Archaeological Lead Findings in the Ukraine

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Abstract. In June-August 2006 an expedition with the aim to look for low-radioactive archaeological lead at the bottom of the Black Sea, near the Crimean peninsula (Ukraine) was organised by a Korean-Ukrainian collaboration. The first samples with ~0.2 tons 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 B.C. This lead was used as ballast in the keel of the ship. The element composition of the samples was measured by means of X-ray fluorescence and ICP-MS analyses. The first preliminary limits on the ^{210}Pb contamination of the samples are less than a few hundreds mBq/kg. The measurements were performed using gamma spectroscopy with HPGe-detectors and alpha spectroscopy with commercial α-detectors. Measurements of ^{40}K, Th/U in the lead samples were undertaken in Kiev and in the underground laboratories of the Laboratori Nazionali del Gran Sasso (LNGS, Italy). If it was found to be radio-clean this lead could be used as high efficiency shield for ultra low-level detectors, and as raw material for growing radio-pure scintillation crystals such as $PbMoO_4$ or $PbWO_4$ for the search for rare processes.

Keywords: Low-radioactivity lead, double beta decay, dark matter, $PbMoO_4$, $PbWO_4$ crystal scintillators.
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1. INTRODUCTION

Some very important contemporary fundamental problems have still to be explained by modern physics. One of main interest is the search for Dark Matter (DM) in the Universe; another important one is the determination of the neutrino nature. Dark matter can manifest itself through interaction with ordinary matter, which would result in a nuclear recoil. Some fundamental neutrino properties could be revealed from the study of neutrinoless double beta-decay. Both of the above mentioned physical processes, nuclear recoil from DM and neutrinoless double beta decay, occur at low and very low energies (keV - MeV region). To solve these problems extremely low-level background techniques and instrumentation are substantial.

To detect such very rare events with the best level of sensitivity one needs to reduce both types of background of the experimental set-up, external and intrinsic. The background due to cosmic rays (mainly muons and neutrons) can efficiently be suppressed by operating the set-up in question deep underground. The effect of the intrinsic radioactivity can be reduced by specially selected materials that surround the detector closely or are used in the construction of the detector parts itself. In order to reduce the external background mostly due to gamma rays of environmental radioactivity, one has to adopt massive shields made of materials with a large atomic number and low intrinsic radioactivity.

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2. IMPORTANCE OF ANCIENT LEAD

In order to reduce the environmental background from external γ-rays one needs to install an effective shield as close as possible to the detector for avoiding free space where radon could travel to then decay and give contribution to the background. Moreover, the detector should be made of selected materials that have high absorption efficiency for gamma rays and a low intrinsic activity. Oxygen free high conductivity copper (OFHC) is very popular, but it is rather expensive and has a rather low atomic number. Above this, it might be activated with cosmogenic radionuclides (e.g. ^{60}Co, ^{54}Mn), when exposed at surface to the cosmic rays. Repeatedly distilled mercury was once very attractive material in spite of its rather high thermal neutrons cross section. But it is expensive, harmful, needs special care and requires appropriate packing. Other heavy elements like tungsten are not suitable because of their radioactive contamination and difficult mechanical properties. So, due to its high Z, its reasonable cost, its mechanical properties and low activation cross section for environmental neutrons, lead continues to be an excellent shielding material. But unfortunately modern lead contains a considerable amount of ^{210}Pb which is a rather long-lived radioactive isotope, which is again decaying into ^{210}Bi which further goes to ^{210}Po which finally decays into stable ^{206}Pb. It is dangerous due to the fact that once you have it inside the lead it's almost impossible to separate it from it again. Below you will find the most important decay data for ^{210}Pb and its daughter nuclides:

^{210}Pb ($T_{1/2}$=22.3 years, β^- (17 keV) + γ (46.5 keV)) →
^{210}Bi ($T_{1/2}$=5.013 days, β^- (1162 keV)) →
^{210}Po ($T_{1/2}$=138.376 days, α (5304 keV)) →
^{206}Pb (stable).

