



Czech Technical University in Prague
Department of Dosimetry and Applications of
Ionizing Radiation



X-ray fluorescence analysis: from spot analysis to 3D imaging

T. Trojek

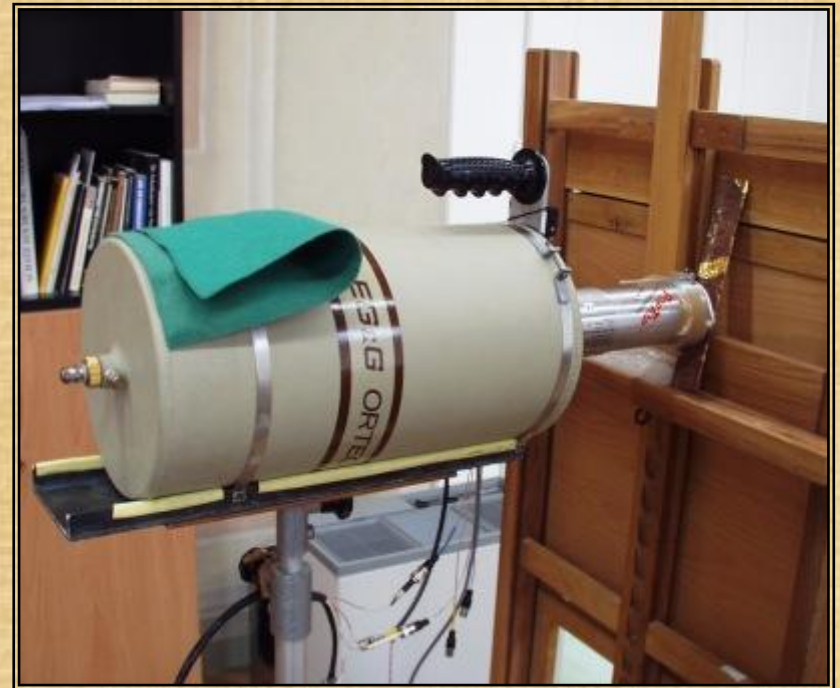
R. Prokeš

H. Bártová

T. Čechák

L. Musílek

X-ray fluorescence analysis 15 year ago



Handheld analysers today



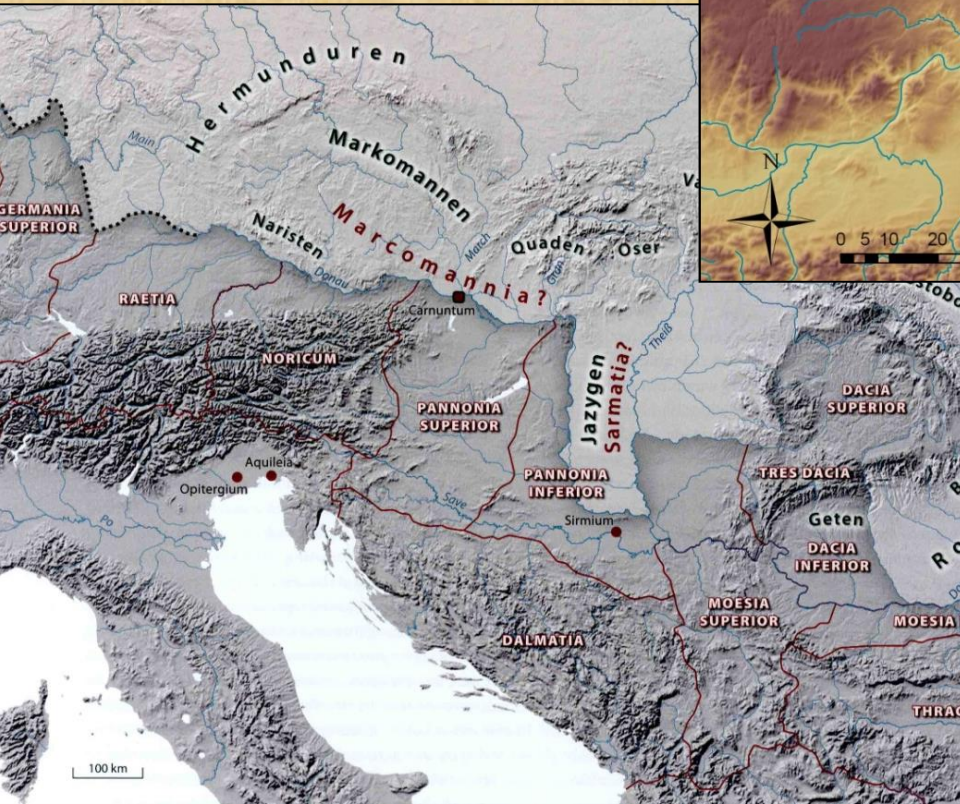
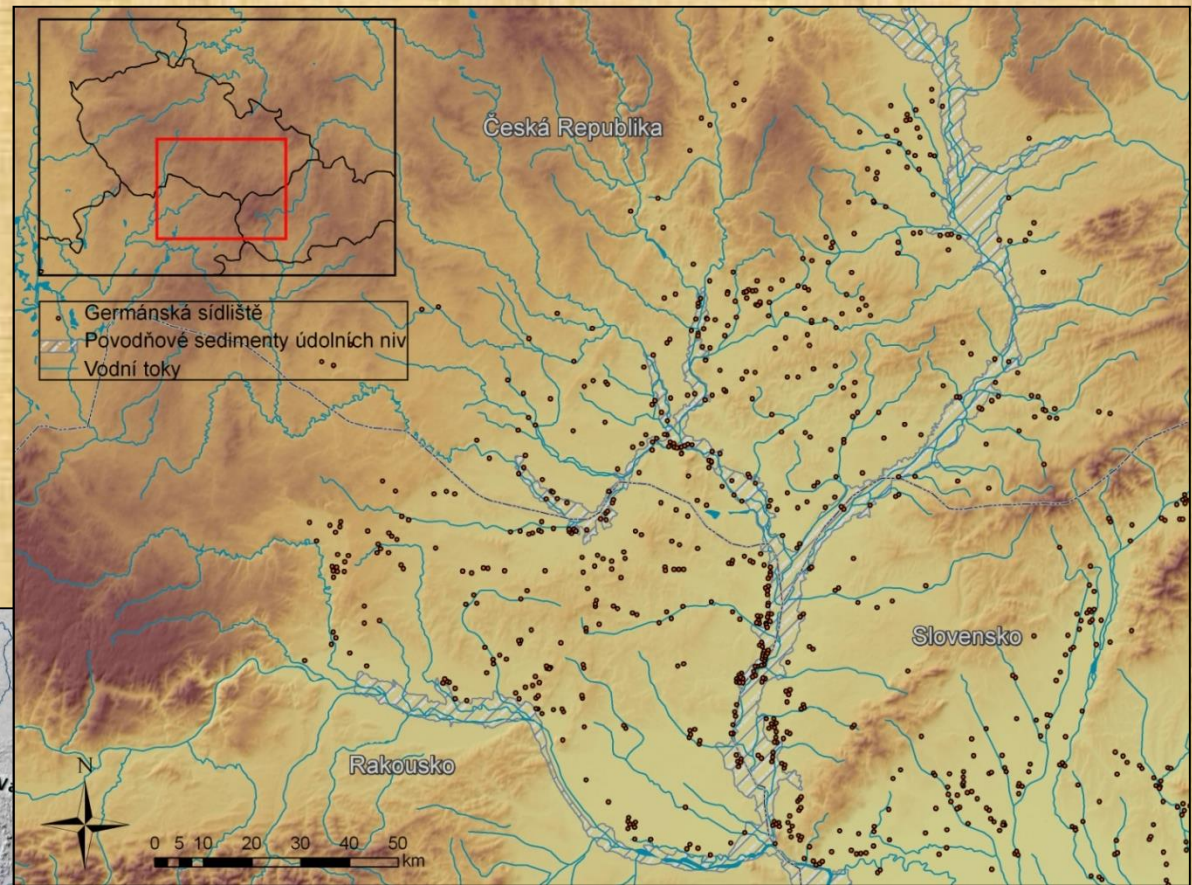
Analysis of inks and pigments

