



U and Th variation in ancient slags, metals and metal ores: Contribution to dating of metals

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Abstract

The variation of uranium-238 (U) and thorium-232 (Th) in metallurgical slags and ores, with extension in metals, is examined using alpha scintillation counting. Data indicate a great variability: 0.1 to 12 ppm for U and 0 to 3 ppm for Th, while Th/U < 1. These isotopic data coupled with the ratio Ra-226/Th-230 in the U-series disequilibrium in ancient metal objects offer a potential means of dating ancient metals.

Keywords: metals, slag, ores, Ra-226, α -counting, dating.

Introduction

Metallurgical slags are very important materials to study since they are direct evidence of pyrometallurgical processes and can provide us with clues regarding way of metal acquisition – from the melting of native copper (or re-melting of different objects) and smelting of ore. This point has particular interest regarding the earliest attempts of metallurgical techniques as far back as the 5th millennium BC (Tylecote, 1970, 1987).

Early metallurgy starts with the exploitation of native copper and gold and copper ores (Piggot, 1999; Hartmann & Sangmeister, 1972; Tylecote, 1987;

Moorey, 1994; Notton, 1974). Native copper and gold were used before Early Bronze Age Europe, unalloyed with other metals, subjected initially to annealing – the first step toward true metallurgy – and next to consolidation by melting and simple casting of molten into molds, and often solely shaped by cold hammering and cutting of the cast piece. Later at some point copper ores were discovered and their smelting which lead to bronzes.

Copper metallurgy has started in different times amongst different cultures flourishing in the Mediterranean and Near East. Archaeological evidence suggests that copper was first used between 8,000-5,000

B.C., most likely in eastern Anatolia to Mesopotamia and –toward the end of this period- the Indian sub-continent (Piggot, 1999).

In Greece it appears during 5th millennium BC known as late Neolithic period and corresponds in the development of an ‘indigenous metallurgy’ in Balkans during Bronze Age (Renfrew and Bahn, 1991; McGeehan, 1996; Arfara, 2007).

These metals replaced lithic tools around 3rd millennium BC. Such ‘invasion’ was realized with the practice of pyrometallurgical technologies of ore melting. At the same time metals become abundant takes place greater development and extension of trade and like handmade artifact specialization, two factors that lied down the basis of the coming ‘first embryonic cultures’ (McGeehan, 1983; Arfara, 2007).

Slags offer important information about ancient technology and are datable by TL. The latter becomes even more useful when it is referred to early metallurgy (Liritzis and Liritzis, 1986). Metal ores on the other hand is the raw material for metal acquisition. Thus, any isotopic method of dating metals should start with the isotopic variation in ores and the slag.

Here we present the first results on U and Th on a group of slag and ore materials employing a well calibrated alpha counting (pairs technique), and refers to the potential dating of metals by a novel ^{226}Ra technique (Liritzis, 2006).

Samples and Preparation

We have measured 15 samples which fall into two major categories, the ore and the copper slag. Metal ores are chosen for the production of copper or its amalgamation, bronze. All samples derive from the Aegean region. These are a) copper oxide Azurite [$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$] (chosen to be of almost 90% pure Cu) from Laurium, b) Galena (PbS), a lead Sulfide from Laurium too (Kohlberger, 1976), c) copper sulphide, Chalkozine (Cu_2S) from Chalkidike, Northern Greece, d) Ore-6 is a copper ore from Fthiotis, and e) slags from prehistoric sites in the islands of Kythnos and Seriphos. In particular Slag1 and Slag 2 (kindly provided by Prof. N. Gale) from Seriphos (Avessalos)

of Bronze Age (not specified the cultural phase). The rest of the Copper slag samples provided by Dr. Y. Basiakos (NCPR Demokritos, Athens) derive from the islands of Kythnos and Seriphos (Avessalos), of the Early Bronze Age (3rd millennium BC).

About 1 gram of each of the fore-mentioned samples was taken and pulverized in fine powder using the appropriate device known as shatter box at the Geology laboratory of the University of Athens. This piece of equipment (the shatter box) was chosen for grinding the samples thus avoiding contamination. An effort was made of those samples powdered to be a representative piece of the solid material they were detached from.

Subsequently, the powder was sieved so that it was in particles finer than $90\mu\text{m}$ and all powdered samples spent 24 hours / 80°C in a drying oven to remove any humidity before we proceed with their analysis. Then, the pulverized samples were placed in specially designed containers and sealed for 12 days to allow build-up of gaseous Radon (Rn-222 , half-life = 3.823 days). The dependence of the alpha counting rate from the distribution of sieved grain sizes has shown a considerable effect, with no any universal trend, in U, and Th dose rate evaluation. However, for an irregular distribution of grain sizes in the sample, for grain sizes less than $90\mu\text{m}$ the higher rates are encountered (Liritzis and Galloway, 1982).

