

# Ultrapurification of Archaeological Lead<sup>1</sup>

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**Abstract**—Based on purification efficiency calculations for lead distillation, we developed a combined process for the ultrapurification of archaeological lead. We obtained pilot amounts of high-purity archaeological lead and PbO with the following contents of detrimental impurities: U, <2 ppb; Th, <1 ppb; Ni, Cu, Fe, Si, Ti, Mg, Al, Mn, Cr, V, Co, <0.1 ppm; K, Ca, Zn, Cd, Ag, Sb, <1 ppm. Lead of such purity can be used in low-background experiments as a protective shield material and in the growth of low-background PbWO<sub>4</sub> and PbMoO<sub>4</sub> scintillator crystals. From an isotope ratio, we were able to identify the origin of the archaeological lead.

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## INTRODUCTION

Studies of the nature of dark matter in the universe and the properties of the neutrino are among the key fundamental issues in modern cosmoastrophysics [1].

The fundamental properties of the neutrino can be understood by investigating neutrinoless double beta decay [2–6], which requires an extremely low detector background, approaching zero.

Radioactive contamination of structural materials and, particularly, of the detector should not exceed 10<sup>-7</sup> to 10<sup>-5</sup> Bq/kg. The radioactive background must also be low in studies of solar and reactor neutrinos, rare alpha- and beta-decays, etc. [7–9]. The choice of the detector material and careful purification of raw materials will ensure a reduction in the effect of internal radioactivity.

Lead is an excellent shielding material. At the same time, it contains the radioactive isotope <sup>210</sup>Pb, whose activity may reach tens and even thousands of Bq/kg. The half-life of <sup>210</sup>Pb is 22.3 years. Therefore, the activity of lead produced hundreds of years ago may be very low. Archaeological lead contains very little <sup>210</sup>Pb [10–12].

Attractive low-temperature detectors for double beta decay and other rare events [13, 14] are PbMoO<sub>4</sub> and PbWO<sub>4</sub> scintillator crystals. The starting lead oxide for the synthesis of PbWO<sub>4</sub> and PbMoO<sub>4</sub> should have not only high radioactive purity but also very low contents of other impurities.

The objectives of this work were to study the behavior of impurities in lead during distillation, to develop a combined procedure for the purification and preparation of radiopure lead from archaeological material and determine its origin, and to select conditions for producing high-purity lead oxide from purified archaeological lead.

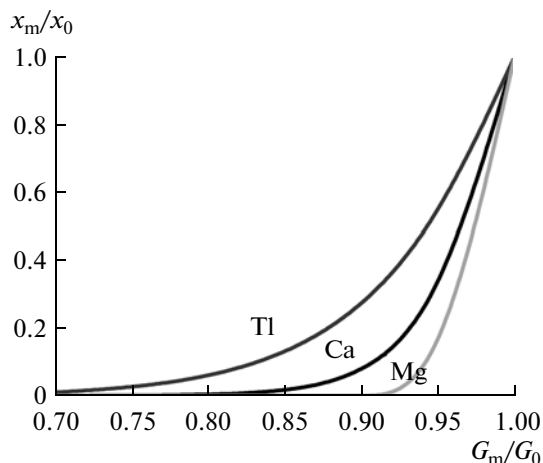
## CALCULATIONAL APPROACH AND EXPERIMENTAL

**Evaluation of the efficiency of lead distillation in vacuum.** A procedure for the purification of archaeological lead should meet stringent requirements. The loss of the valuable, expensive parent material should be minimized, and the yield of purified material should be maximized. The content of a number of transition metals (Cr, Mn, Fe, Co, Ni, and others) should be <1 ppm.