XRF setup from the year 2003
Beam diameter – 0.5 mm



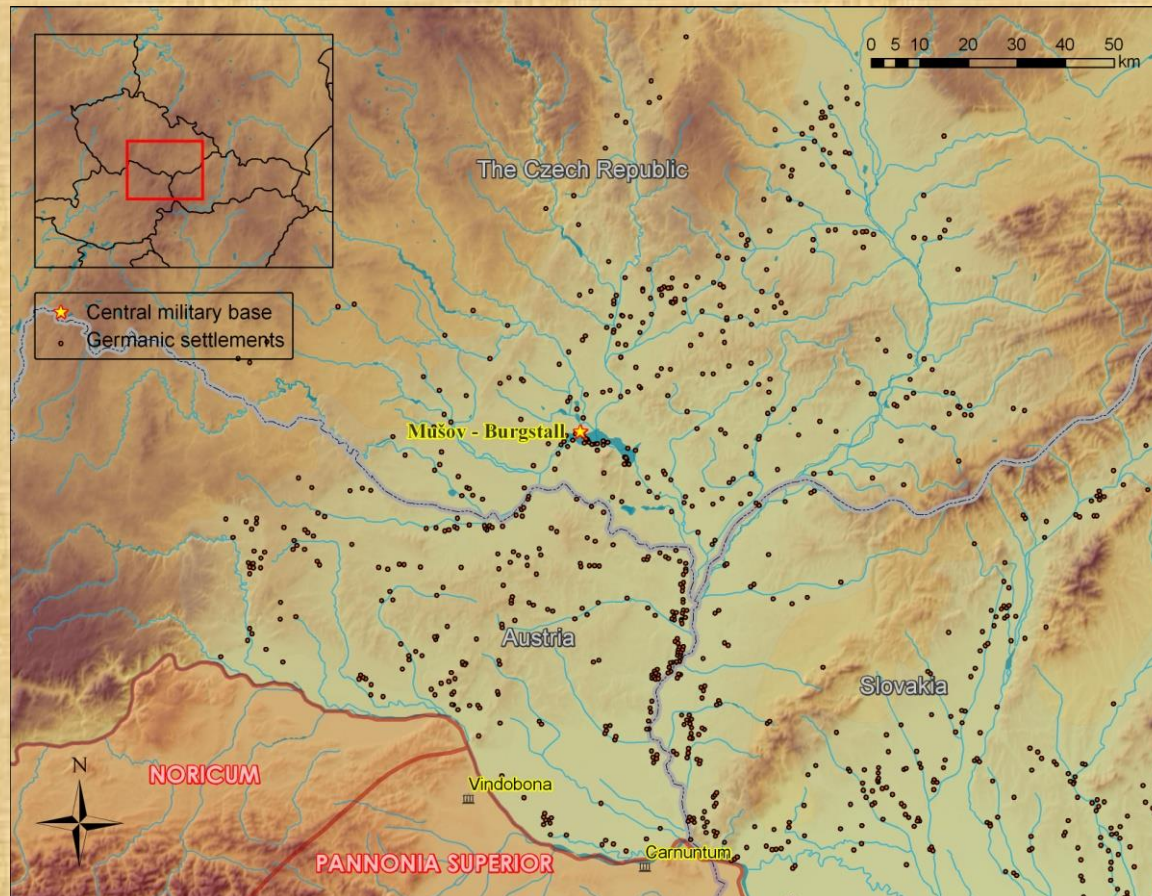
Time of analysis – 5 minutes

Moravia in the Roman period, 0-380 AD



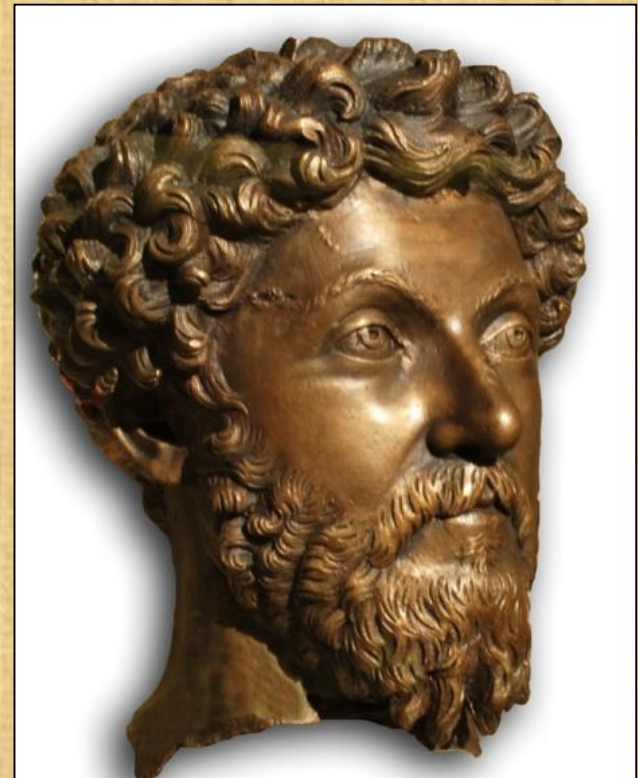
Germanic settlement territory during the Roman period in Moravia, Lower Austria and Western Slovakia.

Roman Military Base at Mušov is an archaeological site on the hill Hradisko (Burgstall) near the Mušov reservoir of the Waterworks Nové Mlýny on the Thaya river. The first excavations, dating back to the 1920s, revealed a Roman military camp from the end of the 2nd century AD. It is one of the most important archaeological monuments in the Czech Republic.



In the second century, the Mušov territory had been strongly affected by a military conflict between Romans and Germans, the Marcomannic Wars.

Emperor
Marcus Aurelius.



166-175 1st Phase of the Marcomannic Wars

166-171 Roman defensive

Invasion of the Obi and Lombards,

The Marcomanni defeat the Romans

Invasion of the Marcomanni and the Quadi through Pannonia to Northern Italy (destruction of Oderzo, siege of Aquileia)

Attacks on Raetia, Noricum, Dacia

171 Extrusion of the invaders from the provincial land

172-175 Roman offensive

172 great offensive against the Marcomanni, “ended” by minting coins with the inscription GERMANIA SVBACTA

173 Combats against the Quadi

174-175 Combats against the Sarmatians

175 Uprising of C. Avidius Cassius in Syria

177/178-180 2nd Phase of the Marcomannic Wars

The main antagonists: the Hermunduri, the Sarmatians, the Marcomanni and the Quadi

179/180 surface control of the Marcomanni and Quadi territories, according to the written sources there were 20 – 30 thousand troops on their territories

17 March 180 death of Marcus Aurelius

April to August 180 4th Imperial acclamation of Commodus.

The so-called Peace of Commodus: the end of the occupation and the withdrawal of the troops, contracts with the individual tribes, partial restrictions on their sovereignties and reductions of their combat potential, free uninhabited zone along the border, the completion of the reconstruction of the fortification system with stone camps.

Mušov-Burgstall

Central Roman Military Base on the Marcomanni territory



The most intensely populated location above the reservoir.



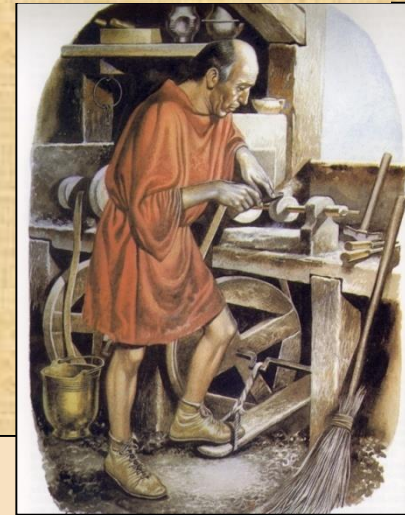
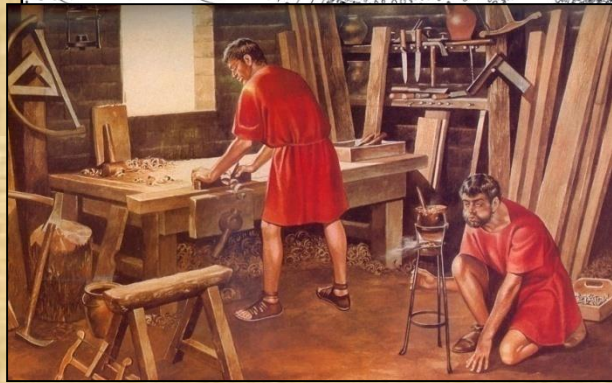
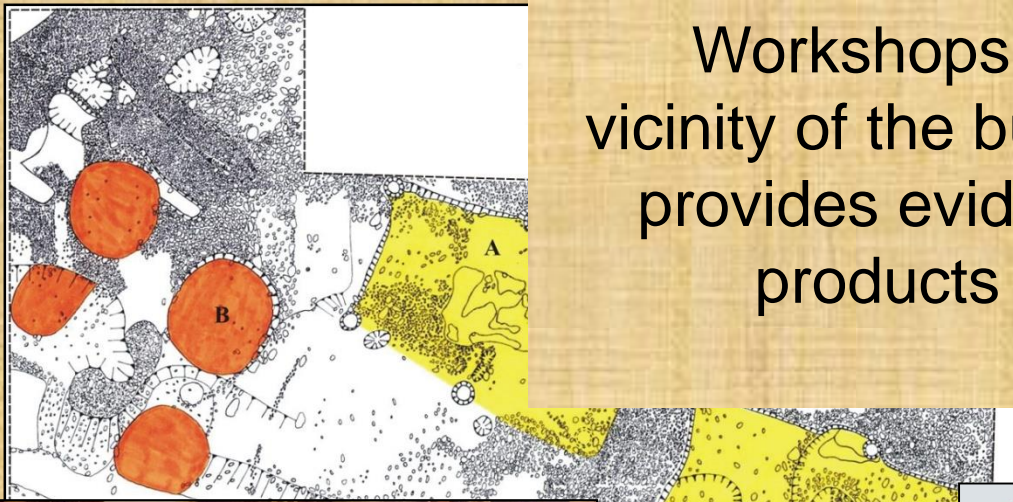
Mušov-Burgstall field research over the past 90 years.



