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# APPLICATION OF X-RAY AND NEUTRON TOMOGRAPHY TO STUDY ANTIQUE GREEK BRONZE COINS WITH A HIGH LEAD CONTENT

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**Abstract**
Highly leaded bronze coins of the Coin Cabinet of the Kunsthistorisches Museum (KHM) show progressive corrosion as a result of unfavourable storage conditions within historic wooden cases. In connection to a research project concerning the preservation and conservation of the antique coins the causes for the sometimes severe corrosion were studied by different analytical techniques. Radiography and tomography investigations using neutrons and X-rays were performed at the Paul Scherrer Institute, i.e. the enrichment of lead in the interior of the objects was studied in a non-destructive manner. The tomography results obtained show that in addition to the lead rich areas on the obverse and reverse of the coins (often already clearly visible on the surface due to the formation of white corrosion products) a varying number of lead containing inclusions could be detected within the antique bronze coins. In addition, some information on their casting technique could be gained.

## Introduction
The Coin Cabinet of the Kunsthistorisches Museum (KHM), Vienna, is one of the largest in the world. It also holds a large collection of ancient Greek bronze coins which were minted during the Roman imperial time. These so-called Greek imperials were produced in the eastern, Greek speaking provinces of the Roman Empire up to c. 280 AD. Other than in the Roman Imperial coinage blanks made of highly leaded bronze alloy were used frequently. Those coins were issued by a great number of municipalities and were primarily used as local currencies; therefore, also their images are of more local character and provide us with unique historic and otherwise unattested information of their cities.
Only a tiny fraction is on display in the permanent exhibition at the KHM, the major part of the collection is stored in wooden storage cabinets (Fig. 1). Due to the release of organic acid pollutions [1] from the wood and together with other air pollutants (i.e. $SO_2$, $NO_2$, $NO_x$, $O_3$) severe corrosion develops on the antique bronze coins showing a high lead and/or tin content [2-4]. A white powder of at first lead acetate and later on lead carbonate develops during this process. The coins start to show some points of whitish, powdery corrosion products on the surface (Fig. 2). For single objects the corrosion even leads to a complete destruction of the coin’s core, by only leaving an intact outer shell of metal and/or patina. When this shell breaks in certain areas it reveals a completely reacted inner part containing only the corroded powdery material [5] (Fig. 2).

## Analysis and results
Within a four years research project the corrosion phenomena of 1,200 coins were studied by different non-destructive analytical techniques to better understand the development of corrosion and to enhance the preservation of the antique coins.

IOP Conf. Series: Materials Science and Engineering **37** (2012) 012011 doi:10.1088/1757-899X/37/1/012011

**Fig. 1** Historic wooden storage cabinets still in use in the Coin Cabinet of the KHM.


**Fig. 2** Different states of typical corrosion phenomena visible on Greek imperials.

UV-fluorescence microscopy was performed in the restoration workshop of the Coin Cabinet using a SteREO Lumar.V12 Zeiss fluorescence microscope equipped with four different UV to red light wavelength filters. Due to their high fluorescence in UV light the formation of mainly carbonates could be observed in the corroded areas at the surfaces of the coins investigated (Fig. 3).

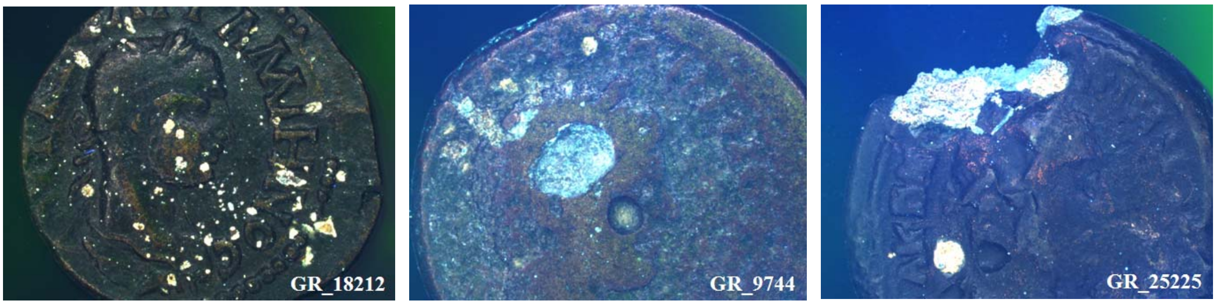


**Fig. 3** UV fluorescence microscopy shows the formation of highly fluorescing carbonates.

Scanning Electron Microscopy with Energy Dispersive X-ray detection (SEM-EDX; Philips XL 30 ESEM; 20 kV) proved the presence of mainly lead containing corrosion products (Fig. 4). Whereas the base alloy contains mainly copper (Cu) and lead (Pb) as well as a low amount of tin (Sn), the white corrosion product is clearly Pb based.