^{210}Pb can contribute to most of the background in the region of interest of experiments which are searching for low energy events like direct interactions of WIMP's or double beta-decay with low transition energies. In modern lead this contamination can vary from 1000 - 20 Bq/kg. Measurements by γ-spectroscopy indicate a very low radioactive contamination from the nuclei of the ^{235}U, ^{238}U and ^{232}Th chains, *when in secular equilibrium,* in all samples of modern commercial lead. Secular equilibrium can however be broken by ^{210}Pb and this can severely affect the sensitivity of experiments searching for low energy rare events, due to the continuum of the bremsstrahlung produced by β-decay of this nucleus and especially of its daughter ^{210}Bi. Lead with reduced ^{210}Pb activity of less than 50 Bq/kg is commercially available [1] but the most recent experiments demand much lower levels. As an example, about half of the counting rate in the low energy region of the spectra obtained in the Heidelberg-Moscow experiment [2] is due to the contribution of ^{210}Pb, although a shielding of modern radio-pure lead was used. On the other hand, ^{210}Pb is almost totally absent in ancient lead due to its half life of 22.3 years, as was shown in [1, 3-5].

Another reason of interest for radio-pure lead is possibility to grow clean scintillating lead tungstate ($PbWO_4$) or lead molybdate ($PbMoO_4$) crystals. Both of them could be used as passive shield with high density, light guides for other scintillation detectors or as active scintillation shield ($PbWO_4$ crystal as light-guide for $CdWO_4$ scintillator show attenuation of only 86% [6]). A very exciting possibility is the use of a $PbMoO_4$ crystal for the search of neutrinoless double beta decay of ^{100}Mo, a very interesting isotope with high Q-value, instead of $CaMoO_4$ which contains at the same time two potential double beta decaying elements – Mo and Ca – and this would create interference of the two decays with a resulting lower sensitivity.

3. ARCHAEOLOGICAL LEAD IN THE UKRAINE

During June-August 2006 an underwater expedition was organised by a Korean-Ukrainian collaboration with the aim to look for archaeological low-radioactive lead at the bottom of the Black Sea near the Crimean peninsula (Ukraine). This work was realised with the kind help of representatives of the Department of the Underwater Heritage of the Institute of Archaeology in Kiev. The first 3 samples with a total mass ~0.2 tons have been located at a depth of 28 m among the relics of a sunken Greek ship (Fig. 1).

Their age was preliminary determined to be originating from the I century BC by analysing fragments of amphorae and other subjects located near the ship. From the geometrical shape of the lead samples the conclusion was drawn that they were used as ballast of the 30 meter long ship and not as an anchor. This hypothesis means that there is the possibility to enlarge the mass of ancient lead looking for the remaining pieces of the ballast. The expedition team hoped to find more lead at this place but they found about 1 meter of sediments. Additional equipment (like e.g. a powerful suction pump) is needed to remove the debris and to look for the remaining pieces

the quantity of which was estimated to be of the order of >1-2 tons. There might exist also other ancient ships sunken near Crimea at rather small depths.

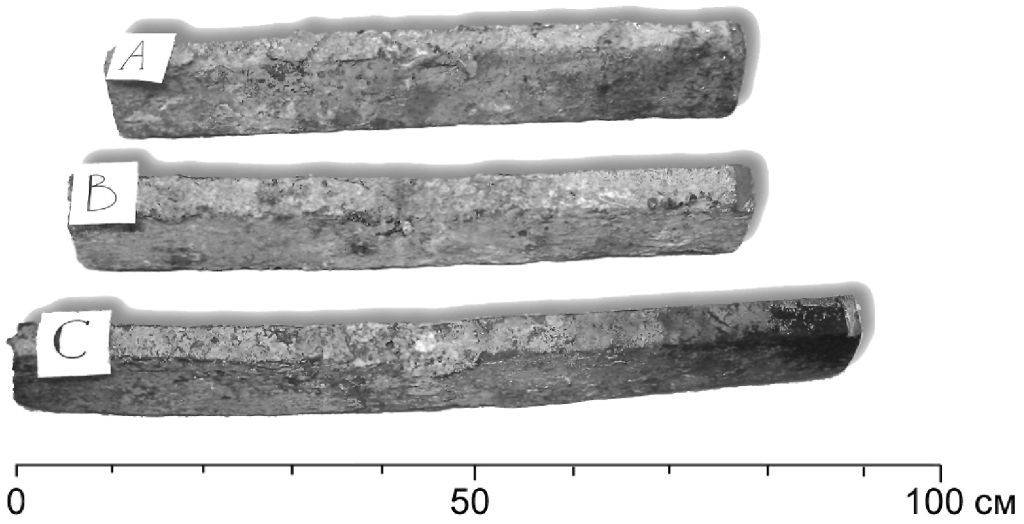

FIGURE 1. Samples of ancient lead found in Ukraine.