Research of A. Gnirs (1927-28). The researches on the site began in the 1920 s. The archaeological research site was visited by the first Czechoslovak President Tomáš Garrigue Masaryk.



Workshops have been uncovered in the vicinity of the buildings. The obtained waste provides evidence for the casting of metal products and the presence of a forge.



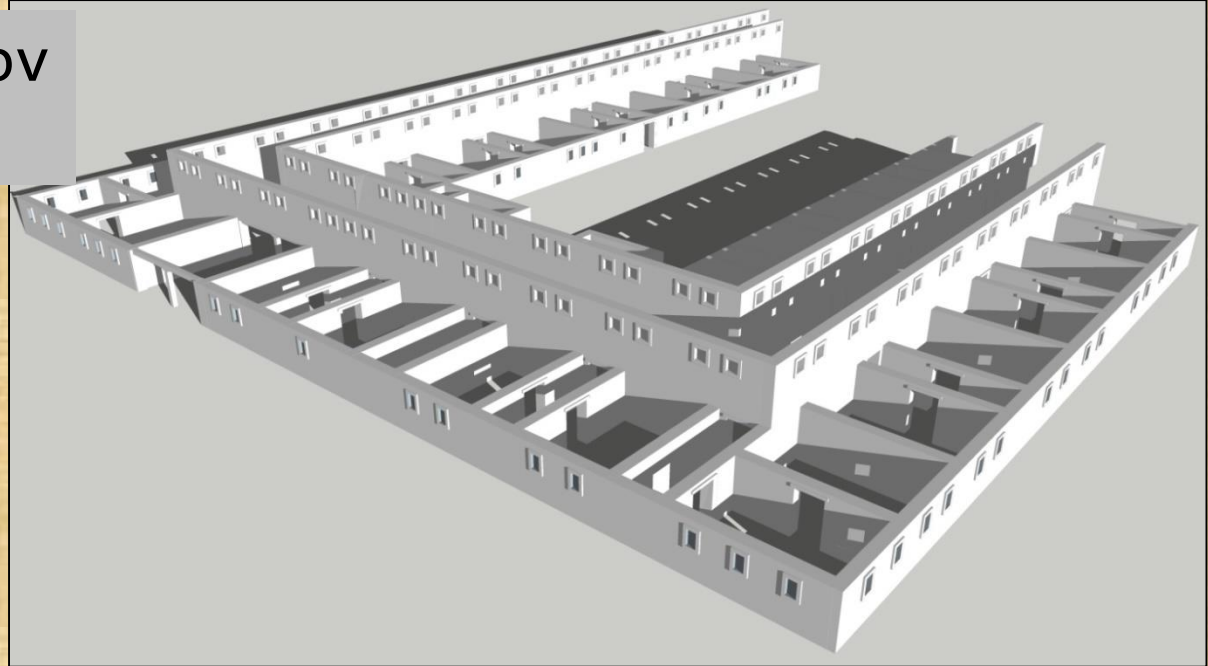
Hradisko near Mušov - Valetudinarium

The hospital, explored in 2012, was part of the military camps.

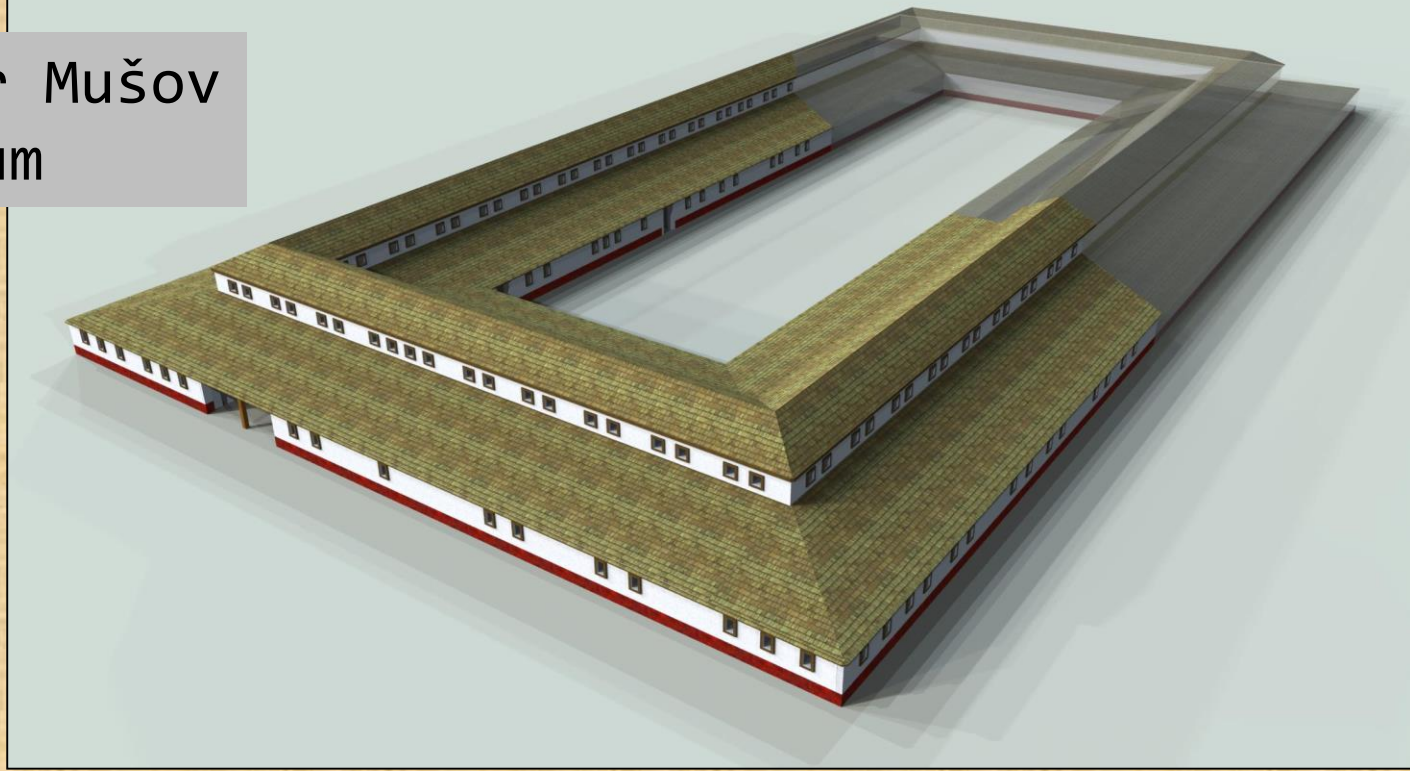
Reconstruction on the basis of the analysis of the ground plan.