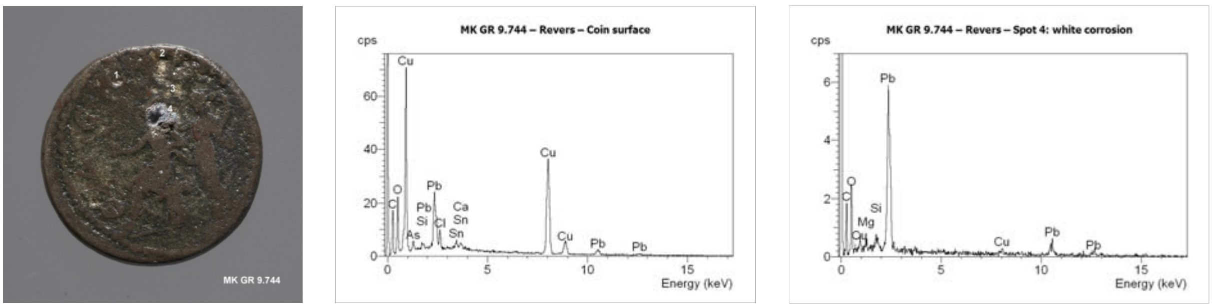


**Fig. 4** Example for the SEM results: Revers of coin GR_9744 together with SEM spectra of the coin's surface (bronze) and the white corrosion spot no. 4 in the centre of the upper half of the coin (Pb based corrosion).

IOP Conf. Series: Materials Science and Engineering **37** (2012) 012011 doi:10.1088/1757-899X/37/1/012011

To further investigate the phases present in the corroded parts of the coins neutron diffraction studies were performed at the GEM and POLARIS diffractometers at the Rutherford Appleton Laboratories, spallation source ISIS, Oxfordshire, Great Britain, for 20 selected objects with different states of corrosion. These investigations confirmed a high lead content of between 20 and over 30 % Pb and a typical tin content of up to 8 % Sn in the bronze alloys. Unfortunately the evaluation of the corrosion phases is still in progress.

In addition, for the same group of objects X-ray (250 kV) and thermal neutron tomography investigations were performed at the NEUTRA beam line, neutron spallation source SINQ, of the Paul Scherrer Institute (PSI) using a max. image size of 5 x 5 $cm^2$ and a resolution of 50 µm (for experimental details see [6]). To get a first overview of the inhomogeneity of the coins X-ray and neutron radiographies were taken from all objects (Fig. 5). Very different results could be obtained from the radiographies for the single objects. For some of them nearly the same image could be detected using either X-rays or neutrons, for others the images looked quite different, e.g. much more information on lead (Pb) containing inclusions within the coins could be seen as black areas in the X-ray image than in applying neutron radiography (Fig. 5, left and middle). Sometimes also the opposite result was detected, i.e. more information was to be seen in the neutron image than using X-ray radiography. These differing results depend on Pb being strongly attenuating X-rays due to the many electrons (Z=82) in its atomic shell. Coins with a high Pb content and/or comparatively thick coins are, therefore, less transparent for X-rays than those with a lower Pb content or thinner coins. Pb aggregates (inclusions) within objects show clearly in X-ray, if their thickness is large compared to the object’s thickness or if the homogeneously distributed Pb content in the matrix is low. On the other hand, for neutrons Pb is more transparent than e.g. bronze. So in neutron radiographs Pb inclusions are usually less visible than in the corresponding X-ray radiographs. Due to varying distributions of the Pb and the different thicknesses of the coins, exceptions are possible (and were sometimes detected). However, in neutron tomography slices, Pb inclusions are visible for all coins irrespective of their Pb content, because the bronze material is contributing mainly to neutron attenuation.

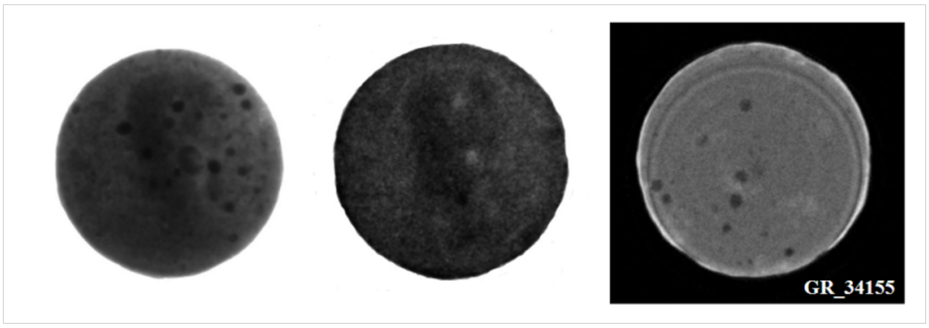


**Fig. 5** X-ray radiography (250 kV, left), neutron radiography (middle) and neutron tomography (right) of coin GR_34155 reveal different information concerning its lead rich inclusions.