4. CHEMICAL COMPOSITION OF LEAD SAMPLES

Chemical impurities different from ^{210}Pb play also an important role in setting up a passive shield, because they could also be radioactive on their own, or they could have large cross sections for neutron capture or cosmic rays activation. These impurities are particularly of interest in the case of using the lead for $PbWO_4$ or $PbMoO_4$ crystal growth. Impurities in the crystal lattice are usually effectively withdrawn during crystal growth; but if there are too many of them or if they diffuse afterwards into the crystal they can make a perfect crystal growth impossible.

First the chemical composition was checked by X-ray fluorescence analysis. A Philips X'Unic II spectrometer was used for this purpose. The results are summarised in Table 1. A slight difference between the results presented in this work and the ones presented by the Fiorini's group [1, 4] should be mentioned. Zn and Cu are present in both kinds of lead (in the so-called Greek one and in the Roman one), but As, Sb, Ni, Ag and W are absent in our samples. The concentration of elements other than lead in the three Greek samples is also a little bit different among the samples themselves. One should underline that sample C is rather different from the samples A and B in shape and dimension and could have different origin (melted in another place or made from a different kind of ore).

TABLE 1. The elemental composition (%) of the three lead samples analysed by X-ray fluorescence analysis.

Element	Sample		
	A	B	C
Pb	99.52	99.53	99.59
Cu	0.36-0.16	0.20	0.116
Al	0.020	-	0.037
Si	0.095	0.061	0.094
Zn	-	0.023	-

Chemical composition of ancient Greek lead samples was additionally verified by ICP-MS (Inductively Coupled Plasma - Mass Spectrometry) analysis at the LNGS. About 0.2 g of each sample was completely dissolved in 10 ml HNO_3 5% solution, after 1 h in ultrasound bath at 70°C. The obtained solutions were diluted 20 times before measurement. The measurements were carried out in the semi-quantitative mode, i.e. the accuracy is on the order of 10-20%. The results are reported in Table 2. Concentration limits were evaluated assuming natural isotopic composition.

TABLE 2. Elemental composition (ppb) of ancient Greek lead determined by ICP-MS analysis at the LNGS

Element	Lead A	Lead B	Lead C
Mg	1200	1500	1100
Al	1200	1000	1100
Ca	4700	3900	3100
Ni	4300	9100	1000
Cu	130000	330000	180000
As	<100	<100	95000
Mo	<1000	2400	<1000
Ru	<10	<15	10
Rh	11000	10000	12000
Pd	<10	<1000	10
Ag	16000	38000	99000
Sb	8200	15000	330000
Sm	<10	<10	13
Au	<10	<10	13

The presence of other elements in the ingots was less than the sensitivity level (Li, Be, V, Mn, Co, Zn, Ga, Ge, Rb, Y, Zr, Nb, Cs, La, Ce, Pr) <10 ppb, (Sc, Sr, Te, Ba) <100 ppb, (Ti, Cr, Ge, Cd, In, Sn) <100-10, and (K, Fe, Se) <1000 ppb. Some additional uncertainties on K and Rh concentrations exist. It must be emphasised that the concentration of the two radioactive elements ^{232}Th and ^{238}U was also found to be less than the sensitivity level ≤10 ppb.

The ICP-MS from Agilent Technologies, model 7500a, is not specific for isotopic ratio measurements and the accuracy of the isotopes abundance determination is usually more than 0.5%. For the identification of the lead mining region the isotopic abundance may be very important, but the accuracy and precision of the semi-quantitative analysis is not enough. Anyway, the lead isotopic ratio carried out from these first measurements is reported in the Table 3.

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

Lead sample	^{204}Pb	^{206}Pb	^{207}Pb	^{208}Pb
A	1.5	24.2	21.6	52.7
B	1.4	24.3	21.4	52.9
C	1.5	24.2	21.7	52.6

It is clear that lead analyzed is pure enough from radioactivity contaminants (Th, U) and only few common (light-medium mass number) elements concentration is higher than 1 ppm. The samples A and B seem very similar while C could be a little bit different (see the As and Sb concentration values). Lead isotopic ratio in the samples is very close.