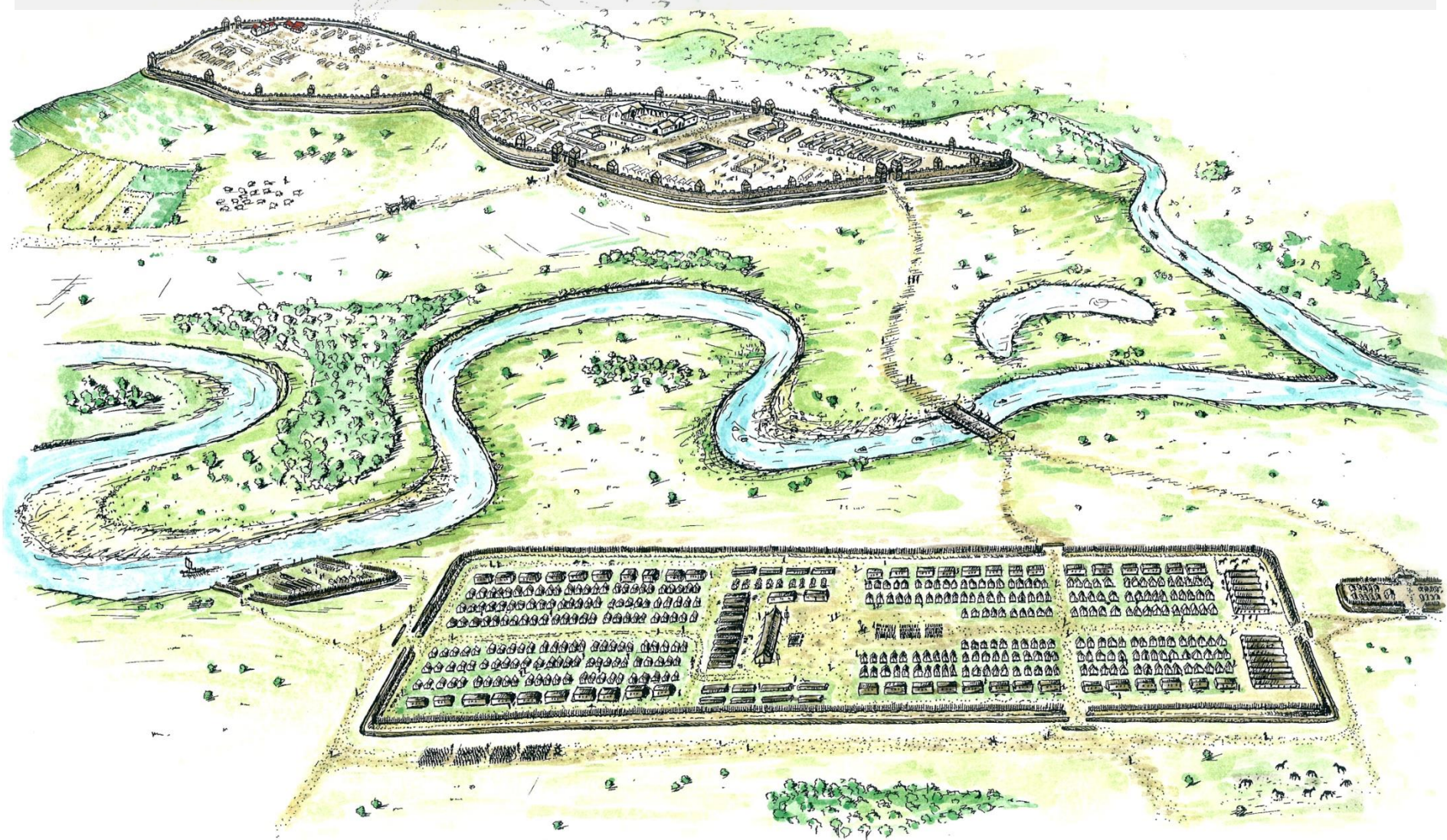
Hradisko near Mušov Valetudinarium



Hradisko near Mušov Valetudinarium



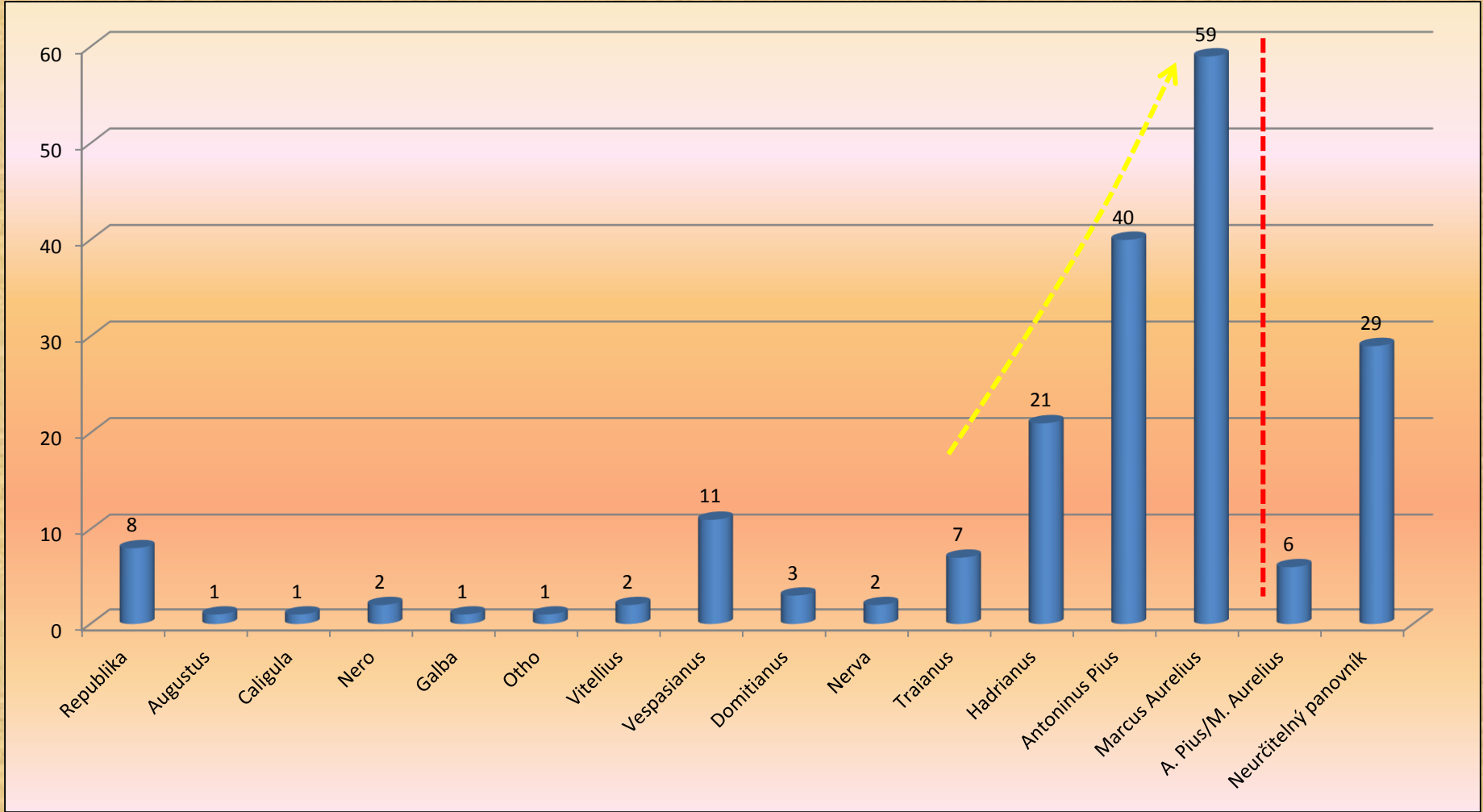
Reconstruction of the Roman military complex on the hill Burgstall at Mušov.



