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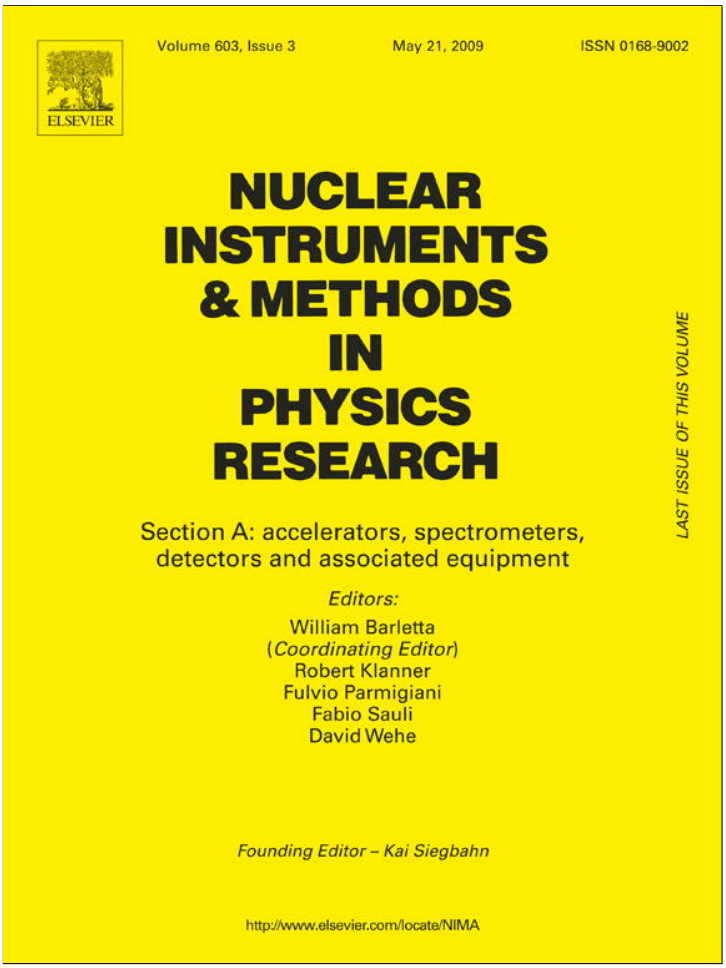

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Ancient Greek lead findings in Ukraine

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ABSTRACT

In June–August 2006 an expedition with the aim to look for archaeological lead with low levels of ^{210}Pb was organised by a Korean–Ukrainian collaboration on the shelf of the Black Sea, near the Crimean Peninsula. The first samples with ~0.2 ton of total mass were found at a depth of 28 m among the relics of an ancient Greek ship. Their age has been dated to the first century BC. The element composition of the samples was measured by means of X-ray fluorescence and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analyses. The radiopurity of the lead was tested using low-level and ultra-low-level γ-spectrometry at a surface laboratory in Kyiv, at the Solotvina Underground Laboratory (Ukraine), and deep underground at the Laboratori Nazionali del Gran Sasso (LNGS, Italy). The samples have been assessed at the LNGS also by means of α-spectroscopy. For all investigated radionuclides, only upper limits could be obtained. Limits on activities of radionuclides in the lead after melting were set at the level of $<(0.2–0.3)\,mBq\,kg^{-1}$ (^{60}Co), $<(0.2–0.7)\,mBq\,kg^{-1}$ (^{137}Cs), $<(0.2–0.9)\,mBq\,kg^{-1}$ (^{226}Ra), $<(0.1–0.9)\,mBq\,kg^{-1}$ (^{228}Th), $<(5–7)\,mBq\,kg^{-1}$ (^{40}K), $<(0.3–1.4)\,Bq\,kg^{-1}$ (^{210}Po), and $<(12–13)\,Bq\,kg^{-1}$ (^{210}Pb). Any ^{210}Pb present in the lead after it was produced ca. 2000 years ago has decayed away. Assuming secular equilibrium in the ^{238}U chain in the lead, the activity of ^{210}Pb due to ^{238}U can be restricted to $<(5–17)\,mBq\,kg^{-1}$ before melting, and $<(0.2–0.9)\,mBq\,kg^{-1}$ after melting.

