Dating metals

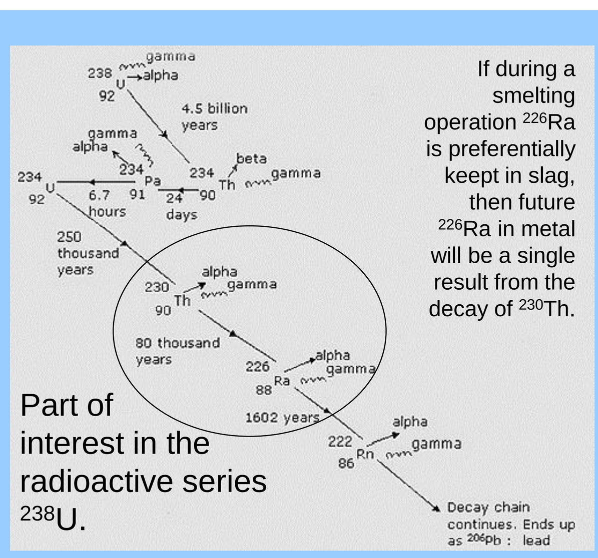
An exploratory project to determine the age of cultural metals using a natural radioactive series

João Cruz[1], Elin Figueiredo[2*,3], Rui J.C. Silva[2], Victoria Corregidor[3], Penka I. Girginova[3,4], Carlos Cruz[3]

[1] DF-FCT-UNL; [2] CENIMAT/I3N-FCT-UNL; [3] IST-UL; [4] FC-UL *e-mail: emf12055@campus.fct.unl.pt

Until present there is no dating method directly applied to metal artifacts that can be used by archaeologists or metallurgists to reveal the age of those ancient artifacts. Such a method would be of high importance to put into context various archaeological finds, to study the introduction/development of metal technological solutions or even to distinguish fake objects from original ones.

In the present project (MetalAge) it is intended to use one of the natural radioactive series (^{238}U) to date metals or, more specifically, metallic artifacts manufactured by man. However, to date these metal pieces which are no more than a few thousand years old, a new approach to the study of this radioactive series is required. Thus, instead of considering the usual ratio $^{206}Pb/^{238}U$, only a small part of this series, the ^{230}Th decay to ^{226}Ra will be considered, based on an isotopic fractionation that may occur during ore smelting, disrupting the secular equilibrium in the ^{238}U series [1].



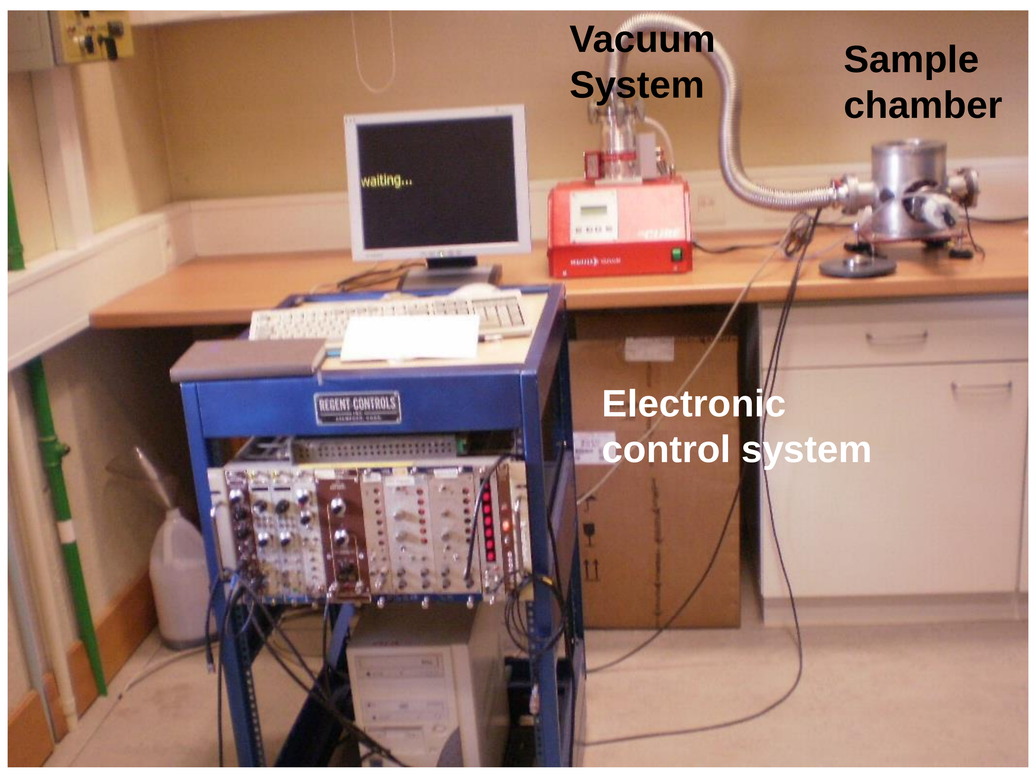
Experimental validation is needed due to:
- uncertainties about homogeneity and fractionation efficiency of U and Th daughter products during smelting between slag and metal.
- extremely low counting rates associated with measuring natural radioactivity.