Only a thin layer of powder is needed, just enough to cover a screen of zinc sulphide (44 mm diameter) which is used as scintillation screen and with which the powdered sample is placed in direct conduct.

The Equipment

The a-counter used for the specific measurements is the ELSEC Low Level Alpha-Counter 7286 with a EMI 6097B PM tube, and ZnS (Ag) on mylar film, incorporating an internal 6502 microprocessor. Alpha counting is highly relevant to dating techniques such as thermoluminescence and optically stimulated luminescence, in each of which the natural dose rate to which samples have been exposed must be known and is regularly calculated from measurement of the ra-

radioactive content of the samples and their surrounding soil (Aitken, 1985). The alpha counter is used to measure the Uranium-238 and Thorium-232 in samples using the "pairs technique". In fact it counts scintillations from a ZnS screen that it is placed on the bottom of the container where the powdered sample is placed before positioned on the a-counter on top of its photomultiplier (PM) (at 1500 volts).

The ZnS(Ag) screen is sensitive to alpha particles (range of energies 4-9 MeV emitted by different members of U and Th series) and it is used as a scintillation screen. Whenever an α -particle strikes the ZnS(Ag) screen light is emitted as the result of transition of the activator Ag atoms. The production of a scintillation is the result of the occurrence of several events, i) ionizing radiation passes through the ZnS crystal, ii) electrons are raised to the conduction band, iii) holes are created in the valence band, iv) excitons are formed, v) activation centers are raised to the excited states by absorbing electrons, holes and excitons, and vi) deexcitation is followed by the emission of a photon. The photons produced in the scintillator enter the phototube and hit the photocathode, which is made of a material that emits electrons when light strikes it. The electrons emitted by the photocathode are guided with the help of an electric field toward the first dynode, which is coated with a substance that emits secondary electrons, if electrons impinge upon it. The secondary electrons from the first dynode move towards the second and so on. The light output affects the number of photoelectrons generated at the input of the PM tube which in turn affects the pulse produced at the output of the counting system. This light produced by the crystal is in fact amplified by the PM tube transformed into an electric current measured as a count. The PM tube is essentially a fast amplifier, which in times of 10^{-9} sec amplifies an incident pulse of visible light by a factor of 10^6 or more. Since the photons are emitted as a result of, a) decays of ionizing atoms, and, b) the decays of excited states, the time of their emission depends on the decay constants of the different states and half lives involved.

Pulses due to beta particles and gamma rays and the PM noise are rejected by setting a threshold.

The a-counter records electrical pulses occurring in "pairs", meaning two counts occurring in time less than 0.21 seconds (slow pairs) or 0.002 seconds (fast pairs). In particular, in the Th chain about 3% of the counts occur in pairs, that is, within about 0.2 sec of each other because polonium-216 has half-life only 0.145 sec and follows immediately after another alpha emitter. Thus, pairs occurring with a time interval less than 0.21 sec is recorded by the electronic coincidence circuit, and the 'pairs rate' observed is a measure of the thorium activity. On the other hand the observed pairs rate by 'fast pairs' due to 0.002 sec half life of polonium-215 in the U-235 series provides the U-238 activity.

Each measurement is in periods of 10ks, which is repeated for as long as it is necessary to have a good statistics, which depends on the concentration of U and Th on the sample (the shorter the time the higher standard deviation).

Prior to counting of any sample series, calibration was made (last in Sept 2005).

A normalization factor for both Uranium and Thorium was calculated in advance, so that the measurements we received from the a-counter could be converted in count rates for U and Th in ppm (parts per million). The normalization factor for U ($N_{f,U}$) was calculated using the knowing rates for Uranium of 3 standard samples with the code names 105A (calibration sand New Brunswick lab.), BC (brick clay NBS), CFA (coal fly ash NBS). The $N_{f,U}$ is the average of the rates of those 3 standard samples equals 11.16 ± 0.63 counts/ppm. The normalization factor for Th ($N_{f,Th}$) was calculated using 12 standard samples with the code names JG2 (granite), OU3 (microgranite), AC-E (granite), 109A (calibration sand New Brunswick lab.), JG3 (granodiorite), OU2 (Belford dolerite), BonnSTD (ceramic archaeological science group Bonn), G94 (Threlkeld microgranite), Monsoil (Montana soil NIST), 105A (calibration sand New Brunswick lab.), BC (brick clay NBS) (Potts et al., 1992). Again the $N_{f,Th}$ is the average rate of the chosen samples equals 3.95 ± 0.16 counts/ppm.