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1. Introduction

Many important fundamental problems still have to be solved by modern physics. Two of the main interesting questions are the explanation of dark matter in the Universe [1] and the determination of the nature of the neutrino. Dark matter particles can manifest itself through interaction with ordinary matter, which would result in nuclear recoil [2]. Fundamental neutrino properties can be revealed from the studies of neutrinoless double β-decay [3]. Experiments to search for both the processes require ultra low levels of background in the experimental set-up. Current dark matter projects call for a background counting rate lower than a few events per keV per 100 kg per year at energies of a few keV [4]. Double β-decay experiments, in order to explore the inverted hierarchy of neutrino mass, need counting rates of the same level at energies of 2–3 MeV [3]. Apart from these extremely rare processes, there is a range of problems, where low levels of radioactive background of a detector are required. Some examples are the investigation of solar neutrinos, the study of rare α- and β-decays, the measurement of natural radioactivity in environmental samples, neutron activation analysis, the search for hypothetical processes like Pauli principle violation, etc. (see, e.g. Refs. [5,6]).

In order to detect such processes, one must reduce both external and intrinsic background of the experimental set-up. The background due to cosmic rays can be efficiently suppressed by operating deep underground. Selecting the materials of the detector can reduce the effect of the intrinsic radioactivity. A massive shield made of radiopure materials efficiently reduces the external background caused by γ-rays of environmental radioactivity. Oxygen-free high conductivity copper (OFHC) is one of the purest materials used for passive shielding. However, copper, irradiated at the Earth's surface by cosmic rays and/or neutrons, may contain cosmogenic radionuclides (e.g. ^{60}Co, ^{54}Mn) [7]. Lead,

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thanks to its high Z, reasonable cost, good mechanical properties, and low activation cross-section for neutrons, is also an excellent shielding material. The main problem of recently produced lead is its high activity (tens–thousands Bq kg^{-1}) in the radioactive isotope ^{210}Pb. As an example, about half of the counting rate in the low-energy region (up to ~1 MeV) in the spectra obtained in the Heidelberg–Moscow experiment [7] is due to internal bremsstrahlung. It comes from the β-decay of ^{210}Bi (daughter of ^{210}Pb, $Q_\beta = 1162$ keV) notwithstanding the fact that a shielding of modern radiopure lead was used. ^{210}Pb is a daughter product in the ^{238}U decay chain, which is present in all rocks and ores. During the melting of the ore, ^{210}Pb concentrates in the metal lead, while all other long-lived nuclides of the ^{238}U decay chain (^{238}U, ^{234}U, ^{230}Th, ^{226}Ra) are chemically very different and are removed to the slag. Because of its half-life of 22.3 years, the activity of ^{210}Pb decreases with time. It can be low in lead produced a long time ago (hundreds of years), depending obviously on the starting activity. In ancient lead, as shown in Refs. [8–11], ^{210}Pb is almost totally absent.

Another reason to have radiopure lead is the possibility to grow radiopure crystal scintillators as lead molybdate ($PbMoO_4$) and lead tungstate ($PbWO_4$). $PbMoO_4$ can be applied as a low-temperature detector to search for double β-decay of ^{100}Mo [12,13]. $PbWO_4$ crystals can be used as active shield detectors and as light-guide for other scintillation crystals, detectors for rare processes. For instance, $PbWO_4$ was proposed in Ref. [14] as an active shield and light-guide for cadmium tungstate ($CdWO_4$) scintillators to search for double β-decay of ^{116}Cd. Radiopure $PbWO_4$ and $PbMoO_4$ crystal scintillators are promising target materials for cryogenic dark matter experiments, as for instance the EURECA project [4,15] where a multi-element target is planned in the search for a dark matter.

The aim of our work was to study the level of purity and radioactive contamination of ancient lead samples discovered at the bottom of the Black Sea, near the Crimean Peninsula in Ukraine. Preliminary results of this project were already reported in Ref. [16].

2. Samples of ancient lead

From June to August 2006, an underwater expedition was organised by a Korean–Ukrainian collaboration with the aim to look for archaeological lead at the bottom of the Black Sea near the Crimean Peninsula, where a few Greek poleis existed 2–2.5 thousands years ago. This work was realised in collaboration with the Department of the Underwater Heritage of the Institute of Archaeology in Kyiv (Ukraine). The first three samples (see Fig. 1) with a total mass of ~0.2 ton have been found at a depth of 28 m among the relics of a sunken Greek ship.