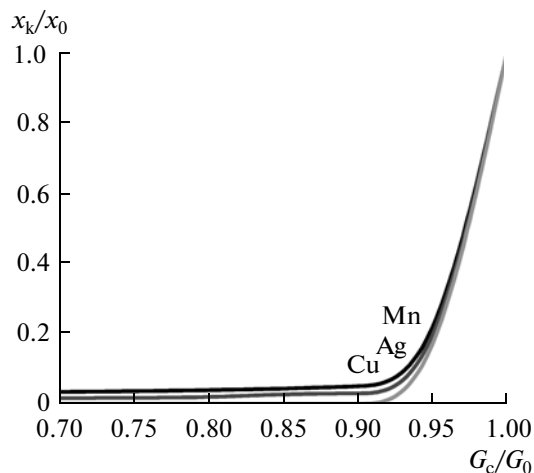
To evaluate the efficiency of lead distillation in vacuum and adjust the temperature and duration of the process, we calculated the thermodynamic partition coefficients of impurities ( $\alpha_i$ ) at the lead distillation and condensation temperatures and plotted the efficiency of melt purification against the weight of the metal and the degree of purification of the condensate against percent distilled.

According to their  $\alpha_i$ , the impurities in lead can be divided into highly volatile (Se, Zn, Te, Mg, Sr, Ba, Tl, Bi, Ca, Sb, and others), with  $\alpha_i \sim 10^{-5}$  to  $10^{-2}$ , and low-volatile (Mn, Ag, Al, Ni, Co, Cu, Sn, Si, Cr, Fe, U, and others), with  $\alpha_i \sim 10^2$  to  $10^9$ . For most elemen-

<sup>1</sup> Ballast from a Greek ship sunk near the southern coast of Crimea in the Black Sea in the first century BC.



**Fig. 1.** Calculated Tl, Ca, and Mg contents in molten Pb against residual fraction at 1000 K:  $\beta(\text{Tl}) = 14.08$ ,  $\beta(\text{Ca}) = 28.57$ ,  $\beta(\text{Mg}) = 2857$  (calculation formula, see text).



**Fig. 2.** Calculated Mn, Ag, and Cu contents in Pb condensate against fraction distilled at 1200 K:  $\beta(\text{Mn}) = 0.02$ ,  $\beta(\text{Ag}) = 0.004$ , and  $\beta(\text{Cu}) = 0.00003$  (calculation formula, see text).

tal impurities,  $\alpha_i$  differs significantly from unity, which ensures efficient purification.

The efficiency of lead purification was assessed using simplified equations for distillation at low impurity concentrations [15]. As an example, Fig. 1 plots the calculated melt purification efficiency ( $x_m/x_0$ ) against weight change ( $G_m/G_0$ ) at 1000 K for Tl, Ca, and Mg, and Fig. 2 plots the degree of condensate purification ( $x_c/x_0$ ) against fraction distilled ( $G_c/G_0$ ) at 1200 K for Mn, Ag, and Cu.

The ratios  $x_m/x_0$  and  $x_c/x_0$  were determined as

$$x_m/x_0 = (G_m/G_0)^{\beta-1}$$

and

$$x_c/x_0 = \frac{(1 - G_c/G_0)^\beta}{G_c/G_0},$$

where  $x_0$  is the initial impurity content of the melt,  $x_m$  and  $x_c$  are the final impurity contents of the melt and condensate (wt %),  $G_0$  is the initial melt weight,  $G_m$  and  $G_c$  are the final weights of the residue and condensate, and  $\beta = 1/\alpha_i$ .

Calculations indicate that the removal of highly volatile impurities from molten Pb through vaporization will be efficient for impurities with  $\alpha_i < 10^{-2}$ . For example, to reduce the Mg content of Pb by an order of magnitude, no more than 5% of the charge should be evaporated. The removal of low-volatile impurities by lead distillation will be efficient for  $\alpha_i > 5 \times 10^1$ . In particular, to reduce the Mn, Ag, and Cu concentration in lead condensate by one order of magnitude, the percent distilled may exceed 90%. These data were taken into account in selecting distillation conditions and designing the distillation apparatus.

**Lead purification, oxide synthesis, and analytical techniques.** To ensure lead ultrapurification, we used molten metal filtration followed by distillation with vapor condensation at a temperature close to the distillation temperature [16]. The distillation apparatus was made from MPG-7 high-purity, dense graphite, with a very low impurity content, nonreactive with lead.