Results

Table 1 gives the U and Th concentration values for all samples. U varies between 0.16 to 10 ppm. Exceptionally high values are for Slags 1 and 2 from Abessalos in Seriphos, quite different from other slags of same site. Higher Th values are for slags from Kythnos 23 and 60 followed by other slag from Kythnos and slag from Abessalos. All other materials gave small amount of thorium. Ores 6 from Fthiotis has low contents and represent the rock bearing copper oxides since the latter had been extracted by hand.

The heated Slag 1 Seriphos at 250°C/24 hrs gave less U beyond the errors (9.11 from 11.74) and higher Th (2.06±0.83 from initial 0.80±1.55). The less U is due to the escape of gaseous daughter products such as the volatile Ra-222 (and Polonium) drawing with it the rest part of the radioactive chain. The Th values are similar within errors.

The repeated measurement for Slag Abessalos 20 gave similar values within errors, satisfying the criterion of repeatability of measurements.

Another interesting observation is the lack of the observed ratio of around 3.4 in Th/U of rocks in general (average U=2 ppm and Th= 6 ppm, see Hansen and Stout, 1968), but a bias of Th/U <1. This observation for slags may be due to a kind of isotopic differentiation occurring during smelting.

The latter lead us to revisit an old suggestion by one of us (Liritzis, 1983) concerning radium separation from metal during ore smelting and investigate its validity (Liritzis, 2006).

The ²²⁶Ra Dating Method in Brief

In melting and smelting procedures of ores in kilns or open air fires (crucibles) and separation of slag from metal phase the radioisotopes are fractionated too. That is, the radioactive equilibrium of ore is unset by the high temperature during smelting in kilns and their casting in molds (Faure, 1986).

For example, the ²²⁶Ra daughter product of the ²³⁸U series is withdrawn by slag products away of the melted metal, as a result of its lower specific gravity, $\epsilon = 5-6$

g/cm³, and its lower melting point (700°C) than that of copper (1083°C). Thus disequilibrium is set with an expected theoretical ratio ²²⁶Ra/²³⁰Th in the metal of zero.

Although the effect of U-series disequilibrium is significant for great ages compared to the half-lives of the involved isotopes and applies to palaeolithic times, the 1600 years half-life of ²²⁶Ra is comparable to the elapsed time since the onset of metallurgy in prehistoric archaeology. Therefore ²²⁶Ra production towards equilibrium with ²³⁰Th follows the known exponential decay law of radioactivity for a time period equivalent to several half-lives which cover the whole of prehistory of the world (about 10,000 to 3,000 years before present). Therefore this growth of ²²⁶Ra back to 'secular' equilibrium with its parent ²³⁰Th is the basis of the new method.

Disequilibrium between ²³⁸U and ²²⁶Ra is common with ²²⁶Ra usually in excess. Once metal is separated from slag and its products, ideally radium (²²⁶Ra) is gone with slag and metal remains free of radium. Although this is accord with theory in practice traces may remain. Thereafter in metal ²²⁶Ra is grown from ²³⁰Th while ²³⁰Th decays. Equilibrium is achieved at around 10,000 years. The equations governing the process are:

$$\text{For the decay of Th-230: } dN_T/dt = -\lambda_R N_R \quad (1)$$

For the growth and decay of Ra-226:

$$dN_R/dt = \lambda_T N_T - \lambda_R N_R \quad (2)$$

Where N_T and N_R are the number of atoms of ²³⁰Th and ²²⁶Ra present at time t , and $\lambda_T = 8.664301 \text{ E-}06 \text{ yr}^{-1}$.

Eq (2) may be solved to give N_T and N_R if the quantities or activity or disintegration rate, of these two atoms present at time $t = 0$ i.e. $N_T(0)$ and $N_R(0)$, are known.

Thus, from eq.(1) and eq.(2):

$$\text{Activity of Th} = \lambda_T N_T = \lambda_T N_T(0) e^{-\lambda_T t} \quad (3)$$

$$\text{Activity of Ra} = \lambda_R N_R = \lambda_R N_R(0) e^{-\lambda_R t} + \lambda_T \lambda_R N_T(0) [e^{-\lambda_T t} - e^{-\lambda_R t}] / (\lambda_R - \lambda_T) \quad (4)$$

Where λ_R , λ_T ($= 8.664301 \text{ E-}06 \text{ yr}^{-1}$) decay constants of ²²⁶Ra and ²³⁰Th respectively (Kokkoris and Liritzis, 1997; Liritzis and Kokkoris, 1992).