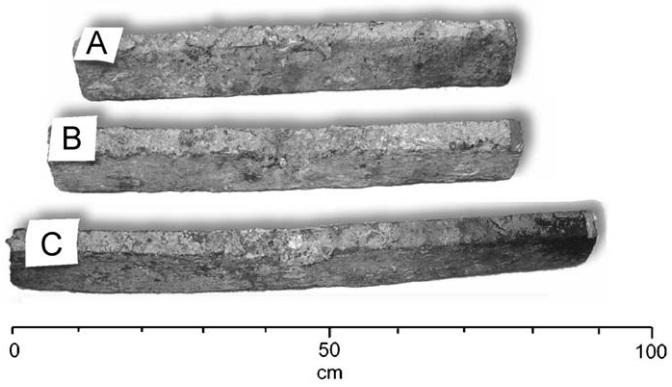

Fig. 1. Three pieces of lead of the ballast of a Greek ship sunken in first century BC near the Crimean peninsula.

The age of the lead was preliminary determined to be originating from the first century BC by analysing fragments of amphorae and other subjects located near the ship. The shape of the lead samples indicates that they were used as parts of the ballast of the ship that had ≈30 m length. Therefore, the remaining pieces of the ballast are expected to be in the sediment around. The amount of the remnant lead can be estimated to ~1 ton. There exist several other ancient sunken ships near Crimea.

3. Cleaning and melting of the lead pieces

The samples were cleaned with a metallic brush in order to remove all surface pollution and stratification. Then the samples were cut into portions with a mass of about 10–15 kg, etched in high-purity nitric acid, and thoroughly rinsed with bi-distilled water.

The melting procedure consisted of two stages. In the first step, the lead was melted in the oven inside a quartz crucible. Dirt was removed from the surface of the melt with the help of a stainless steel spoon covered with polytetrafluoroethylene (PTFE) tape. This removed different pollution and inclusions (stones[1], sand, etc.) from the lead. In the second step, the melted lead was poured into a PTFE container. The second melt was then carried out in a closed stainless steel crucible and poured into a stainless steel fill-out form in order to obtain bricks with a size of 5 cm × 10 cm × 20 cm. The different samples (A, B, and C) were melted separately. During all the stages of work the pieces of the lead were packed into polyethylene in order to avoid pollution with dust. The bricks of the lead were vacuum-packed with polyethylene sheets and placed in plywood cases for storage. Dedicated samples for X-ray fluorescence, mass spectrometry, α- and γ-spectrometry were prepared from the samples before and after melting.

4. Contamination of the lead samples

4.1. X-ray fluorescence analysis

Chemical impurities play an important role, when lead is used for passive shield, because they could have large cross-sections for neutron capture or cosmic-ray activation. Some elements, especially transition metals, are particularly undesirable when growing $PbWO_4$ and $PbMoO_4$ crystal scintillators. The element composition of the lead samples before and after melting was checked by X-ray fluorescence analysis. A Philips X'Unic II spectrometer was used for this purpose. The results of the measurements are presented in Table 1.

4.2. Mass spectrometry

4.2.1. Measurements of impurities

The Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis of the samples, before and after melting, was performed at the LNGS. A mass spectrometer of Agilent Technologies®, model 7500a, was used. About 0.2 g of each sample was completely dissolved in 10 ml of 5% HNO_3 solution, for 1 h in an ultrasonic bath at 70 °C. The obtained solutions were diluted 20

[1] We have found a few stones inserted into the lead that had not been visible from outside. Special efforts had to be undertaken to sink the stones into the heavy lead liquid. One could suppose that this was done on purpose (e.g. to "save" material, as lead was relatively expensive).

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Table 1
The elemental composition (%) of the three lead samples analysed by X-ray fluorescence analysis before/after melting.