Hradisko near Mušov

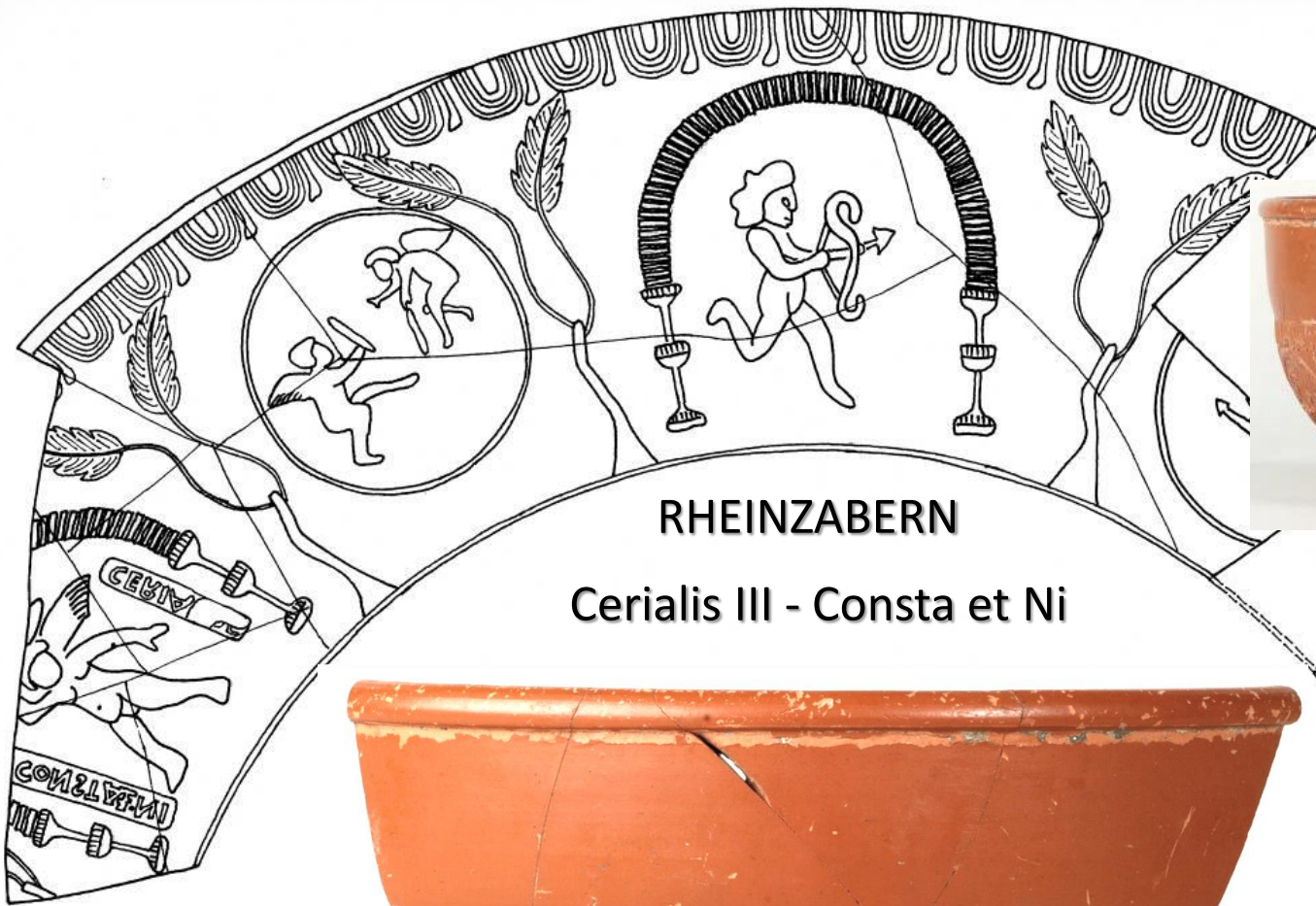
Coins





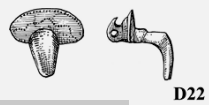
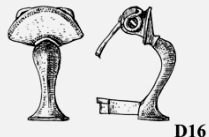
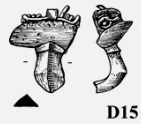
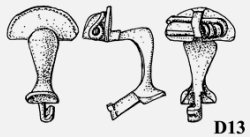
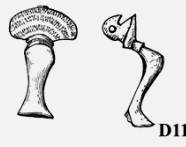
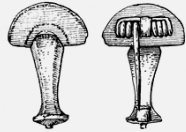
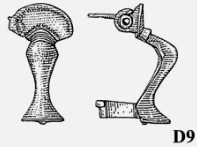
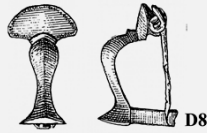
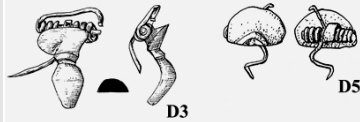
Hradisko near Mušov
terra sigillata





