooth enamel. Using the 5×10^{-5} threshold, we removed all the samples that might have gone through post-mortem diagenetic processes (Figure 3), leaving us with 39 samples (hereinafter, Ba/Ca-corrected samples) from which we reconstruct lead pollution over historical times around Rome (Figure 2).

Table 2. Comparison of Pb/Ca and Ba/Ca in Teeth and Petrous Bones[a]

	type	sub-type	molar ratio	
			Pb/Ca	Ba/Ca
ind #1	enamel	?	2.1E-07	3.3E-06
	petrous	right petrous	1.8E-07	2.7E-05
			6.1E-07	2.4E-05
			2.3E-07	3.3E-05
		average	3.4E-07	2.8E-05
		stdev	2.4E-07	4.6E-06
		RSD (%)	70	16
ind # 2	enamel	2nd M LL	1.2E-07	1.0E-05
	petrous	right petrous	3.5E-07	5.4E-04
			3.2E-07	5.0E-04
			4.0E-07	6.3E-04
			5.9E-07	9.5E-04
			2.6E-07	6.2E-04
		average	3.8E-07	6.5E-04
		stdev	1.3E-07	1.8E-04
		RSD (%)	33	27

[a]In red are enamel data and averages, standard deviations, and relative standard deviations (standard deviation/average) of the petrous samples. 2nd M LL = 2nd molar tooth, lower left position.

Lead to Ca ratios in the analyzed petrous bones follow Settle and Patterson's record[1] of lead production over millennia (Table S1; Figure 2). This match is further improved when only Ba/Ca-corrected samples are considered. In general, however, both noncorrected (all samples) and Ba/Ca-corrected samples depict a similar trend (Figure 2). As predicted, we observe a clear rise in Pb/Ca petrous-bone levels approximately 5000 years ago, at the time of the discovery of cupellation. Pb/Ca levels then remain constant until the Bronze Age, when they start to slowly increase until the Iron Age. From the Iron Age on, a steeper increase in Pb/Ca is evident, leading to a clear peak during the Roman period, followed by lower, but still high, Pb/Ca values during the decline of the Roman Empire and then in the late Medieval Period. Settle and Patterson[1] report approximately four orders of magnitude increase in lead production between the discovery of cupellation and the height of the Roman Empire (Figure 1). We observe an increase in Pb/Ca ratio in petrous bones that is nearly as large, approximately 4000-fold, for the same period. Thus, our record provides a clear demonstration of how lead pollution in humans has closely followed past anthropogenic lead production. Unlike the calculation of Settle and Patterson,[1] our record of lead pollution shows less dramatic increase during the past 1000 years. This is likely a result of the fact that worldwide lead production has increased in places that are remote from Italy, such as the New World, which should not be reflected as increased pollution in a Roman population.

The close correspondence between Pb production rates and Pb levels in humans in the past suggests that this might happen nowadays and in the future in less regulated regions of the World. More so, numerous studies have shown that Pb pollution in people and especially in children takes place through various pathways, including diet, air-pollution, resuspension of urban soils, and exposure to other types of industrial Pb (refs 46−48 and references therein). These and other studies have emphasized the effect of living conditions and socioeconomic status on the concentrations of Pb in children, and a few studies also demonstrated their adverse, long lasting effect on children's neurobehavioral functioning.[49,50]

In the near future a mounting demand is expected for metals for the manufacturing of new products such as solar panels and wind turbines,[51] and electronic devices.[52−55] For example, a 300% increase in the demand for lead, nickel, silver, and indium in solar photovoltaics, and 1200% increase in the demand for lead, cobalt, and nickel for energy storage technologies are expected in order to achieve 2 °C rather than 6 °C increase in global world temperature by 2050.[51] In

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addition, there has been growing concern about the environmental and toxicological impacts of metal mining in a few African and Asian countries, and the need to curb illegal trade and introduce certification processes was repeatedly advocated (e.g., refs 56−58).

This raises the concern that the current increasing use of several toxic metals (including Pb) in electronic devices and the transition to low-carbon energy production may soon be reflected in elevated concentrations of these metals in humans, predominantly in those that are not fortunate enough to live in regulated and monitored regions. This also strengthens the case that increased use of metals should go hand in hand with augmented industrial hygiene, maximum metal recycling, and the consideration of environmental and toxicological aspects in the selection of metals for industrial use.[59,60]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c00614.

Table S1, sample names, age, and Ca, Li, Na, Mg, Al, K, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Ag, Cd, Sn, Ba, and Pb concentrations (XLSX)

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Author Contributions

Y.E., R.P., and L.C. designed and supervised the study; Y.E., O.T., and A.T. performed and supervised laboratory work; A.C. designed collection strategy for archeological material; A.C. and R.P. assembled archeological material and advised on historical background and interpretation; Y.E. and L.C. analyzed data with input from O.T. and A.T.; and Y.E. and L.C. wrote the manuscript with input from all coauthors.

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Notes

The authors declare no competing financial interest.

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