Interaktion ohne Grenzen

Interaction without borders

Band 1 | Volume 1

Interaktion ohne Grenzen

Beispiele archäologischer Forschungen am Beginn des 21. Jahrhunderts

Interaction without borders

Exemplary archaeological research at the beginning of the 21st century

herausgegeben von | edited by

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Band 1 | Volume 1

Schleswig 2017

Gedruckt mit Unterstützung von

Archäologisches Landesmuseum in der Stiftung
Schleswig-Holsteinische Landesmuseen Schloss Gottorf, Schleswig

Carlsbergfondet, København

Dronning Margrethe II's Arkæologiske Fond, København

Farumgaard-Fonden, København

Verein zur Förderung des Archäologischen Landesmuseums e. V.
Schloss Gottorf, Schleswig

Zentrum für Baltische und Skandinavische Archäologie in der Stiftung
Schleswig-Holsteinische Landesmuseen Schloss Gottorf, Schleswig

Redaktion
Angelika Abegg-Wigg und Isabel Sonnenschein
unter Mitarbeit von Ronja Mücke und Nele Voß
sowie Wilson Huntley (englische Lesekorrektur)
und Annika Sirkin sowie Birte Anspach (Ortsverzeichnis)

Einbandgestaltung
Jürgen Schüller

Foto Seite V
Stiftung Schleswig-Holsteinische Landesmuseen
Schloss Gottorf, Schleswig

Layout und Herstellung
Wachholtz Verlag, Kiel/Hamburg
www.wachholtz-verlag.de

Vertrieb
Archäologisches Landesamt Schleswig-Holstein (ALSH), Schleswig
www.archaeologie.schleswig-holstein.de

Bibliografische Information der Deutschen Nationalbibliothek
Die Deutsche Nationalbibliothek verzeichnet diese Publikation in der
Deutschen Nationalbibliografie; detaillierte bibliografische Daten
sind im Internet über http://dnb.dnb.de abrufbar.

ISBN 978-3-00-057735-2

Festschrift für Claus von Carnap-Bornheim

zum 60. Geburtstag

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The axe from Ahneby – non-destructive view with X-rays inside the object

Mechtild Freudenberg and Leif Glaser

Metalworking has been a driving force in our development. In particular, copper and bronze objects from our past represent first key development steps in technical and social aspects and thus are invaluable as part of our cultural heritage. Being in use as tools, weapons and status symbols, these objects feature state of the art in metalworking of the respective time and place. Originating from a time without written documents in northern Europe, stone, copper and bronze objects in particular, being generally well preserved, are a very important source of knowledge when discovering our past and especially concerning the craft of metalworking. Naturally it is reasonable that we should study and conserve those precious objects, learning all we can at the time, while preserving them ideally undamaged for future generations and for possibly

Fig. 1 The axe from Ahneby.

Fig. 2 The coat of arms of the parish of Ahneby.

more advanced investigation techniques. Unfortunately when investigating the fabric of an object, the easiest and therefore oldest and most common method is sampling, cutting and the inspection of polished sections. Methods improved with time and the objective when investigating objects began to emphasize more the preservation of the objects than the mere scientific result of a single investigation. Neutron time-of-flight diffraction measurements are used to investigate strain and structure (Arletti et al. 2008; Caspi et al. 2010; Berger et al. 2013; Kiss et al. 2015). Those non-invasive neutron scattering experiments allow high-resolution crystallographic phase retrieval, with bulk sensitivity, allowing the measurement of the object without any disturbance from surface treatment or corrosion, with the converse argument of not being surface sensitive if need be. Two slight limitations of neutrons are: first, the relatively low flux of the sources and the impossibility to focus the beam, causing the need to use larger areas (cm^2) of an object for a measurement to keep measuring times reasonable; second, the possibility of neutrons to activate material (in some cases this can of course be used as features) restricts the methods to materials that are more or less immune to neutron activation. When using X-rays, as we have done, the advantage to tune the X-ray energy for different measurements and thus change the attenuation length (below 20 µm at 6 keV and 2 cm at 100 keV for copper), as well as the option to focus the beam from cm^2 down to μm^2, comes with the trade-off of being less accurate than neutrons in measuring the crystallographic phase.

It should be noted that sample penetration depth of X-rays depends on the photon energy applied and one of the methods presented (surface reflectance XRD) is surface sensitive with less than 100 µm penetration depth. Likewise the sampling depth of XRF spectroscopy depends on the primary X-ray energy and the element specific XRF of the material under investigation, which leads to less than 100 µm for lighter metals or low excitation energy, up to several mm or even cm, when exciting with 100 keV and detecting heavy element (like lead) XRF from K-shell electrons.

