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DETERMINATION OF CHARACTERISTIC TRACE ELEMENTS IN A MIDDLE AGE BRONZE DOOR OF THE AUGSBURG CATHEDRAL BY USING NEUTRON ACTIVATION ANALYSIS (NAA)

The Romanic bronze portal of the Augsburg Cathedral is dated to the first half or at the latest from the middle of the 11th century. It is one of the twelve major Romanic bronze gates in Europe and one of the best examples of medieval casting art north of the Alps. It is the best-preserved component of the old Ottonian church consecrated in 1065. Its original place is unknown. It was first mentioned in a paper source during a transgression (alleged theft of a plate and subsequent repair) in 1593. During the last ten centuries, the door was placed at different locations of the cathedral (Weis/Mach/Brendel 2005). As one of the major works of the Diocesan Museum of Augsburg, the door has finally received a hall of its own designed especially for providing the best conservation conditions since 2004.

The two door wings with different size consist of a total of 35 bronze plates, two door pullers, 18 decoration heads and 89 borders. The relief panels depict mythological, symbolic and several Biblical scenes. Quite different from those at other medieval cathedrals in Germany, e. g. Hildesheim Cathedral (1015), the 35 panels are relatively plain with just a single figure occupying the space. This makes it somewhat difficult to identify the scenes. The consecution, context and the origin of the reliefs have been an unsolved puzzle since long time (Chevalley 1995).

An extensive restoration was carried out in the late 1990s in the restoration department of the Bavarian State Department of Monuments and Sites under scientific guidance. During the restoration, hundreds of samples were collected from the relief panels and the borders for further scientific investigations. The alloys could be analysed by using scanning electron microscopy with energy dispersive X-ray spectros-copy (SEM/EDX). Different contents of the major elements (tin, lead and zinc) could be determined quantitatively. However, due to the very low sample quantities, trace elements in the samples could not be analysed (Mach 2009). Art historians hope that at least a part of the numerous questions, e. g. the production place of the old bronze door and above all the context of the bronze panels, may be solved by means of other modern scientific analysis, when more information about the chemical and physical properties of the materials will be known.

Neutron Activation Analysis (NAA) is a very sensitive multi-element analytical technique used for both qualitative and quantitative analysis of major, minor and trace elements. It is based on an extensive spectrometry of characteristic g-rays after sample irradiation in a neutron field with high neutron flux, such as in a research reactor. Up to 30 or even 40 elements can be determined simultaneously, which of course depends on the elemental composition of the samples. The great advantage of NAA is that elements which were not expected before are also detected. In many cases, this has been of practical use: especially in scientific applications, the presence of such unexpected trace elements often has enormous consequences. The method works for a very wide concentration range, from percent level down to the ppt (parts per trillion e. g. one part in 1012) and even sub-ppt level. NAA is in an unbeatable position in analysis of the rare earth elements (REE) and other metal elements in low concentration level measurements. NAA can perform non-destructive analyses or with minimal sample amounts. In archaeology, NAA can give useful information about the origin of the findings according to the so-called

Fig. 1 Bronze heads (top: Kl09 and Kl10; below: Kl11 and Kl12) on the left door leaf. – (Photos B. Diepold).

fingerprint of the individual element composition in their raw materials (Harbottle 1990). Many ancient bronze samples, e. g. old Chinese bronze mirrors, have been analysed by using NAA to understand their production procedures and origins (Li 1981; Gilmore/Ottaway 1980; Nezafatis 2006; Kuleff/Pernicka 1995; Höltta/Rodenberg 1987).

Irradiation and analysis

Samples collected from four bronze heads (Kl09, Kl10, Kl11 and Kl12; **fig. 1**) on the left door wing were analysed at the research reactor FRM II of Tech-

nische Universität München in Garching, Germany. Only several milligrams (1.8-4.5 mg) of samples were packed in polyethylene (PE)-bags and loaded into a PE-irradiation capsule. The samples were irradiated together with a neutron flux monitor of ca. 10 mg (AuAl-wire IRMM-530R, with $0.1003 \pm 0.0012\%$ Au) at the irradiation position RPA-2 with a thermal neutron flux of $1.5 \cdot 10^{13}/cm^2 s$ for 30 min.