RHEINZABERN
Cerialis III - Consta et Ni



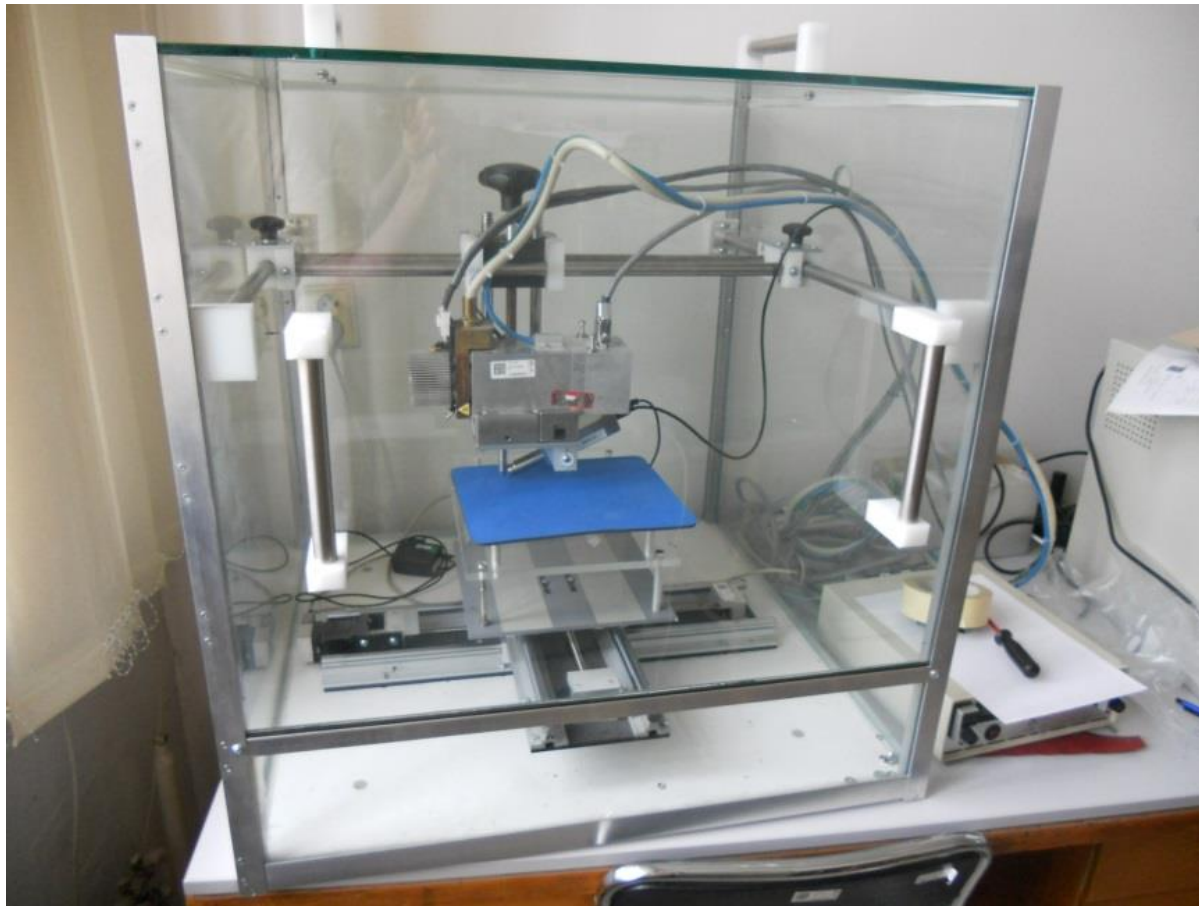


Hradisko near Mušov
Roman fibulae

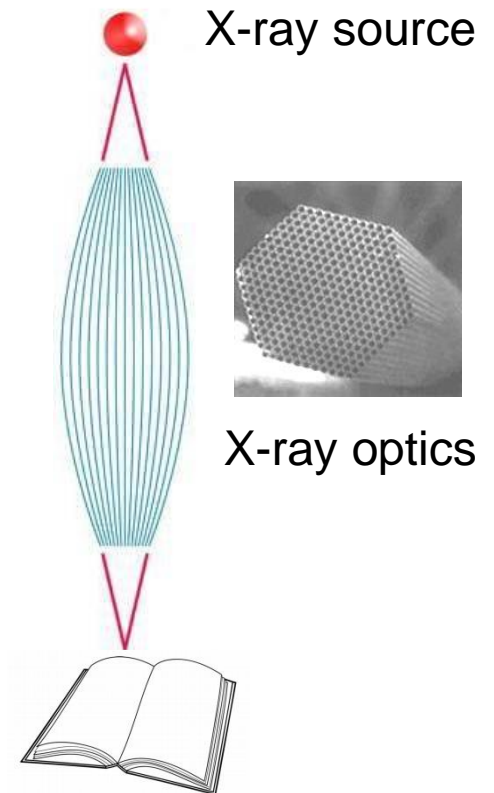


X-ray fluorescence micro-analysis

Diameter of a beam spot: 0.02 mm – 0.5 mm



Maximum dimension of an object: 70 cm



X-ray fluorescence micro-analysis

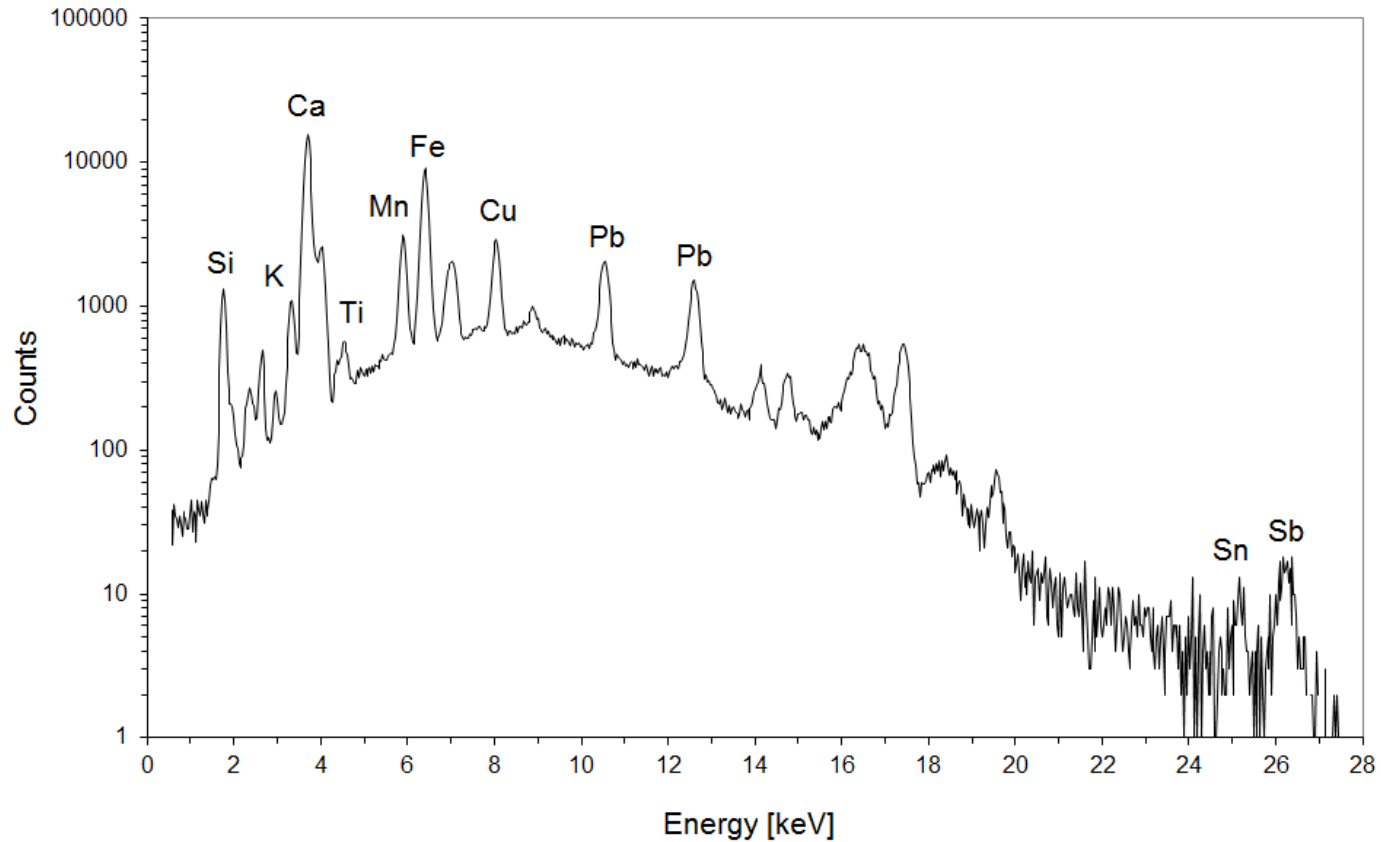
Photograph of a bronze belt fitting

- decorated by enamel and a combination of enamel and millefiori technique



X-ray fluorescence micro-analysis

XRF spectrum of blue enamel



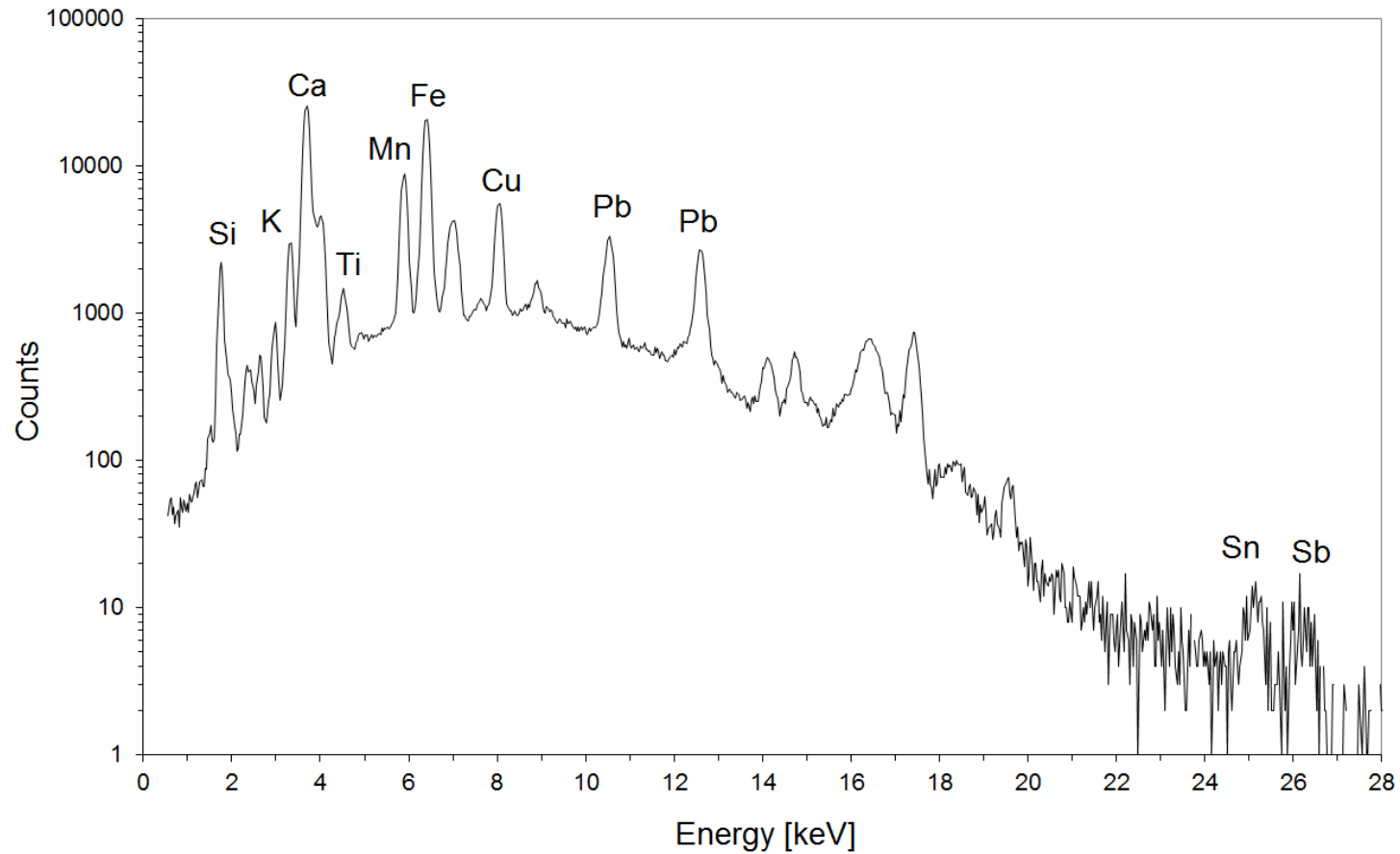
X-ray fluorescence micro-analysis

Photograph of a unique fibula decorated by enamel technique
(locality Mušov – Burgstall)



X-ray fluorescence micro-analysis

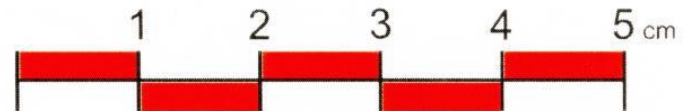
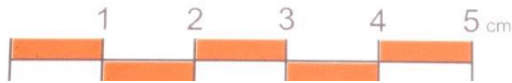
XRF spectrum of blue enamel



X-ray fluorescence micro-analysis

Composition of blue enamels

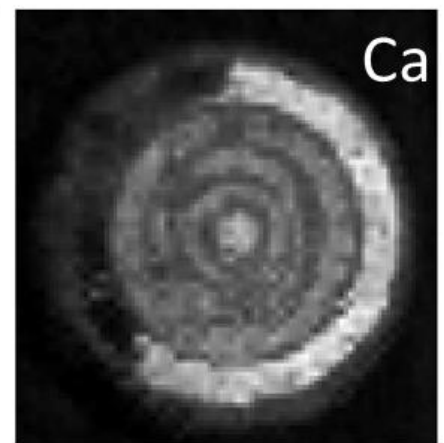
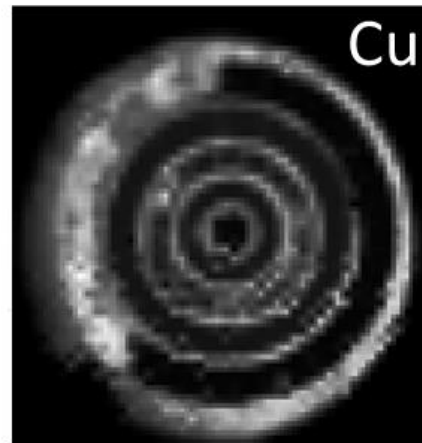
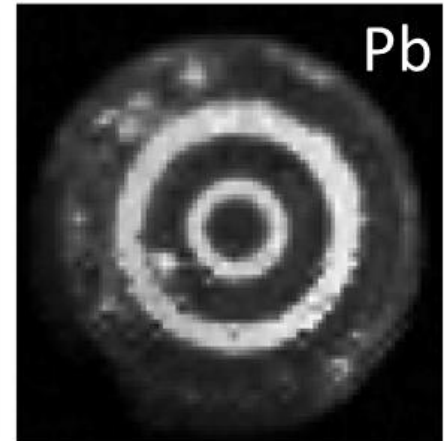
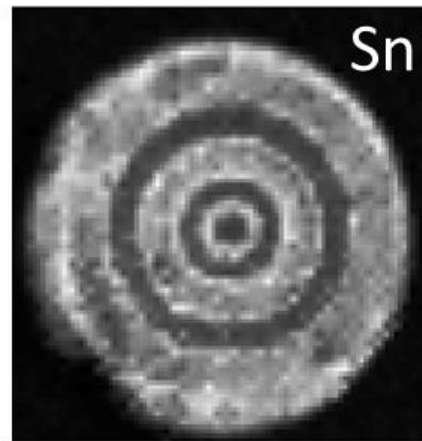
The concentrations of oxides varied between 1-1.5% for lead and tin, 1-3% for antimony, and above 0.5% for copper. Concentration of cobalt oxide was lower than 0.1%.



It is well known that mixtures of cobalt and copper oxides were added to glass to achieve blue colouring. In these particular cases, the **colorizing of blue enamels with a cobalt oxide was excluded** because its concentration is much lower than for a copper oxide.