Element	Sample A	Sample B	Sample C
Pb	99.8/99.8	99.8/99.8	99.8/99.8
Cu	0.15/0.08	0.11/0.07	0.08/0.06
Ag	<0.006/<0.006	<0.006/<0.006	0.03/0.02
Sb	<0.004/<0.004	<0.004/<0.004	0.07/0.04

Table 2
Element composition (in units of 10^{-6} g/g) of ancient Greek lead determined by ICP-MS analysis at the LNGS before/after melting.

Element	Sample A	Sample B	Sample C
Mg	1.2/<1	1.5/<1	1.1/<1
Al	1.2/<1	1.0/<1	1.1/<1
K	<10/<10	<10/<10	<10/<10
Ca	4.7/<3	3.9/<3	3.1/<3
Fe	<10/<10	<10/<10	<10/<10
Ni	4.3/11	9.1/13	1.0/1.5
Cu	130/380	330/510	180/200
As	<0.1/0.4	<0.1/0.6	95/51
Mo	<5/<5	<5/<5	<5/<5
Ag	16/39	38/44	99/78
Sb	8.2/3.9	15/7.4	330/230
Th	<0.01/<0.002	<0.01/<0.002	<0.01/<0.002
U	<0.01/<0.001	<0.01/<0.001	<0.01/<0.001

times before measurement. The measurements were carried out in the semi-quantitative mode, i.e. the uncertainty is of the order of 10–20%. The results are reported in Table 2. Concentration limits were evaluated assuming natural isotopic composition.

The concentration of other elements in the ingots was below the sensitivity level: for V, Mn, Co, Zn, Rb, Y, Zr, Nb, Ru, Pt, Au $<1\times10^{-8}$ g/g; for Sc, Cr, In, Sn, Te, Ba $<1\times10^{-7}$ g/g; and for Se, Pd, Cd $<1\times10^{-6}$ g/g.

As can be seen, the lead contains mainly Cu, Ag, and Sb (Tables 1 and 2). The contamination of sample C is particularly different in Ni, As, and Sb from samples A and B. Taking into account that this sample is also different in shape and dimension, one could suppose that it is of different origin (made of a different kind of ore). It was added to the ballast of the ship maybe at a later moment.

The concentrations of Ni and Cu show a slight increase after the melting. We cannot exclude contamination of the lead during the melting process (for instance, due to the use of a stainless steel crucible). However, the systematic uncertainties of the ICP-MS are rather large, so that this increase might not be a real effect.

As regards radionuclides, the limit on the natural potassium concentration of $<10^{-5}$ g/g corresponds to a limit in the ^{40}K activity of <0.3 Bq kg^{-1}. This limit is two orders of magnitude worse than that was obtained by ultra-low-background γ-spectrometry. The concentrations of Th ($<2\times10^{-9}$ g/g) and U ($<10^{-9}$ g/g) correspond to activities of <8 mBq kg^{-1} (^{232}Th) and <12 mBq kg^{-1} (^{238}U), respectively. These numbers are valuable as they give a direct estimate of the concentrations of these radionuclides. γ-Spectrometry cannot measure directly ^{238}U and ^{232}Th, but only their daughters ^{234}Th+^{234m}Pa and ^{228}Ac, respectively, which could not be in equilibrium with their parent isotopes after the melting of lead (see Section 5.3 where results of ultra-low-background γ-spectrometry are presented).

4.2.2. Isotopic composition of the ancient lead

To identify the lead-mining region where the lead is originating from, the isotopic abundance could be very important. The ICP-MS instrument used in this work is not designed for precision measurements of the isotopic ratios, and the accuracy is usually not better than 0.5%. Nevertheless, the lead isotopic abundance has been measured and is reported in Table 3. The recommended natural isotopic composition of lead [17] is also given for comparison. The isotopic composition of the Greek lead is equal to the average natural one within measured uncertainties.

Table 3
Isotopic composition (%) of ancient lead samples determined by ICP-MS analysis.