A high purity Ge-detector with a relative efficiency of 40% was used for the g-countings. A digital signal analyzer of type LynxTM made by CANBERRA and the GENIE2000 software belonged to the gamma spectroscopy system. The detector efficiency was calibrated and calculated using a mixed nuclide reference source QCY48 and the LabSOCSTM soft-

ware. The first measurements were performed with very high dead time (up to 50%) even at a distance of 30 cm from the detector after a cooling time of two hours. Although the spectra were dominated by the activation product of copper ^{64}Cu ($T_{1/2} = 12.7$ h), some other minor and trace elements with short-lived isotopes, such as ^{116m}In ($T_{1/2} = 54$ min), ^{65}Ni ($T_{1/2} = 2.52$ h) and ^{56}Mn ($T_{1/2} = 2.58$ h) could be detected, however, with large counting uncertainties. Nickel could not be identified in the sample KI09, due to the high concentration of Mn. Its detection limit was calculated by means of the minimum detectable activity (MDA) in the gamma counting.

Over the following days, the samples were measured again after the most short-lived nuclides had decayed. The long-lived nuclides could be identified without interference. Each sample was measured three or four times with different cooling times, in order to determine different nuclides with different half-lives. Already during the first countings, the different radioactivities provided an indication of different chemical compositions in the samples. In total, more than 20 elements were determined quantitatively or their detection limits were calculated by using the computer program MULTINAA (Lin/Baumgärtner/Li 1997). Based on the k_0-method (Lin/Lierse/Wahl 1997), no correction for the influence of the epithermal neutrons needed to be done due to the very high thermal neutron flux ratio at the reactor FRM II (Li/Lierse 2014). Not all related elements could be analysed, e. g. Pb, which is one of the important major elements in ancient bronze samples. The half-life of its activation product ^{207m}Pb ($T_{1/2} = 0.85$ s) is too short for the gamma counting under the condition for routine works at the research reactor FRM II. A fast sample transfer system would solve this problem (Li/Henkelmann/Baumgärtner 2004).

Discussion

Table 1 shows the contents (mass fractions) of the major and trace elements determined in the four bronze samples. Usually, it is not easy to find out a clear relationship between many results, especially when the range extends over several orders of magnitude from percentage to ppb (parts per billion). A direct comparison of all elemental contents in a logarithmic diagram cannot really reflect the similarity between different materials, because the real ratio of the data is more or less distorted through the logarithm. A simple relative comparison with a reference sample can partly solve this problem, but the smaller values can hardly be shown in the same ratio as the larger values (fig. 2).

We developed a new method to compare the different elemental contents over several orders of magnitude. Firstly, one sample, for example the KI12 is selected as reference randomly. For each element x, its mass fraction [kg/kg] values in all the other samples are compared to the value in the sample KI12 and then, normalised to unity. In order to display the smaller values as well as the larger with the same fair weighting in the same plot, the comparison ratio c and its sign will be changed, if the reference value of KI12 is greater than the value in the sample to be compared. The advantage of this change is that the smaller values of mass fraction can be demonstrated more clearly in a linear diagram (fig. 3).

$$c = \frac{w(x)}{w(x_0)} - 1, \text{ if } w(x) > w(x_0) \text{ or } c = 1 - \frac{w(x_0)}{w(x)}, \text{ if } w(x) < w(x_0).$$

It is easy to see from figure 3 that the elemental contents of KI12 and KI10 are most similar, except for iron and antimony, although these objects look quite different (fig. 1). This discovery confirms the result of the SEM/EDX performed by the Bavarian State Department of Monuments and Sites, which determined the major elements tin (Sn), zinc (Zn) and lead (Pb) in the samples. This result supports the presumption that the objects KI12 and KI10 most probably originated from the same material.

The contents of Sn and Zn in the two samples are higher than in the other samples. However, the values of nickel (Ni) cannot really be compared, because they have large uncertainties due to the high activities of other short-lived isotopes in the measurements after short cooling time. Very good agreement between the samples KI12 and KI10 can be found for the trace elements arsenic (As), selenium (Se) and indium (In). The higher contents of iron (Fe)