The chosen historic object had the patina completely removed when found and the replicated objects were all manufactured identically and cleaned to investigate the effects of post-cast treatment. The specimens investigated were replicated objects from the experimental archaeological group at Gottorf Palace. They were made in well-defined production conditions, using replicated historic tools and an original axe, the Late Neolithic axe from Ahneby (District of Schleswig-Flensburg, Schleswig-Holstein, Germany). The measurements were performed at DESY (Deutsches Elektronen-Synchrotron, Hamburg, Germany) using beamlines G3 (Wroblewski et al. 1999), L and W2 at DORIS III, as well as P07 at PETRA III.

The axe from Ahneby

In spring 1967, the farmer Johannes Hansen discovered, after harrowing on the surface of his field, a low-flanged axe on the slope of a soggy depression. No other objects were found nearby. It seems to have been a deposit of just a single axe in an area of wet ground. The axe came into the possession of a dealer in agricultural machines, who cleaned it and removed most of the patina and some parts of the ornamentation as well (Aner/Kersten 1978, 5). In 1977, the axe was given to the State Archaeological Museum at Gottorf Palace. By then it had become so popular that it was integrated into the coat of arms of the parish of Ahneby (**Figs. 1–2**).

The axe belongs to the group of so-called Anglo-Irish axes and dates to the Late Neolithic (Aner/Kersten 1978, 5) or to the early phase of the Early Bronze Age (Vandkilde 1996, 87–91). The basic form and ornamentation are quite characteristic for axes of the Anglo-Irish type. They belong to the Scrabo Hill type of axe (Schmidt/Burgess 1981, 63–65) or type A10, 'Anglo-Irish-developed flat axes' as defined by Helle Vandkilde (1996, 87–91). Ornamented axes with side loops are known from Ulstrup (Region Midtjylland, Denmark; Butler 1963, fig. 4) and a tiny one (*c.*10 cm) with unknown provenance from the National Museum of Antiquity (National Museum of Scotland) in Edinburgh is listed by Harbison (1969, no. 1185 pl. 53,18). Shape and side loops from Ulstrup are very close to those from Ahneby. Both are large axes with lengths of 25 cm (Ulstrup) and 27 cm (Ahneby) respectively, with a rounded butt, and they curve out to the cutting edges with edge corners. The cutting edge of the Ahneby axe is asymmetrical, probably the result of casting problems; the mould could perhaps not be filled properly. Both axes are largely covered with ornaments more or less from the butt to the cutting edge (Ulstrup) or down to 5 cm above the cutting edge (Ahneby). The geometric ornaments differ. Ahneby is covered above the side loops with a simple herringbone ornament and below that with triangle ornaments that differ on front and rear sides. The Ulstrup axe is decorated with casually applied large Xs and triangular ornaments covering the whole surface. The function of those axes might perhaps not be profane as Kibbert has already assumed for the axe from Frankenthal (Rheinland-Pfalz, Germany; Kibbert 1980, 54). The largely decorated faces and the side loops give no hint about how the axe might have been fixed to the handle if it had a handle at all. There is no conclusive evidence that Ahneby has ever been used as an axe. It might be questioned if the quality of the cast is good enough for more than a decorative purpose of a precious object coming from far away. It is quite interesting that both axes, though they are obviously foreigners in Denmark or Schleswig-Holstein with at least a strong Anglo-Irish influence, have no parallels in Ireland or Great Britain. Were they just made for trading?

The surface of the axe has been thoroughly cleaned and shows only a few small spots of bog patina. The surface damage is severe on the raised parts of the flanges and loops[1], so the parts where the surface is more or less untouched are few. Still some traces of tools can be found. Most obvious are traces of hammering on the faces of the low flanges. The drawings by Aner and Kersten show that they obviously interpreted them as a kind of ornament (Aner/Kersten 1978, pl. 1). But that does not seem to have been the intention; the impacts are less regular on the original than shown on the drawing. The traces do not cover the entire surface of the flanges and the edges of the impacts are smoother than well defined, but that may be a result of the cleaning process.

The surface of the faces, including the cutting edge and the areas that are not decorated, do not show any visible traces of hammering. The ornaments are very subtle and some losses are obviously due to rough cleaning. The traces of hammering could have been destroyed during this process too, but as they are still visible on the flanges they should at least be partially preserved on the faces as well.