Pb isotope	Sample A	Sample B	Sample C	[17]
^{204}Pb	1.5(5)	1.4(5)	1.5(5)	1.4(1)
^{206}Pb	24.2(5)	24.3(5)	24.2(5)	24.1(1)
^{207}Pb	21.6(5)	21.4(5)	21.7(5)	22.1(1)
^{208}Pb	52.7(5)	52.9(5)	52.6(5)	52.4(1)

5. Radiopurity measurements

5.1. Low-level γ-spectrometry

The measurements were performed using a low-background high-purity germanium (HPGe) γ-spectrometer (ORTEC® GWL-100/210, well-type) in the Institute for Hydrometeorology Research (Kyiv, Ukraine). It is difficult to detect the presence of a tiny contamination of ^{210}Pb by means of γ-spectrometry because of the low yield (4.25%) of the only γ-line emitted. Moreover, the γ-quanta have low energy (46.5 keV), which results in a low detection efficiency due to self-absorption in the sample and the absorption in the end-cap and the dead layer of the detector. Samples A, B, and C (with masses of 4.77, 3.56, and 3.50 g, respectively) were assessed in the form of cylinders with a thickness of ~0.4 mm. They were measured in the experimental set-up located in a basement of building for about 60 h each. The full energy peak (FEP) detection efficiency for the 46.5 keV γ-quanta was calculated using the GEANT4 package [18]. It ranged from 3% to 5% depending on the sample. No evidence of any radioactivity could be seen in all the measured spectra. Thus only upper limits on the radioactive contamination by ^{210}Pb as well as for ^{40}K, ^{60}Co, ^{137}Cs, ^{228}Th were determined. They are listed in Table 4. The measurements were made in order to have a first rough estimate of lead radiopurity.

5.2. Low-background measurements with a large-volume $CdWO_4$ scintillation detector

The radioactive contamination of the lead samples before and after the melting was measured in the low-background set-up installed in the Solotvina Underground Laboratory (Ukraine, depth of 1000 m water equivalent). In the set-up, a scintillation $CdWO_4$ crystal ($\varnothing70\,\text{mm}\times70\,\text{mm}$) was connected to a special low-radioactive 5 in. photomultiplier tube (EMI D724KFLB) through a high-purity quartz light-guide ($\varnothing100\,\text{mm}\times330\,\text{mm}$). A passive shield made of PTFE (thickness of 3–5 cm), Plexiglas (6–13 cm), high-purity copper (3–6 cm), lead (15 cm), and polyethylene (8 cm) surrounded the detector. Energy scale and resolution of the detector were determined in calibration runs with a ^{207}Bi γ-source. The energy resolution of the detector was 16.0%, 14.4%, and 13.3% for γ-quanta of the ^{207}Bi source at the energies of 570, 1064, and 1770 keV, respectively. Three samples with a mass of ≈1 kg were placed on the $CdWO_4$ detector. The time of measurement was in the range of 46–62 h. The detection efficiency of the detector was calculated using the GEANT4 code

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Table 4
Upper limits (given with $k = 1$, ca. 68% confidence level) of the concentration of selected radionuclides in the ancient Greek lead before melting obtained from measurements by low-level HPGe γ-spectrometry in the Institute for Hydrometeorology Research.

Isotope	Activity (Bq kg^{-1})		
	Sample A	Sample B	Sample C
^{210}Pb	$\leqslant$77	$\leqslant$37	$\leqslant$15
^{40}K	$\leqslant$22	$\leqslant$20	$\leqslant$13
^{60}Co	$\leqslant$1.2	$\leqslant$1.1	$\leqslant$0.9
^{137}Cs	$\leqslant$1.2	$\leqslant$1.1	$\leqslant$0.8
^{228}Th	$\leqslant$0.9	$\leqslant$3.3	$\leqslant$0.3

Table 5
Upper limits (given with $k = 1$, ca. 68% confidence level) of the concentration of selected radionuclides in the ancient Greek lead before/after melting measured by scintillation γ-spectrometry in the Solotvina Underground Laboratory.

Nuclide	Activity (mBq kg^{-1})		
	Sample A	Sample B	Sample C
^{228}Th	$<22/<21$	$<31/<23$	$<27/<25$
^{226}Ra	$<90/<120$	$<130/<120$	$<110/<160$
^{40}K	$<310/<210$	$<320/<220$	$<380/<120$

Table 6
Upper limits (given with $k = 1.645$, ca. 90% confidence level) of the concentration of selected radionuclides in the ancient Greek lead before/after melting obtained via γ-spectroscopy at the LNGS.