Evaporation of 95% of the lead from the crucible ensures the removal of low-volatile impurities, which remain in the residual melt in the crucible. Highly volatile impurities arrive at a heated condenser together with the host. Since the condenser and metal are maintained at an elevated temperature during purification, the highly volatile impurities vaporize and leave the condenser through special holes. Thus, in this purification procedure, low- and high-volatile impurities are removed simultaneously, which raises the process rate and the yield to specification.

The purified metal was converted to PbO by dissolving the metallic lead in 20% HNO<sub>3</sub>, followed by neutralization of the acid solution with ammonia gas until complete Pb(OH)<sub>2</sub> precipitation (pH 10–11). After calcination in a muffle furnace at 300°C, the precipitate had the form of yellow PbO powder.

The elemental composition of the lead and the purity of the oxide were determined by inductively coupled plasma mass spectrometry (ICP-MS)<sup>2</sup>. In addition, impurity concentrations were determined by laser mass spectrometry (LMS)<sup>3</sup>.

**Identification of the origin of the archaeological lead.** To this end, we used the isotope dilution tech-

<sup>2</sup> Mass spectra were taken at the Gran Sasso National Laboratory (GSNL) (Italy) and at the Semenenko Institute of Geochemistry, Mineralogy, and Ore Formation (IGMOF), National Academy of Sciences of Ukraine.

<sup>3</sup> Impurity concentrations were determined at the Kharkov Institute of Physics and Technology (KIPT), National Academy of Sciences of Ukraine.

**Table 1.** Isotopic composition and isotope ratios in archaeological lead samples

Sample	$^{204}\text{Pb}$	$^{206}\text{Pb}$	$^{207}\text{Pb}$	$^{208}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
	Isotopic composition				Isotope ratios		
<i>A</i>	1.348(7)	25.398(7)	21.086(7)	52.168(15)	18.830(5)	15.633(5)	38.677(5)
<i>B</i>	1.348(8)	25.388(8)	21.083(8)	52.180(15)	18.838(6)	15.644(6)	38.717(6)
<i>C</i>	1.347(4)	25.371(5)	21.071(5)	52.211(12)	18.832(2)	15.640(3)	38.754(3)

**Table 2.** Main elemental impurities in archaeological lead before and after refining and in PbO prepared from refined archaeological lead

Element	Content, ppm						
	before refining		after refining			PbO	
	ICP-MS	LMS	ICP-MS		LMS	ICP-MS	ICP-MS
	GSNL	KIPT	GSNL	KIPT	GSNL	KIPT	IGMOF
Mg	<1	0.09	<5	–	<0.04	<5	–
Al	<1	1.5	<1	–	0.04	<1	–
Si	<25	1.0	<25	0.4	0.08	<25	0.15
K	<10	0.5	<10	–	0.3	<10	–
Ca	<5	0.6	<5	–	0.3	<5	–
Ti	<0.5	<0.09	<0.5	–	<0.09	<0.5	–
V	<0.01	<0.07	<0.01	–	<0.07	<0.01	–
Cr	<0.1	<0.09	<0.1	–	<0.09	<0.1	–
Mn	<0.05	<0.08	<0.05	–	<0.08	0.1	–
Fe	<10	<0.09	<10	0.14	<0.09	<10	0.2
Co	<0.01	<0.09	<0.01	0.002	<0.09	<0.02	0.002
Ni	<0.1	<0.2	<0.1	0.014	<0.09	<0.1	0.04
<b>Cu</b>	<b>200</b>	<b>6</b>	<b>0.3</b>	<b>0.4</b>	<b>&lt;0.1</b>	<b>&lt;0.2</b>	<b>0.03</b>
Zn	<0.3	3	<0.3	2	<0.2	<0.3	4
<b>Ag</b>	<b>80</b>	<b>30</b>	<b>0.7</b>	<b>0.08</b>	<b>&lt;0.6</b>	<b>&lt;0.2</b>	<b>0.02</b>
Cd	<0.05	5	<0.05	–	<0.8	<0.05	–
Sn	–	<0.08	–	0.03	<0.08	–	0.02
<b>Sb</b>	<b>230</b>	<b>5</b>	–	<b>0.01</b>	<b>&lt;0.6</b>	–	<b>0.005</b>
Th (ppb)	<2	–	<1	–	–	<1	–
U (ppb)	<1	–	<2	<2	–	<1	<1