To explore/validate this dating method alpha-spectrometry and analyses by SEM-EDS, XRD, PIXE and RBS will be performed on materials obtained from recent smelting experiments simulating ancient and traditional technologies, as well as on coins from different chronological periods.

The project interconects the fields of nuclear physics and metallurgy and the work is a collaboration between CENIMAT/I3N, Department of Physics-FCT-UNL, CTN-IST-UL, FC-UL and the Portuguese Numismatic Museum.

The MetalAge project can have notable consequences in several scientific areas that deal with metallic heritage, such as archaeometallurgy, materials and conservation sciences and museology.

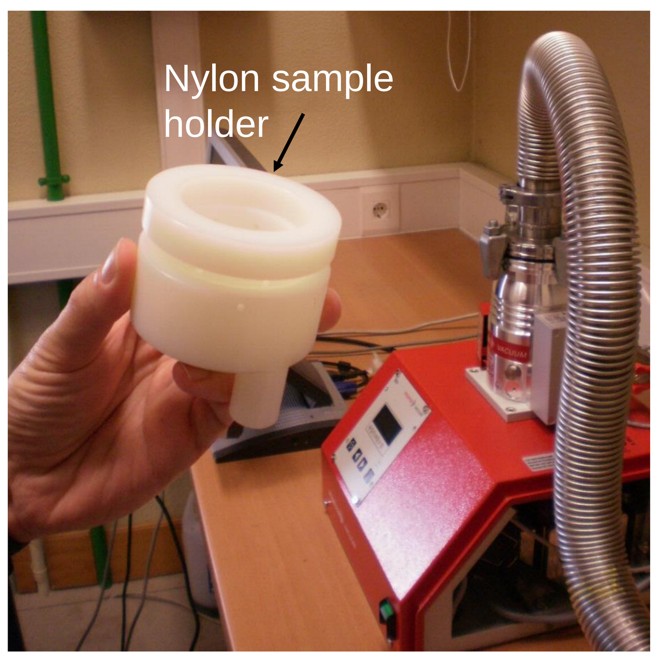
Experimental setup

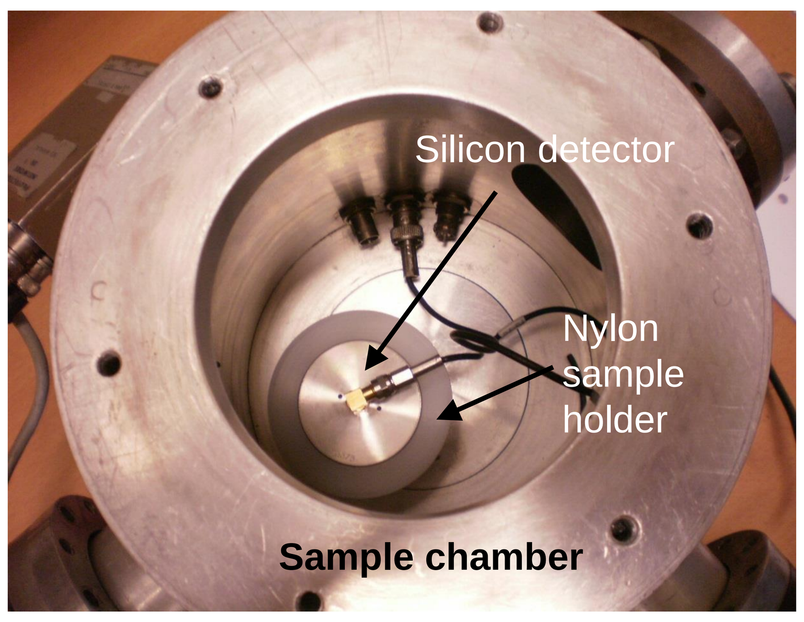


Thick Source Alpha Counting (TSAC) spectrometry technique

using a silicon detector for ^{226}Ra and ^{230}Th quantification

- sensitive to all alpha emitters from the uranium and thorium series
- uses a simple and easily portable setup
- accurate and non-destructive
- gives a good signal to background ratio
- allows the study of samples with several centimetres and of different masses (large sample yield, higher counting ratio and better statistics improving the signal to background ratio)