element	KI12	±	1.80	mg	KI10	±	4.56	mg	KI11	±	3.68	mg	KI09	±	4.36	mg
Sn	7.95	±	0.61	%	9.78	±	0.72	%	4.82	±	0.50	%	3.92	±	0.47	%
Zn	1.76	±	0.12	%	1.95	±	0.14	%	0.857	±	0.060	%	0.191	±	0.014	%
Ni	0.30	±	0.08	%	0.23	±	0.09	%	0.16	±	0.08	%	<0.38			%
Fe	0.28	±	0.03	%	0.13	±	0.01	%	0.15	±	0.02	%	1.2	±	0.1	%
Sb	0.16	±	0.01	%	0.094	±	0.01	%	0.51	±	0.04	%	0.092	±	0.006	%
As	0.11	±	0.01	%	0.10	±	0.01	%	0.16	±	0.01	%	0.021	±	0.002	%
Ag	0.040	±	0.003	%	0.033	±	0.002	%	0.046	±	0.003	%	0.054	±	0.004	%
Se	110	±	10	ppm	130	±	10	ppm	4.6	±	1.6	ppm	3.6	±	0.4	ppm
Au	9.0	±	0.7	ppm	5.3	±	0.4	ppm	26	±	2	ppm	3.3	±	0.4	ppm
Co	6.5	±	0.6	ppm	3.6	±	0.5	ppm	22	±	2	ppm	31	±	2	ppm
In	3.0	±	0.3	ppm	3.9	±	1.3	ppm	2.3	±	0.5	ppm	34	±	4	ppm
Br	2.3	±	0.8	ppm	1.5	±	0.6	ppm	1.4	±	0.4	ppm	6.5	±	0.8	ppm
La	0.047	±	0.010	ppm	0.021	±	0.004	ppm	0.029	±	0.006	ppm	2.6	±	0.3	ppm
Ir	14	±	4	ppb	<7.0			ppb	120	±	10	ppb	<6.3			ppb
Mn	76	±	5	ppm	<2.1			ppm	6.9	±	0.8	ppm	130	±	10	ppm
Sc	250	±	30	ppb	<23			ppb	68	±	21	ppb	910	±	70	ppb

Tab. 1 NAA results of the analysis of four ancient bronze samples. Element contents are given in mass related units-%, ppm (=mg/kg) and ppb (=µg/kg).
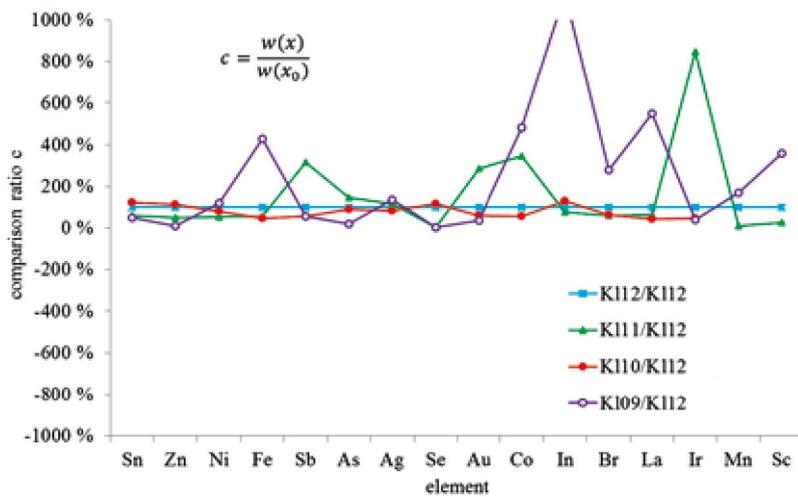
Fig. 2 A simple relative comparison of the other three samples with KI12. The content of each element determined in KI12 is set to 100 % as reference. The smaller values (c. <100 %) cannot be shown in the same ratio as the larger values.

$$c = \frac{w(x)}{w(x_0)}$$

(Legend: KI12/KI12, KI11/KI12, KI10/KI12, KI09/KI12)
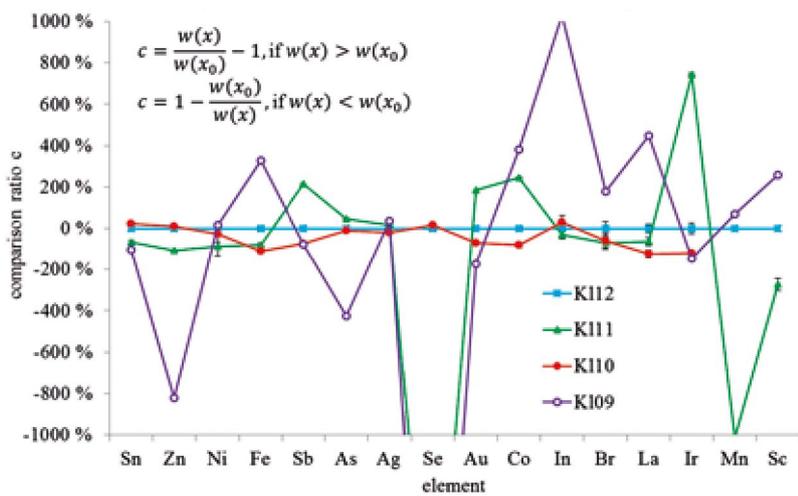
Fig. 3 The mass fractions of the same element in different samples are normalised to unity. The values in sample KI12 are selected as reference randomly. The material of KI12 and KI10 seems very similar. Comparison ratios c are calculated as described in the text.