nique, which is employed in dating minerals and rocks.<sup>4</sup>

Lead isotope methods for dating minerals take advantage of radioactive conversion of uranium and thorium into stable lead isotopes, which results in wide variations in the isotopic composition of the lead. Depending on the uranium and thorium concentration in the starting ore and on its geological age, the  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios have particular values, characterizing the occurrence [17, 18]. To recover

lead with the minimum possible impurity content, we used ion-exchange chromatography by a procedure designed for recovering lead and uranium from zircon [19]. The analytical results for three lead sample from ingots *A*, *B*, and *C* (see [12]) are presented in Table 1.

## RESULTS AND DISCUSSION

The contents of elemental impurities in the archaeological lead before and after purification and in the lead oxide, are listed in Table 2.

The impurity concentrations in the purified lead are below the detection limits of the analytical techniques used:  $< 1 \times 10^{-8}$  ppm for Rb, Y, Zr, Nb, Ru, Pt,

<sup>4</sup> The isotopic composition of the archaeological lead was determined at the Radiogeochronology Department, Semenenko Institute of Geochemistry, Mineralogy, and Ore Formation, National Academy of Sciences of Ukraine.

and Au;  $< 1 \times 10^{-7}$  ppm for Sc, In, and Te; and  $< 1 \times 10^{-6}$  ppm for Se and Pd.

It follows from Table 2 that the purity of the archaeological lead is 99.94+ wt %, which corresponds to S2 commercial lead (RF State Standard GOST 3778-98). After purification, the purity is 99.9996+ wt %. This corresponds to S000 high-purity lead (RF State Standard GOST 22861-93).

The major impurities in the archaeological lead were Cu, Sb, and Ag. Refining markedly reduced their concentrations, by more than a factor of 10–500. The K and Ca contents were below the detection limit of ICP-MS analysis. According to LMS, it was 0.3 ppm.

It follows from Table 2 that the composition of the lead oxide was not impaired in comparison with the purified Pb. The Cu and Ag concentration even decreased, which can be accounted for by the solubility of the copper and silver ammonia complexes that were formed during the neutralization of the lead nitrate solution in nitric acid with ammonia. The lead oxide obtained corresponds to the requirements for the purity of starting materials for the crystal growth of lead tungstate and lead molybdate scintillators.

Comparison of the present results with known isotope ratios in different antique occurrences [17, 18] indicates that the lead under investigation was extracted from silver–lead ores on Mount Lavrion (Attica, 40 km south-west of Athens). Note that the  $^{210}\text{Pb}$  activity in the Greek lead is  $< 0.2\text{--}0.9$  mBq/kg [12], which is orders of magnitude lower than that in special, low-radioactivity lead [10, 11].

## CONCLUSIONS

Archaeological lead with a low radioactive contamination level ( $^{40}\text{K}$ ,  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$ , and  $^{228}\text{Th}$  activity on the order of 1 mBq/kg) is the best material for the fabrication of passive protection in low-background systems and for the crystal growth of  $\text{PbWO}_4$  and  $\text{PbMoO}_4$  scintillators.

We obtained a pilot amount of archaeological lead of 99.9996+ % purity, with an upper limit of the concentrations of major elements at a level of  $< 0.1\text{--}1$  ppm. The purified lead was converted to PbO for the growth of low-background lead tungstate and lead molybdate scintillator crystals with a residual activity of  $< 10^{-5}$  Bq/kg.

The  $^{204}\text{Pb}/^{206}\text{Pb}$  ratio determined by mass spectrometry leads us to assume that the archaeological lead was extracted from silver–lead ores on Mount Lavrion (Attica, Greece).

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