TABLE I. Samples, mean counts, counting time in No of periods (one period 10ks), and U, Th content (heated: at 250°C/24hrs)

SAMPLES	Mean counts U	Mean counts Th	Number of periods	U (ppm)	Th (ppm)
Azourite-Laurium	7.36±0.38	0.18±7.36	93	0.66±0.03	0.05±1.86
Galena-Laurium	9.56±0.98	2.16±0.88	65	0.86±0.10	0.55±0.22
Chalkozine-Chalkidike	1.8±1.12	3.7±1.08	69	0.16±0.10	0.94±0.28
Ore-6	11.55±0.33	0.03±0.18	156	1.04±0.07	0.01±0.05
Slag1- Seriphos	130.95±6.71	3.16±6.13	18	11.74±0.60	0.80±1.55
Slag2- Seriphos	101.69±4.74	0.65±4.19	21	9.11±0.67	0.16±1.06
Slag1- Seriphos-heated	110.24±3.54	8.13±3.25	61	9.88±0.64	2.06±0.83
Slag-Kythnos-7	43.86±2.1	7.18±1.91	66	3.93±0.29	1.82±0.49
Slag-Kythnos-8	55.16±2.38	5.62±2.13	62	4.94±0.35	1.42±0.54
Slag- Kythnos-60-no16	44.77±2.39	10.86±2.22	68	4.01±0.31	2.75±0.57
Slag-Kythnos-23 no11	37.99±1.67	10.01±1.55	121	3.40±0.24	2.53±0.40
Slag-Kythnos-46a	22.51±1.16	7.63±1.16	164	2.02±0.15	1.93±0.30
Slag-Avessalos-no 18	17.64±0.86	2.53±0.75	118	1.58±0.12	0.64±0.19
Slag-Avessalos-no19	21.97±1.11	4.49±1.01	117	1.97±0.15	1.14±0.26
Slag-Avessalos-no20	18.43±1	3.33±0.89	108	1.65±0.13	0.84±0.23
Slag-Avessalos no20 (repeat)	20.52±1	3.68±0.89	122	1.84±0.14	0.93±0.23
Slag-Avessalos-no24	29.52±1.26	0.91±1	51	2.65±0.19	0.23±0.25

It is assumed that initially in the deposited metal ^{226}Ra is not present, $N_{\text{R}}(0) = 0$, and then at any time, the age equation is:

$$\text{Activity of Ra} / \text{Activity of Th} = \lambda_{\text{R}} [1 - e^{-(\lambda_{\text{R}} - \lambda_{\text{T}})t}] / (\lambda_{\text{R}} - \lambda_{\text{T}}) \quad (5)$$

For the long-lived parents of uranium or thorium it is clear that when secular equilibrium has been established the quantities of successive products present are given by the equations:

$$\lambda_{\text{T}} N_{\text{T}}(0) = \lambda_{\text{R}} N_{\text{R}} = \lambda_{\text{Rn}} N_{\text{Rn}} \dots = \text{constant} \quad (6)$$

that corresponds to ^{230}Th , ^{226}Ra and ^{222}Rn in the U-238 series (the stable end product of ^{206}Pb is excluded from this constancy since it continually accumulates). The activities are constant throughout and the relative amounts of different products are inversely proportional to their decay constants (Burcham, 1973).

Thus, from measured activities of ^{226}Ra and ^{230}Th in metals eq. (5) is the age equation.

Measurement of ^{226}Ra and ^{230}Th can be achieved

by using various techniques such as refined radiochemical and mass spectrometric techniques, thermal ionization mass spectrometry (TIMS), or Multiple collector ICP-MS, Laser Ablation-quadrupole ICP-MS and SHRIMP-SIMS. Another technique to measure them is by alpha counting pairs technique or thick source alpha counting with silicon pin detector (Michael & Zacharias, 2000). Work should be focused on radium homogeneity issues and investigation of remaining traces in metals.

Accordingly, $^{226}\text{Ra}/^{234}\text{U}$ disequilibrium - ^{226}Ra deficiency (absence) and ^{234}U presence- was found for contemporary metal finds of aluminium, copper and iron (using TSAC system with surface barrier detector kindly measured by Drs Michael and Zacharias at NCPR Demokritos for us), reinforcing the validity of the new dating method. Secular equilibrium was found for Bronze Age slags from Seriphos and modern outdoor experiment.

A detailed account of this method is given in Liritzis (2006).

Conclusion

The U and Th content in ancient metal slags from two prehistoric sites in Kythnos and Seriphos show a fractionation in U series isotopes mainly due to smelting, with $\text{Th}/\text{U} < 1$. The U varies between 0.1 – 12 ppm and Th varies between 0-3 ppm. Three copper ores have very low U and Th values both less than 1 ppm, while two of them have Th near zero. The segregation of Ra-226 from the metal provides a sound theoretical background for a novel dating method. Initial results of modern metals indicate zero Ra-226 which reinforces this working hypothesis.

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