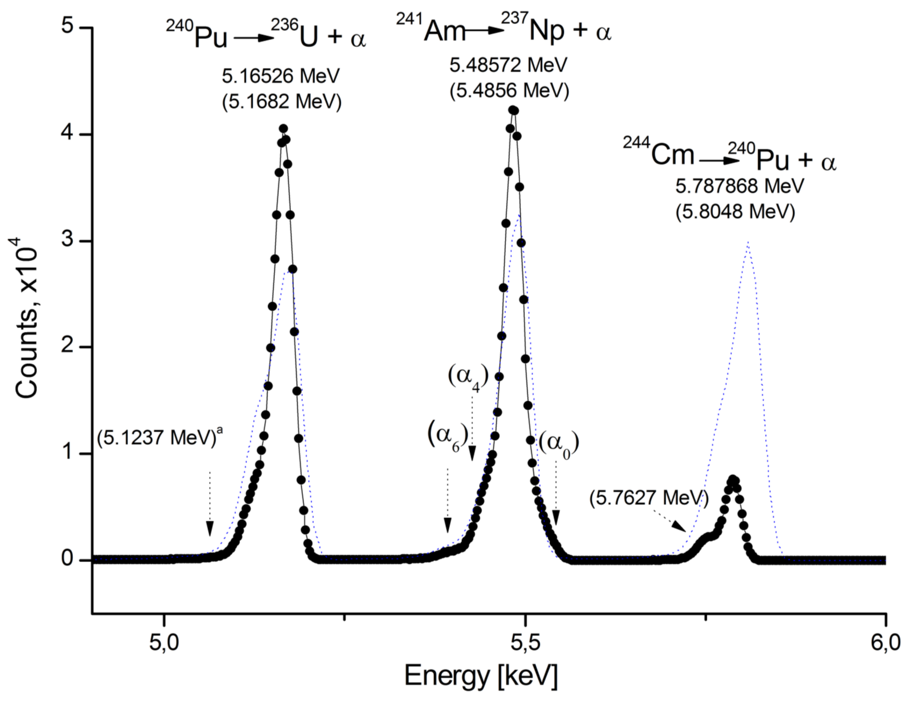




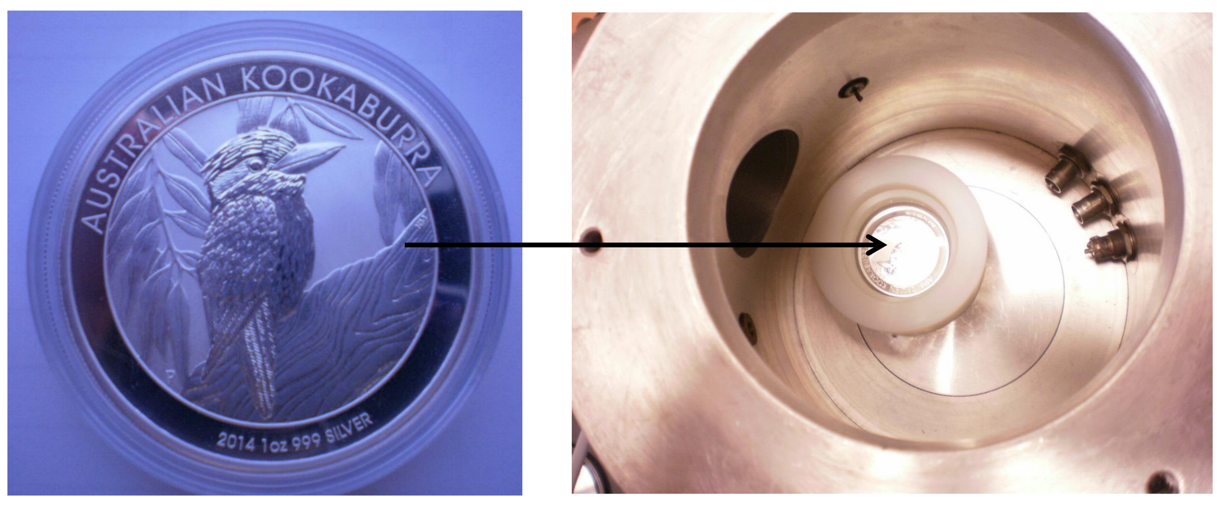
Ideal samples should be pressed forming pellets. For the measurements of α particles emitted by these samples, a 1200 mm² silicon detector with a resolution of 32 keV is placed at around 5 mm from the sample in vacuum conditions (P=1.4×10⁻⁶ mbar). The silicon detector is energy calibrated with a triple-alpha source (^{244}Cm, ^{241}Am and ^{240}Pu).

Background and first experimental runs

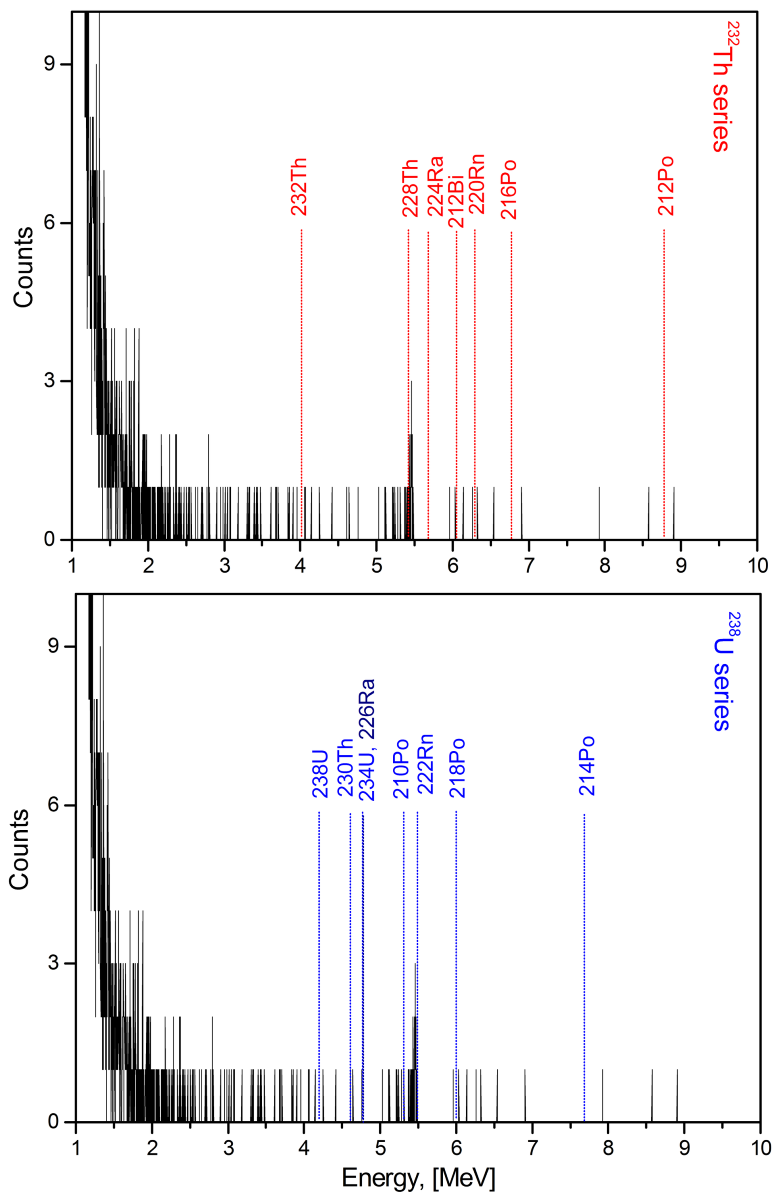
Triple-alpha source (^{244}Cm, ^{241}Am and ^{240}Pu) energy spectrum measured with the 1200 mm² silicon detector