Following these first investigations the coins were divided in three stacks of six to seven coins, respectively. These stacks were investigated by neutron tomography overnight (360°, 625 images, 60 sec/image), enabling further study of the distribution of the Pb containing inclusions in the core of the objects. For the majority of the coins the presence of two phases within the alloy, one rich in copper the other one rich in lead (darker in the neutron tomography images) could be detected by neutron tomography (Fig. 5, right). As shown on selected tomography slices in Fig. 6 the Pb containing inclusions of varying size are inhomogeneously distributed over the width and depth of the coins (typical thickness about 3 mm; Fig. 7).

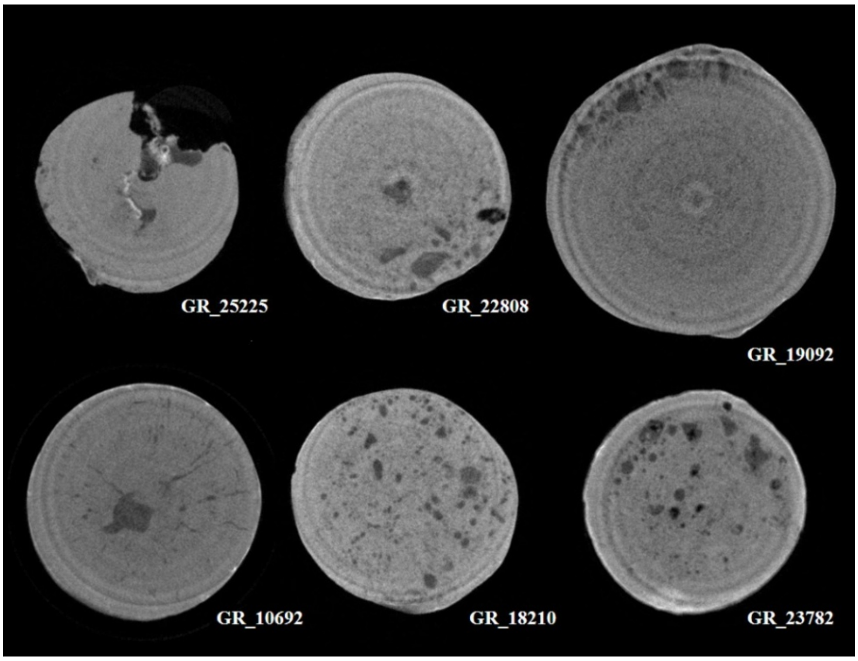


**Fig. 6** Casting the flans in vertical moulds leads to a Pb enrichment (darker) at one end of the coins (upper row); for other objects, presumably cast using horizontal moulds, the inclusions seem to be more evenly distributed.

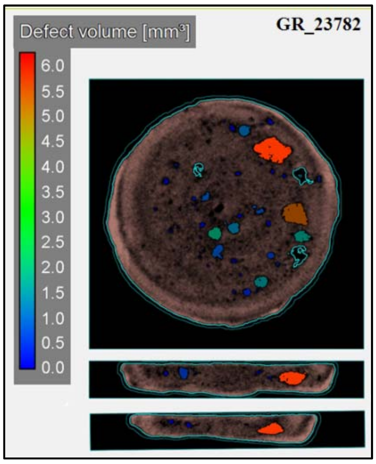


**Fig. 7** In this example about 20 % of the coin's volume consists of the Pb rich phase.

During the evaluation of the neutron tomography data it became obvious that additional information on the casting technique – not studied for antique bronze coins so far – can be gained by this non-destructive technique. Due to their high lead content no homogeneous alloy can be formed in the production of the coin blanks used for minting the coins later on. Dependent on the casting technique chosen in antiquity – vertical or horizontal [7-9] – the Pb containing phase can be found in different parts of the object. Using the vertical casting technique a row of upright blanks is received within a closed mould by pouring the hot alloy in from the top. On the other hand, the horizontal casting technique produces lying blanks using open moulds. So the position of the blanks is different between horizontal and vertical casting techniques. Hints for the technique used can sometimes even be seen on the original antique coins, e.g. a nearly perfect round shape for the horizontally cast objects or typical casting marks on two opposite edges of the coins for applying the vertical technique. For the vertically cast blanks a clear enrichment of the Pb rich phase at one end of the coins is often visible (Fig. 6, upper row). Other objects show a more even distribution of the inclusions suggesting a horizontal casting technique. Further studies using self-made replicas applying different ancient casting techniques are still in progress.
The different distribution of the two phases within the coins, together with varying burial conditions and environmental influences, explains the irregular development of corrosion in the core and on the surface of the different coins investigated. To enhance the future preservation of the vulnerable objects a nitrogen flooded metal storage cabinet has been installed in the Coin Cabinet of the KHM recently.

## Conclusion

By applying light and electron microscopy the development of lead containing corrosion products (most probably carbonates) could be confirmed for a set of antique bronze coins with high lead content. Using neutron tomography the development of two different phases during the casting process (one rich in copper and one rich in lead) could be proven and the inhomogeneous distribution of the Pb rich inclusions inside the coins could be shown. The assumption that the scattering of the Pb rich phase is connected to the casting techniques used in antiquity will be further studied using self-made replicas in the future.

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