Chain	Nuclide	Activity (mBq kg^{-1})		
		Sample A	Sample B	Sample C
^{232}Th	^{228}Ra	$<16/<0.44$	$<13/<0.40$	$<18/<0.56$
	^{228}Th	$<20/<1.1$	$<11/<0.46$	$<13/<0.14$
^{235}U	^{235}U	$<19/<6.4$	$<12/<5.1$	$<13/<6.7$
^{238}U	^{234m}Pa	$<460/<21$	$<690/<13$	$<650/<25$
	^{226}Ra	$<17/<0.87$	$<12/<0.37$	$<4.8/<0.24$
	^{210}Pb	$<66\,000/<13\,200$	$<85\,000/<12\,900$	$<36\,000/<12\,400$
	^{40}K	$<129/<7.0$	$<173/<4.7$	$<239/<5.9$
	^{60}Co	$<7.5/<0.22$	$<6.0/<0.26$	$<5.9/<0.31$
	^{137}Cs	$<7.0/<0.24$	$<3.9/<0.38$	$<7.3/<0.68$

[18] and the event generator DECAY0 [19]. In the energy spectrum of the detector there are no peaks that could be attributed to γ-activity of ^{40}K, ^{226}Ra, and ^{228}Th. Therefore, only upper limits for the activity of these radionuclides in the lead samples were determined. They are reported in Table 5.

5.3. Ultra-low-level γ-spectrometry

Three samples of the lead (before melting), each in the form of a disk ($\varnothing$ 50 mm $\times$ 0.5 mm), were measured in the LNGS underground laboratories (average overburden of 3500 m water equivalent) [5,6] with a p-type HPGe detector (468 cm^3, 120% efficiency relatively to a 3 in. $\times$ 3 in. NaI(Tl)). This detector has a rather thin Cu window of 1 mm thickness. The spectra were measured for 326 h (sample A, 8.4 g), 395 h (sample B, 9.5 g), and 324 h (sample C, 9.8 g). The samples were positioned directly on the end-cap of the detector. The detection efficiency of the detector was calculated using the GEANT4 code [18]. The upper limits found for the concentration of selected radionuclides are listed in Table 6.

Table 7
Upper limits (given with $k = 1.645$, ca. 90% confidence level) of the activity concentration of ^{210}Po in ancient Greek lead before/after melting, obtained via α-spectrometry at the LNGS (values are given in Bq kg^{-1}).

Sample A	Sample B	Sample C
$<0.36/<0.25$	$<0.48/<0.45$	$<0.27/<1.4$

In a later stage, three samples of the lead after the melting were measured again with the same HPGe detector. Data were accumulated over 467 h with a sample of lead A (877 g), over 500 h with sample B (775 g), and over 460 h with sample C (899 g). The results are again summarised in Table 6. It should be stressed that the GeCris detector was developed for effective measurements of middle- and high-energy γ-quanta. This explains the relatively low sensitivity at the low-energy γ-line of ^{210}Pb. The worse sensitivity achieved for the lead samples before melting is due to the smaller mass of the samples ($\approx$8–10 g) compared with the samples of the lead after melting ($\approx$0.8–0.9 kg).

5.4. Low-background α-spectrometry

The α-activity of the lead was measured in the LNGS using commercial counting devices from CANBERRA/EURYSIS® and ORTEC®, each equipped with a Passivated Implanted Planar Silicon (PIPS) detector of 1200 and 900 mm^2 active surface, respectively. The spectra showed no positive signal for ^{210}Po and allowed deriving upper limits for the intrinsic ^{210}Po contamination of the lead. The results are listed in Table 7.