5. RADIOACTIVITY MEASUREMENTS

The presence of a tiny contamination of ^{210}Pb is difficult to reveal by γ-spectroscopy. The only measurable γ-rays due to this nucleus or to the nuclei produced by the further decays have energies of 46.5 (^{210}Pb) or 304.9 and 265.8 keV (^{210}Bi). The first is strongly absorbed by the cup of the Germanium detectors, while the branching ratios of the latter are very low (around 10^{-6}). Measurements based on α- and X-ray spectroscopy and on the bremsstrahlung are more promising [1]. They can however hardly reach sensitivities better than one Bq/kg. To be sure before undertaking further time- and efforts-consuming steps, 3 samples were taken from the different pieces A, B, C (with mass 4.77, 3.56 and 3.50 g), having the form of cylinders with a thickness of ~0.4 mm. They were measured in Kiev with a well-type, low-background HPGe-spectrometer, ORTEC GWL-100/210, for about 60 h each. The spectra of the background and of the samples were almost indistinguishable. A small difference was seen in the low energy region due to the additional shield of the detector by the samples themselves. An example of measured spectra is shown in Fig. 2.

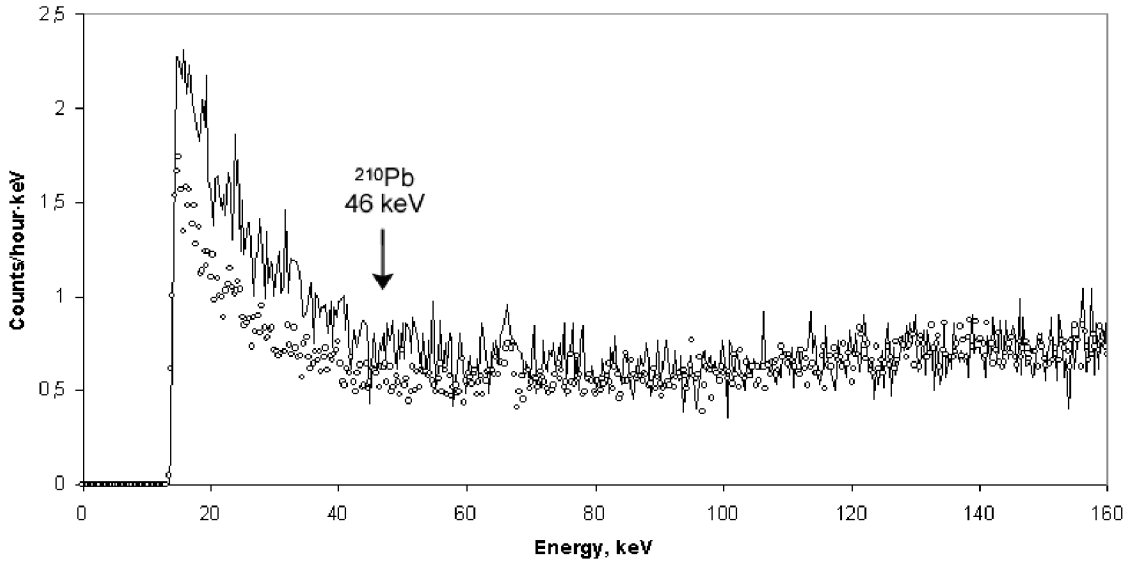

FIGURE 2. Fragment of low-energy region γ-spectra of background (dots) and Greek lead (sample A, line) measured in Kiev.

The efficiency of the ^{210}Pb 46.5 keV γ-rays in this geometry was calculated using the GEANT package and is 3-5% for the different specimens. No evidence of additional radioactivity was seen in all the measured spectra, so only limits on the radioactive contamination of the Greek lead (Bq/kg) could be established, which are listed in Table 4.

TABLE 4. Limits on radioactive contamination of Greek lead (Bq/kg) from gamma spectrometric measurements in Kiev.

Isotope	Lead sample		
	A	B	C
^{210}Pb	≤77	≤37	≤15
^{40}K	≤22	≤20	≤13
^{60}Co	≤1.2	≤1.1	≤0.9
^{137}Cs	≤1.2	≤1.1	≤0.8
^{208}Tl	≤0.9	≤3.3	≤0.3

At the next stage 3 samples of the lead, each in the form of a disk (∅ 50 mm; height 0.5 mm), were measured in the LNGS underground laboratories with an ultra low-level p-type HPGe-detector, total volume 465 cm^3. This detector has a rather thin Cu window of 1 mm thickness. The spectra measured had a counting time of 326 h for sample A (8.4 g), of 395 h for sample B (9.5 g), and 324 h for sample C (9.8 g). The sample were positioned directly on the endcap of the detector inside a polyethylene bag. No positive signal was found. The detection limits are listed in Table 5.