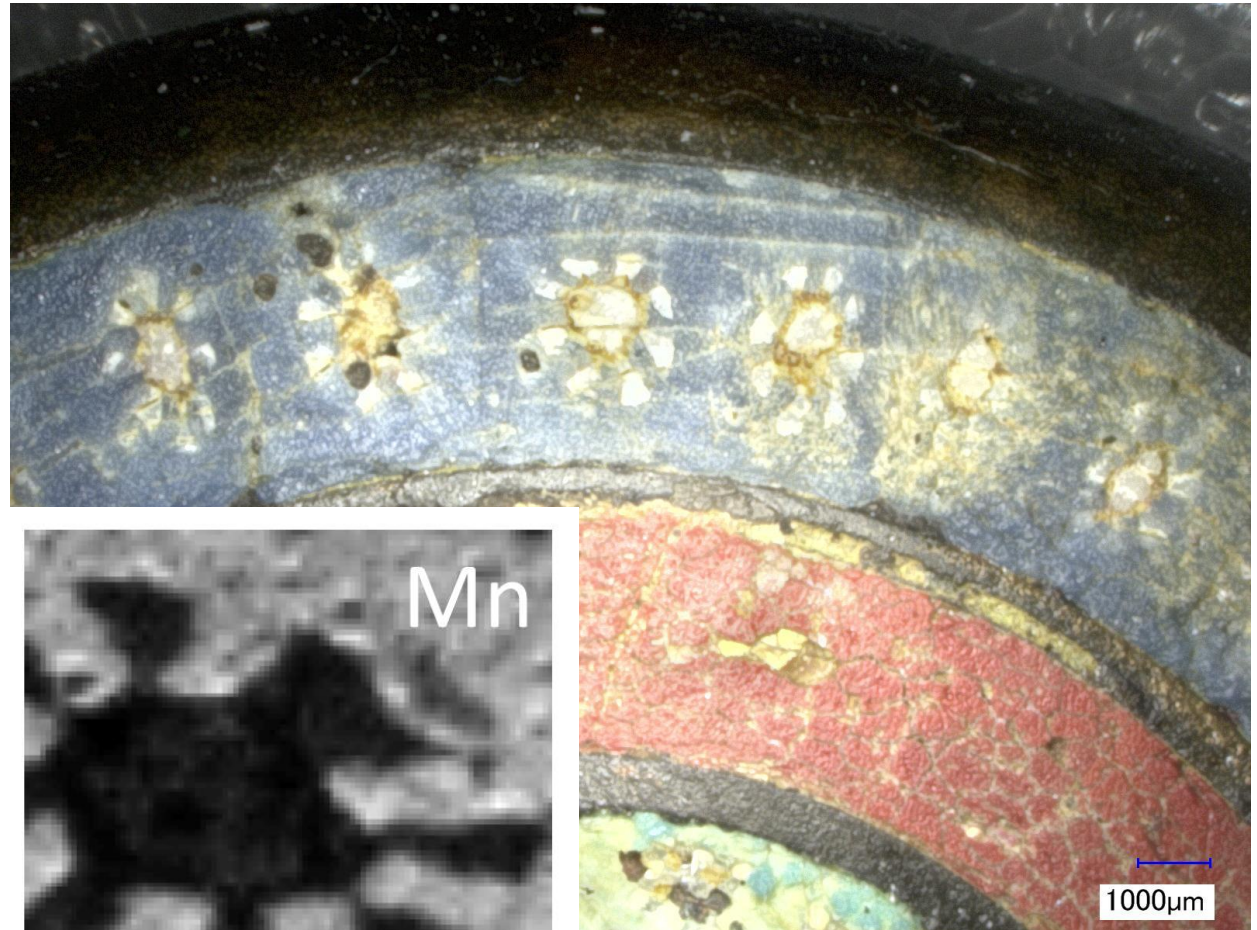
Macro – XRF scanning

Disk-shaped belt decoration (locality Mušov – Burgstall)
and results of macro-XRF scanning

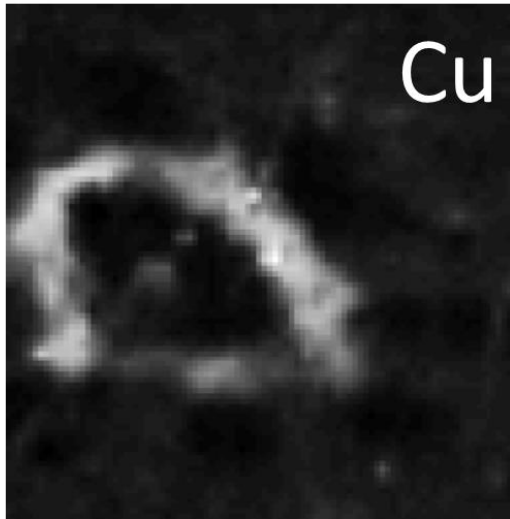


Micro –XRF scanning of paintings

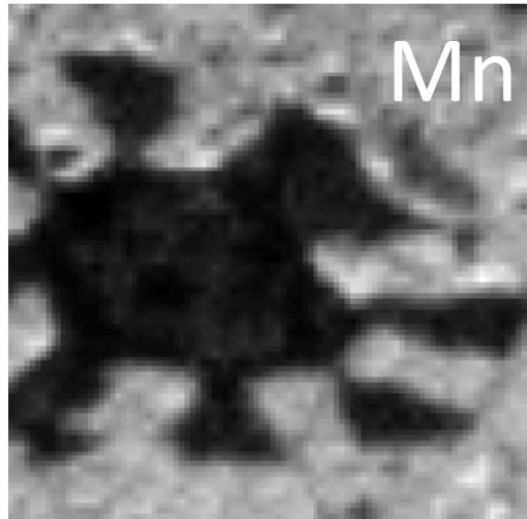
Micro-XRF scanning of decoration in blue enamel in the outer band



Cu

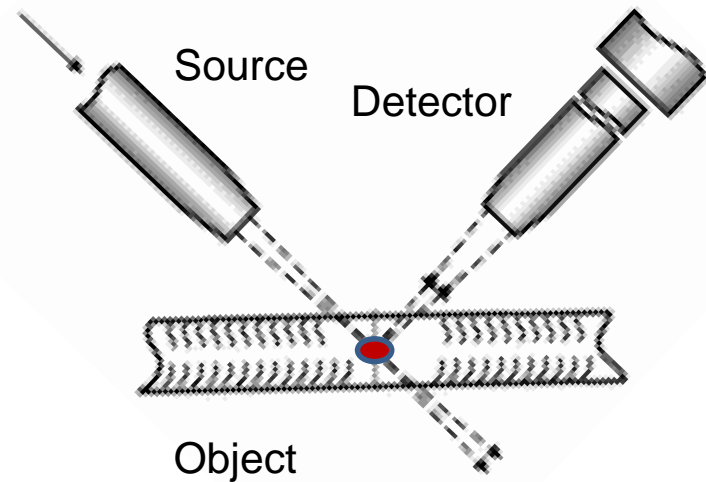
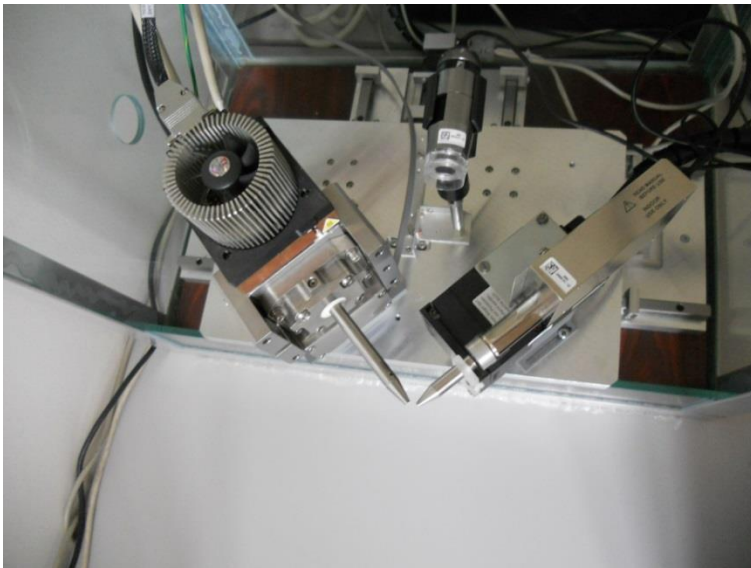