6. Discussion

The radiopurity of the ancient Greek lead satisfies the requirements for present-day ultra-low-level spectrometry as material for passive shielding. At the same time the direct sensitivity to ^{210}Pb is not high enough, due to obvious constrains in the measurement techniques used. However, assuming secular equilibrium of the ^{238}U decay chain in the lead, the activity of ^{210}Pb can be restricted using the limit on the activity of ^{226}Ra, $<$(5–17) mBq kg^{-1} before melting, and $<$(0.2–0.9) mBq kg^{-1} after melting. This is a much stronger limit than the one obtained via direct measurements. It should be emphasised, however, that such an assumption looks valid before the melting process because of the greater age of the lead samples, while one can suppose again a breaking of the secular equilibrium in the U chain after melting. In the latter case both the activity of ^{210}Pb and of ^{226}Ra could occasionally increase due to pollution, for instance, by Rn, dust from air, etc. Similarly the activity of ^{232}Th can be constrained to $<$(11–20) mBq kg^{-1} before, and $<$(0.1–1) mBq kg^{-1} after melting. The γ-spectroscopic measurements show that ^{228}Ra and ^{228}Th are in equilibrium. As ^{232}Th should behave chemically in the same way as ^{228}Th, no future increase in ^{228}Ra is to be expected. Much higher sensitivity to ^{210}Pb can be reached by using radiochemical separation of ^{210}Po and low-background α-spectroscopy. In this way the limit on ^{210}Pb activity could be improved by at least two orders of magnitude. R&D to develop such a technique is in progress at the Laboratori Nazionali del Gran Sasso.

We hope to reach much higher sensitivity to the different radionuclides, and first of all to ^{210}Pb directly, doing measurements with $PbWO_4$ crystal scintillators, which would act simultaneously as source and as detector (an example of such measurements can be found in Ref. [14]).

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However, the chemical purity of the lead is far from the specifications for raw compounds used for growing $PbWO_4$ and $PbMoO_4$ crystal scintillators. In order to produce high-quality crystals, one should provide at least a 99.995% level of purity for raw compounds. For this purpose, in the Institute of Solid State Physics, Materials Science and Technologies (Kharkiv, Ukraine) the R&D work to purify the archaeological lead is in progress. A sample of lead of 1 kg weight was purified using vacuum distillation and filtration to the level of 99.999%. Only upper limits on the level of $0.1–1\times10^{-6}$ g/g were measured for a wide range of elements [20]. Such level of purity is sufficient to produce a high-quality raw compound for crystal growing. As a next step, together with the Institute for Scintillation Materials (Kharkiv, Ukraine), we will be growing $PbMoO_4$ and $PbWO_4$ crystal scintillators. They will allow measuring radioactivity concentrations in lead with a sensitivity on the level of $\mu Bq\,kg^{-1}$ [10].

7. Conclusions

Searches for ancient lead, which is known to have very low levels of ^{210}Pb impurity, were performed on the Black Sea shelf. Three samples of ancient Greek lead with a total mass of ~0.2 ton have been found near the Crimea Peninsula on the south shore at the depth of 28 m. They were dated to the first century BC. The total quantity of ancient lead expected in this region in the form of anchors and ballast can be estimated to several tons.

The chemical composition of the lead before and after melting was determined using X-ray fluorescence and ICP-MS analyses. The main impurities are Cu, Ag, Sb and Ni. Sample C showed differences in the chemical composition, in particular for As and Sb. The radiopurity of the lead, tested at a surface laboratory in Kyiv, at the Solotvina Underground Laboratory (Ukraine), and deep underground at the Laboratori Nazionali del Gran Sasso (Italy), satisfies the requirements of present-day ultra-low-level spectrometry set-ups as material for passive shielding. Only upper limits were found in the lead after melting for possible radioactive contaminants at the level of $<(0.2–0.3)\,mBq\,kg^{-1}$ (^{60}Co), $<(0.2–0.7)\,mBq\,kg^{-1}$ (^{137}Cs), $<(0.2–0.9)\,mBq\,kg^{-1}$ (^{226}Ra), $<(0.1–0.9)\,mBq\,kg^{-1}$ (^{228}Th), $<(5–7)\,mBq\,kg^{-1}$ (^{40}K), $<(0.3–1.4)\,Bq\,kg^{-1}$ (^{210}Po), and $<(12–13)\,Bq\,kg^{-1}$ (^{210}Pb). Assuming secular equilibrium of the ^{238}U decay chain in the lead, the activity of ^{210}Pb due to ^{238}U can be restricted to $<(5–14)\,mBq\,kg^{-1}$ before melting, and, with a caveat, $<(0.2–0.9)\,mBq\,kg^{-1}$ after melting.

The R&D work concerning radiopure $PbWO_4$ and $PbMoO_4$ crystal scintillators produced from the ancient lead is ongoing. Low-background measurements with such crystals as detectors could allow reaching sensitivity to internal radioactive contamination on the level of a few $\mu Bq\,kg^{-1}$.

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