TABLE 5. Limits on the radioactive contamination of ancient Greek lead from gamma spectroscopic measurements at LNGS.

Nuclide	Sample A		Sample B		Sample C	
	mBq/kg	g/g	mBq/kg	g/g	mBq/kg	g/g
^{232}Th	<34	$<8.5\cdot 10^{-9}$	<27	$<6.7\cdot 10^{-9}$	<34	$<8.3\cdot 10^{-9}$
^{238}U*	<28	$<2.2\cdot 10^{-9}$	<22	$<1.8\cdot 10^{-9}$	<25	$<2.0\cdot 10^{-9}$
^{40}K**	<0.25	$<8.1\cdot 10^{-6}$	<0.20	$<6.4\cdot 10^{-6}$	<0.22	$<7.2\cdot 10^{-6}$
^{137}Cs	<8		<7		<9	
^{210}Pb***	<4000		<2700		<3100	

* - starting from ^{226}Ra
** - concentration in g/g given for natural K
*** - for gamma line of 46.5 keV

At the LNGS underground laboratories, also measurements of the α-activity were performed. Commercial counting devices from Canberra/Eurysis and Ortec have been used, each equipped with a Passivated Implanted

Planar Silicon (PIPS) detector, of 1200 mm^2 active surface. The spectra show no positive signal for ^{210}Po, which permits, assuming of course secular equilibrium in the chain, to give detection limits on the intrinsic ^{210}Pb contamination of the ancient Greek lead. The results are listed in Table 6.

TABLE 6. Limits on the radioactive contamination in ^{210}Pb of ancient Greek lead from alpha spectroscopic measurements of ^{210}Po at LNGS.

Nuclide	Sample A Bq/kg	Sample B Bq/kg	Sample C Bq/kg
Ortec detector	-	<0.37	<0.34
Canberra detector	<0.46	-	<0.33

Only sample C was measured in both detectors. In all samples a peak-like statistically significant structure could be identified corresponding to an alpha energy of 5.8 MeV. Careful analysis of possible candidates could yield as result only the transuranium elements ^{243}Cm ($T_{1/2}$ = 29.1 y, E_α=5.785 MeV, p=73.0%) and ^{244}Cm ($T_{1/2}$ = 18.1 y, E_α=5.804 MeV, p=76.4%). In the next future will be investigated whether this peak is related to a surface contamination, which occurred during the samples preparation at the INR.

6. PERSPECTIVES

For the future the lead can be further purified from contaminants as ^{232}Th and ^{238}U by melting, in radon-free atmosphere in lead-free melting pots, where these heavier elements are separated efficiently. The plan is to melt the present lead samples for the purpose of further purification with an specially designed electrical furnace with quartz vessel and quartz cap.

Another very efficient procedure to measure the lead contamination by ^{210}Pb, besides a bolometric technique, is growing a scintillator crystal. Crystals as $PbWO_4$ or $PbMoO_4$ [7] made from clean lead can determine with an efficiency of almost 100% the internal ^{210}Po α-activity. A sensitivity level of $\propto$Bq/kg could be realised. This was shown in [8] where the activity of ^{210}Pb was less than 0.4 mBq/kg. The advantage of clean lead is illustrated in Table 7 comparing the results of real measurements performed with $PbWO_4$ [6] and $CdWO_4$ crystals [8]. If to assume that the Greek lead is clean from the U/Th, one would obtain a possibility to reach the level of purity similar to that of $CdWO_4$.

TABLE 7. Radioactive contamination in $PbWO_4$ and $CdWO_4$ crystal scintillators.

Chain	Source	Activity (mBq/kg) $PbWO_4$	Activity (mBq/kg) $CdWO_4$
^{232}Th	^{228}Th	≤13	≤0.004-0.039(2)
^{238}U	^{226}Ra	≤ 10	≤0.004
	^{210}Pb	(53-79)×10^3	≤0.4

7. SUMMARY

The first samples of ancient Greek lead found in the Ukrainian part of the Black Sea, with a total mass of ~0.2 tons were obtained and their study will be continued. A real possibility exists to enlarge the present quantity to up to 1-2 tons. Preliminary checks have shown that this lead is clean from natural radioactivity at a level of less than several tens of mBq/kg for U/Th. An improvement of measurement's sensitivity is in progress. The possibility of growing new clean scintillator crystals for fundamental physics researches of rare events is at hand.

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