$$c = \frac{w(x)}{w(x_0)} - 1, \text{ if } w(x) > w(x_0)$$
$$c = 1 - \frac{w(x_0)}{w(x)}, \text{ if } w(x) < w(x_0)$$

(Legend: KI12, KI11, KI10, KI09)

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and antimony (Sb) in KI12 compared to KI10 could mean an inhomogeneity of the element distribution in the samples during the casting procedure in the past or a possible contamination during the sampling in the late 1990s. This could be also the reason for the discrepancies between the values of some trace elements such as manganese (Mn), scandium (Sc) and lanthanum (La) in the two similar samples.

On the other hand, as we know, the content of tin in the bronze made in the later centuries was mostly higher than in the historical bronze made in the Middle Ages (Riederer 1982). Certainly, there are exceptions, e. g. many old bronze church bells show also high contents of tin. Generally, the alloying process could be more easily controlled, and the resulting alloy was stronger and easier to cast, when tin was mixed in the copper. Due to the high tin content of nearly 10 % in the samples KI10 and KI12, compared to the low values (<5 %) in the other two samples, both objects seem to be produced probably later than the other two and might be cast as copies of the other »original« bronze heads KI11 and KI09 in the later period. Anyway, it is an important indication for an early, local, and therefore probably »careful« preservation in the past (Mach 2009).

Because the element compositions in KI11 and KI09 are quite different, it seems improbable that the two objects were produced from the same row material at the same time. Especially, sample KI09 has much lower contents of Zn with (0.19 ± 0.01) %, and As with (214 ± 18) ppm but higher content of Fe (more than 1 %) than the other materials.

High iridium (Ir) content was found in sample KI11. Iridium is a one of the rarest elements in the Earth's crust and often can be found naturally in some nickel-copper ores (Xiao/Laplante 2004). The high iridium content in KI11 and KI10 might also be correlated with the presence of gold (Au). High content of iridium was also found in some ancient gold samples in our past analyses and by other authors (Brostoff et al. 2009).

Conclusions and outlook

Our positive results show that the NAA is a quite useful technique for the analysis of element composition and can give more details about the materials. If the experiment conditions can be optimised, e. g. by irradiating the samples with different irradiation durations to analyse isotopes with different half-lives or by using special counting techniques to determine nuclides with interferences, then even more trace elements can be determined in the future. By using the fingerprint method, the relation and origin of different objects can be identified exactly. We hope that more mysteries of this historical bronze door of the Augsburg Cathedral will be solved in the near future by means of neutron science.

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Summary / Zusammenfassung

Determination of Characteristic Trace Elements in a Middle Age Bronze Door of the Augsburg Cathedral by Using Neutron Activation Analysis (NAA)

Neutron activation analysis (NAA) was used to analyze samples from an old bronze door of the Augsburg Cathedral, in order to establish a reliable screening method for a total of 35 different reliefs and more than 100 other bronze components on this object, manufactured in the 11th century. Based on the fingerprint method, two bronze heads could be confirmed as copies of their neighboring counterparts. This result is an important indication for an early, local, and probably »careful« preservation in the past.

Bestimmung von charakteristischen Spurenelementen in einer mittelalterlichen Bronzetür des Augsburger Doms mithilfe der Neutronenaktivierungsanalyse (NAA)

Die Neutronenaktivierungsanalyse (NAA) wurde verwendet, um Proben einer alten Bronzetür des Augsburger Doms zu untersuchen und damit eine verlässliche Klassifizierungsmethode für die im 11. Jahrhundert hergestellten 35 verschiedenen Reliefs und mehr als 100 anderen Bronzekomponenten auf diesem Objekt zu etablieren. Basierend auf der Fingerabdruckmethode konnten zwei Bronzeköpfe als Kopien ihrer benachbarten Gegenstücke bestätigt werden. Dieses Ergebnis ist ein wichtiger Hinweis auf eine frühe, lokale und wahrscheinlich »sorgfältige« Konservierung in der Vergangenheit.

Keywords