Ongoing experiment: analysis of a contemporary Silver coin (99.9%Ag)



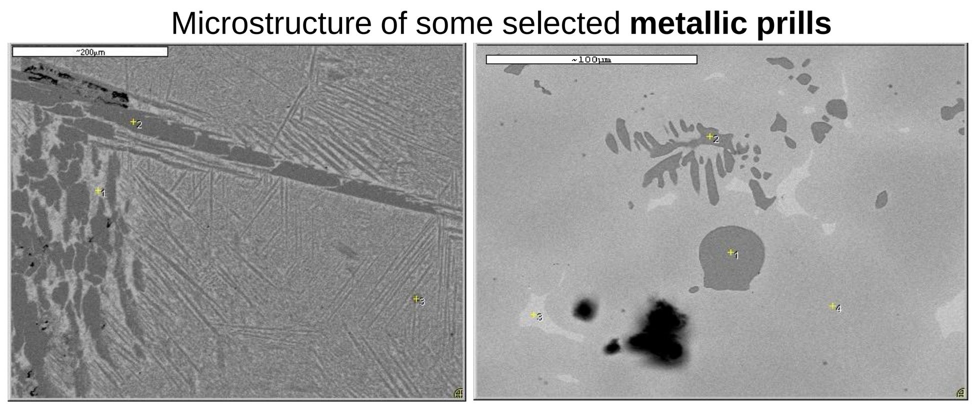
Background spectrum measured for 5 days and 20 h



SEM-EDS analyses of slags and metals

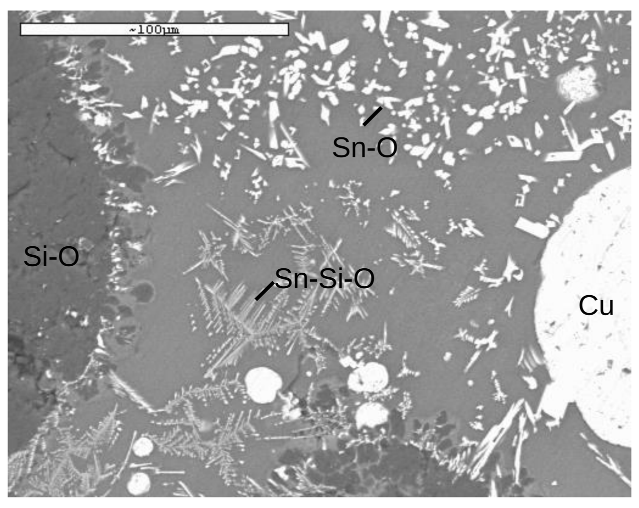
Products obtained by co-smelting cassiterite and malachite to produce bronze in a simillar way as it could have been produced in ancient times

Microstructure of some selected **metallic prills**



Sn-31wt%Cu
p1. Sn rich (η+δ-Sn ?)
p2. Cu~42-45Sn (ε+η ?)
p3. Cu-Cl-O inclusion

Cu-6wt%Sn
P1 and 2 Cu-S-Fe inclusion
p3. Cu~29Sn (α+δ eutectoid)
p4. Cu-Cl inclusion
p5. Cu-Sn (α)