Mn



Confocal X-ray fluorescence analysis

Determination of depth distribution of elements



Confocal XRF of paint layers

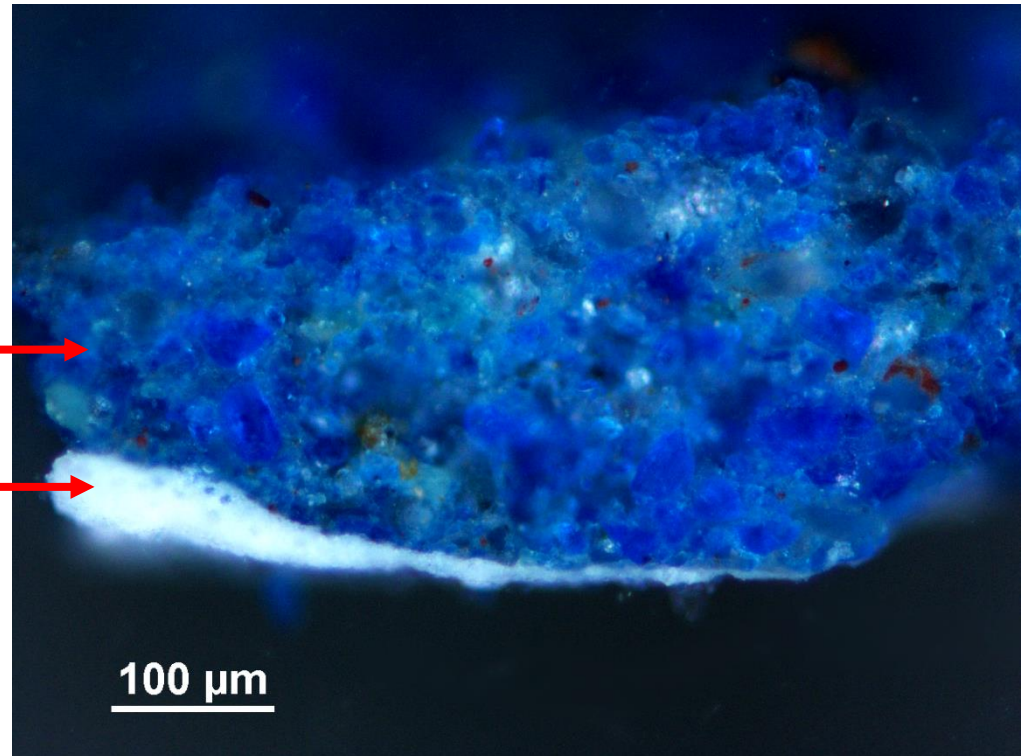


Azurite on lead white

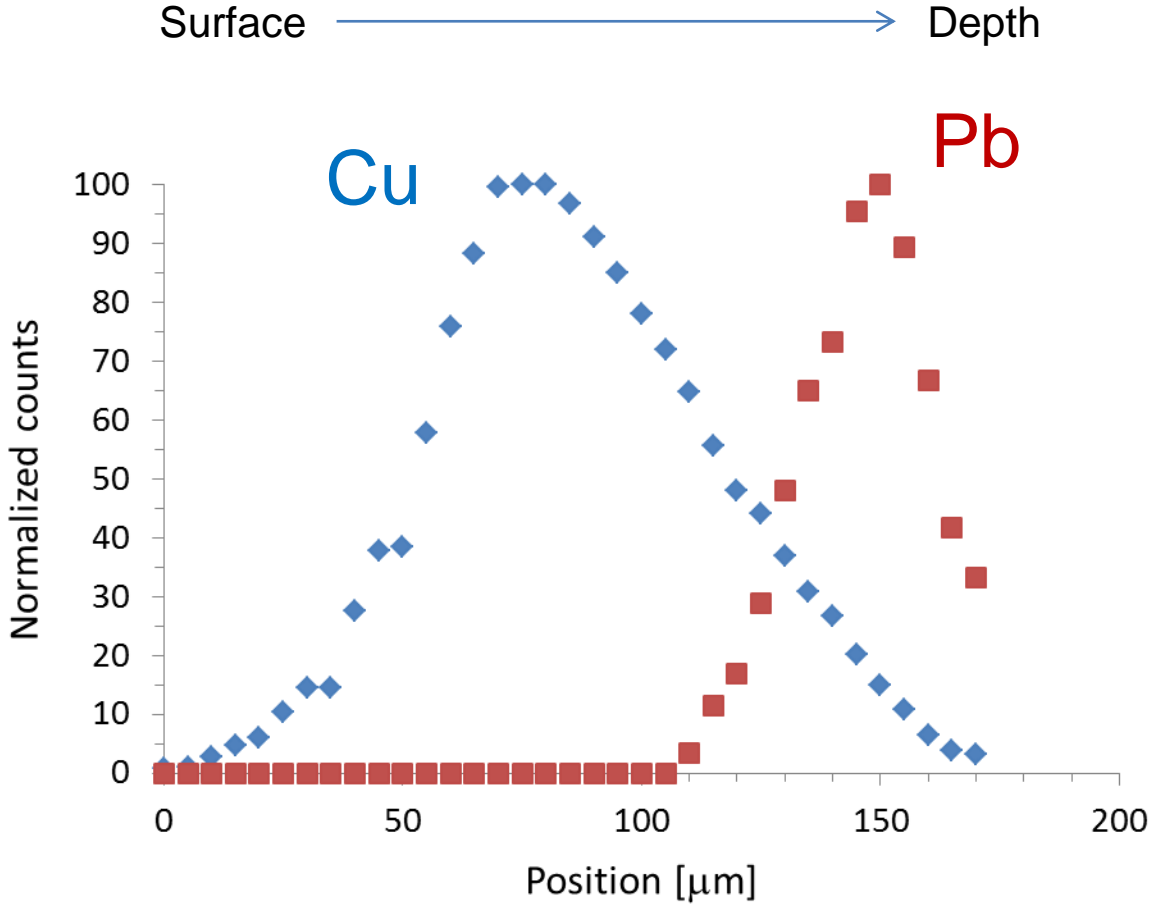
Cross-section of a sample

Azurite – $2 \text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ →

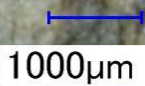
Lead white – $2 \text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ →



Confocal XRF of pigment layers - result

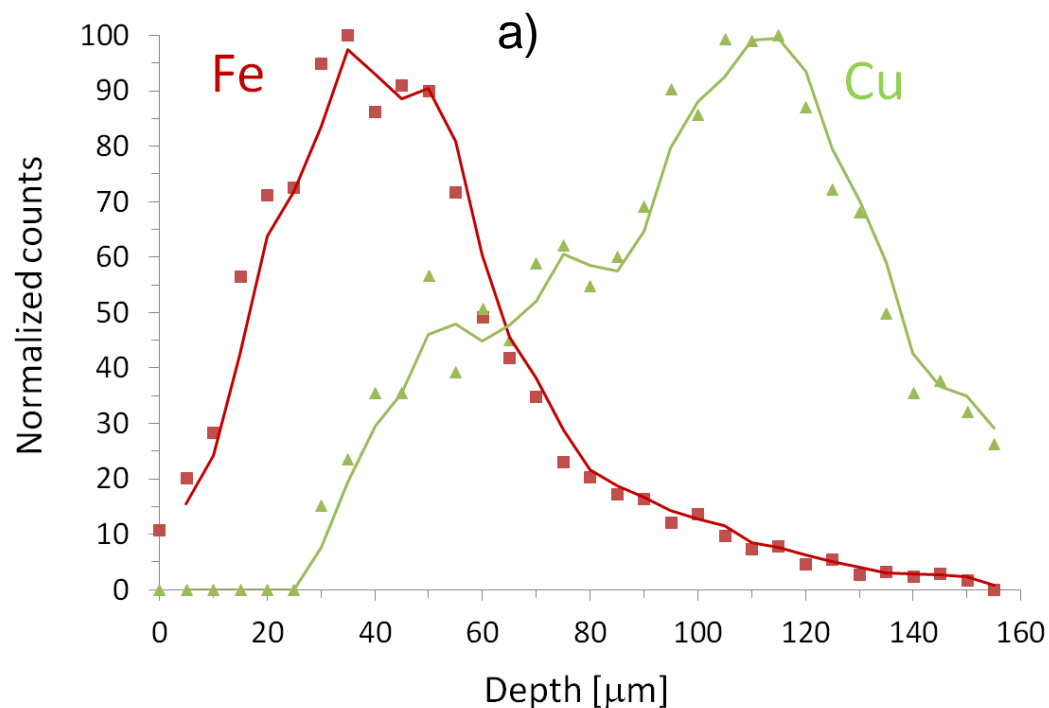


Small disk-shaped belt decoration (locality Mušov – Burgstall)



Small disk-shaped belt decoration (locality Mušov – Burgstall)

Confocal XRF depth profiling of the small disk-shaped decorative artefact in the place of the red line



Small disk-shaped belt decoration (locality Mušov – Burgstall)

It indicates that the red line rich in iron was painted with a brush on a green copper-based enamel layer.



Conclusions

The finds analysed within the presented research, can be placed in the situation of the Roman army. In spite of the fact that enamel-decorated finds rarely occur in South Moravian sites inhabited by Germans.

Analyses performed with micro-XRF techniques show that oxides used in colourizing enamels can have much more varied chemical compositions than previously assumed. We excluded colourizing of blue enamels with cobalt oxides and we proved that the blue hue was achieved by copper, tin, and antimony.

Also the surface XRF scanning of the artefacts played an important role in the identification of chemical compositions of artefacts decorated by the combination of millefiori and enamel-painting techniques. Due to large dimensions of the examined artefacts, the application of SEM-EDX or EMPA is meaningless.