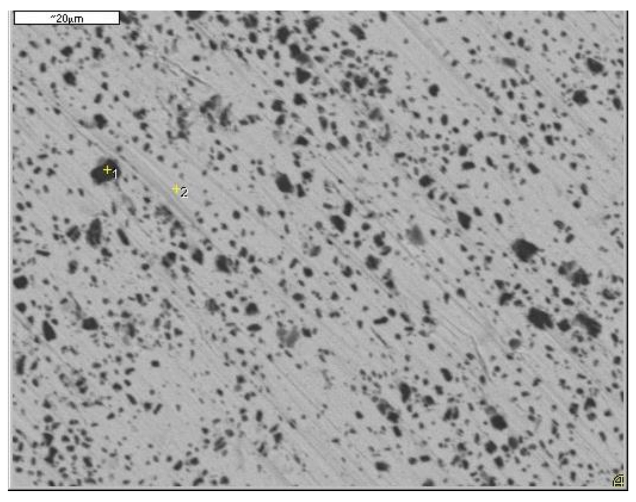


Slag

with heterogeneous microstructure and small metallic prills entrapped

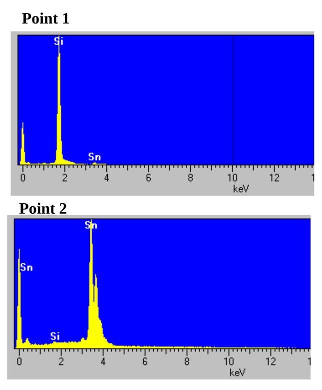
BSE images

Products obtained by smelting cassiterite to produce tin in a traditional small scale operation

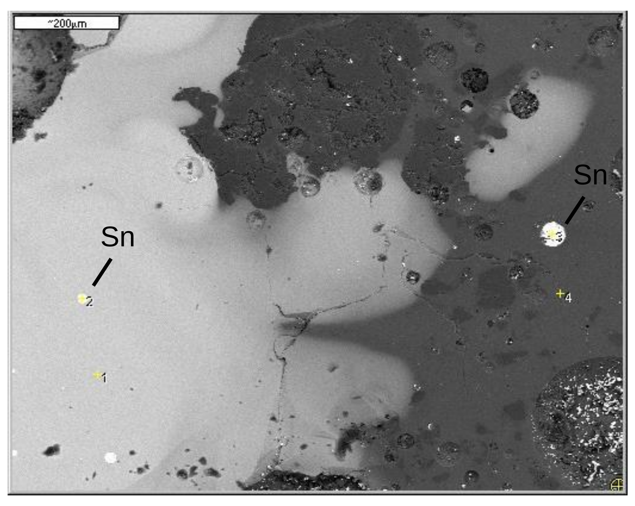


Tin ingot

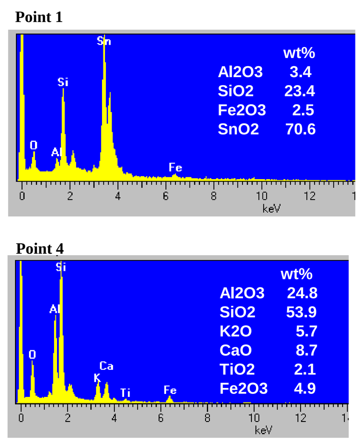
Sn-7wt%Si



BSE images



Slag



Some preliminary results

Alpha spectrometry background test showed a 17 counts/day background yield for the energy range of interest (3 – 8 MeV), meaning that expected yield from ancient metallic artifacts is much higher than background.

Current alpha spectrometry analysis of a 99.9% silver coin is still undergoing, but preliminary results point out to the absence of specific radiation emitted by the coin, as expected from modern fabrication techniques.

SEM-EDS analysis of slags and metals produced by ancient and traditional techniques show that very heterogeneous materials can be produced: slags with very complex and heterogeneous microstructures can result from a single smelt; in a co-smelting experiment, metallic prills with different compositions and inclusions were produced.

References: [1] I. Liritzis, *Mediterranean Archaeology & Archaeometry* 6, 93-98 (2006).

Acknowledgements: MetalAge is a research project financed by FCT (EXPL/EPH-ARQ/1015/2013). V. Corregidor acknowledges FCT for the Ciência program, P.I. Girginova acknowledges the grant from Project EXPL/EPH-ARQ/1015/2013 and E. Figueiredo the grants SFRH/BPD/73245/2010 and SFRH/BPD/97360/2013. Cooperation with B. Comendador Rey, A. Lackinger and C. Fernández from the GEAAT of University of Vigo is also acknowledged for producing and documenting metals obtained by ancient and traditional techniques. CENIMAT/I3N acknowledges the Strategic Project Pest-C/CTM/LA0025/2013-2014.

www.cenimat.fct.unl.pt

UNINOVA

FACULDADE DE CIÊNCIAS E TECNOLOGIA UNIVERSIDADE NOVA DE LISBOA