There are some traces left of the casting process. They give information mostly about its problems. There are several cavities on the surface and more may be assumed to be in the bulk. Some were filled with metal after casting. Some smaller ones were just left as they are (**Fig. 3**). Several other indicators of casting problems were found near the cutting edge. There are irregular linear grooves parallel as well as at right angles to the cutting edge where the mould was not filled properly (**Fig. 4**). The asymmetry of the cutting edge is, as already mentioned above, probably a result of casting problems as well. The cast probably included the ornaments; there is no sign of ornamentation in the filled-in cavities as should be expected if the ornaments were done after the casting. The decoration runs over the cavities without trying to include or avoid the flaws in the surface. So the axe was probably cast using the lost wax technique. There are no signs of a casting burr of a two-piece mould to contradict this theory. The surface of the faces was probably just cleaned and polished after casting. The small faces were hammered. There are no visible signs of a special treatment for the hardening of the cutting edge. To get further information about the production process a look inside the axe was needed. Furthermore we needed experiments to learn more about the production process to identify traces of the different techniques.

The chemical composition of the axe

The first analyses were done to determine the alloy for the casting of replicates. They took place at the Institute of Material Science, Division of Microanalysis of Materials of the Christian Albrechts University (CAU) in Kiel in 2009 when we started our experiments[2]. The analyses gave

Fig. 3 Ahneby, detail of the filled blowholes and cavities from casting.

a result with an average of 80.3 % copper and 19.7 % tin. The data ranged between 88 %–70 % copper and 12 %–30 % tin. The percentage of tin varied without having a recognizable purpose. The preliminary XRF analyses executed in 2010 at the Deutsche Elektronen-Synchrotron in Hamburg (DESY) supported the wide range of data. The chemistry of the axe is not constant throughout the object. Most obviously different are those spots where cavities were filled with a different material from the matrix. But the matrix itself is inhomogeneous too.

Measurements with storage ring based X-ray fluorescence (SR-XRF) performed at the beamline L of storage ring DORIS III at DESY in 2011 confirmed the CAU measurements and allowed us to investigate blowhole fillings with XRF mapping (**Fig. 5**).

The experiments and measurements

The replicas to test the method were produced by the State Archaeological Museum, Gottorf Palace (Schleswig, Germany), in cooperation with the Industriemuseum Howaldtsche Metallgießerei ([Howaldt Foundry Industrial Museum]

1 That gave the advantage of being able to have a close look at the chemical composition with microanalyses without being hindered by corrosion or oxides.

2 We would like to thank Wolfgang Jäger for the chance to use the equipment at his institute and Christel Dieker and Christiane Zamponi for the analyses and the discussion of the results.

Fig. 4 Ahneby, detail of the cutting edge with shrinkage lines from casting.

Kiel, Germany). The original bronze axe came from the State Archaeological Museum. A special focus was on the effects of possible cold working on the Late Neolithic axe from Ahneby.

The replicas had a bronze stoichiometry of the average of the axe of Ahneby and were cast using modern techniques. The copper was molten at 1300 °C and then tin added and mixed for 1–2 minutes, before the axes were cast with the sand casting technique using a foundry ladle. No additives were used for the bronze, except a little carbon and quartz sand to bind the scoria for removal prior to adding tin. The objects were cleaned using brushes and water. After the first measurements, the objects were cold-worked using stone tools, replicated after Neolithic finds (Freudenberg 2006; 2009) and tempered in a muffle furnace at 700 °C (the temperature is comparable with a charcoal fire with moderate airflow; **Fig. 6**). After each treatment cycle, a strain measurement was performed and a surface picture of aligned grains taken. The results were compared with measurements performed with the axe of Ahneby.

In this context two related experiments were performed at the DORIS G3 beamline at DESY: one for strain analysis and one for spatially resolved analysis of aligned reflexes. A detailed description of those experiments is published in Glaser et al. 2016.

To investigate the blowhole filling of the blade of the axe from Ahneby, the specific section of the axe surface was mapped with a 32 keV monochromatic X-ray beam of 150 µm diameter, while an XRF measurement was taken every 300 µm. Those mapping experiments were done at the DORIS beamline L at DESY.

Additionally the hardening of the blade's edges and the general grain structure of the axe from Ahneby were investigated using X-ray diffraction in transmission geometry. For this task monochromatic X-rays between 91 and 120 keV were used at the DESY beamlines W2 (DORIS) and P07 (PETRA) with beam sizes between 10 µm and 1 mm in diameter. During those experiments the XRF signal emitting from the axe's surface was parasitically recorded.

All XRF spectra were recorded using a Vortex-EM detector together with an XIA map-based multi-channel analyser. At beamline L, XRF element mapping was recorded at 7 Hz in reflectance geometry (**Fig. 7** [b]) with a primary photon energy of 32 keV and a spot size of 150×150 µm^2. The XRD data recorded at W2 in transmission geometry (**Fig. 7** [c]) was taken with a MARCCD 555 detector, using a 1×1 mm^2 spot of 101 keV X-rays. At P07 likewise in transmission geometry (**Fig. 7** [c]), the diameter of the spot size of the 91 keV photons was varied between 10 µm and 600 µm, while data was recorded using a Photonic Science X-ray VHR detector.

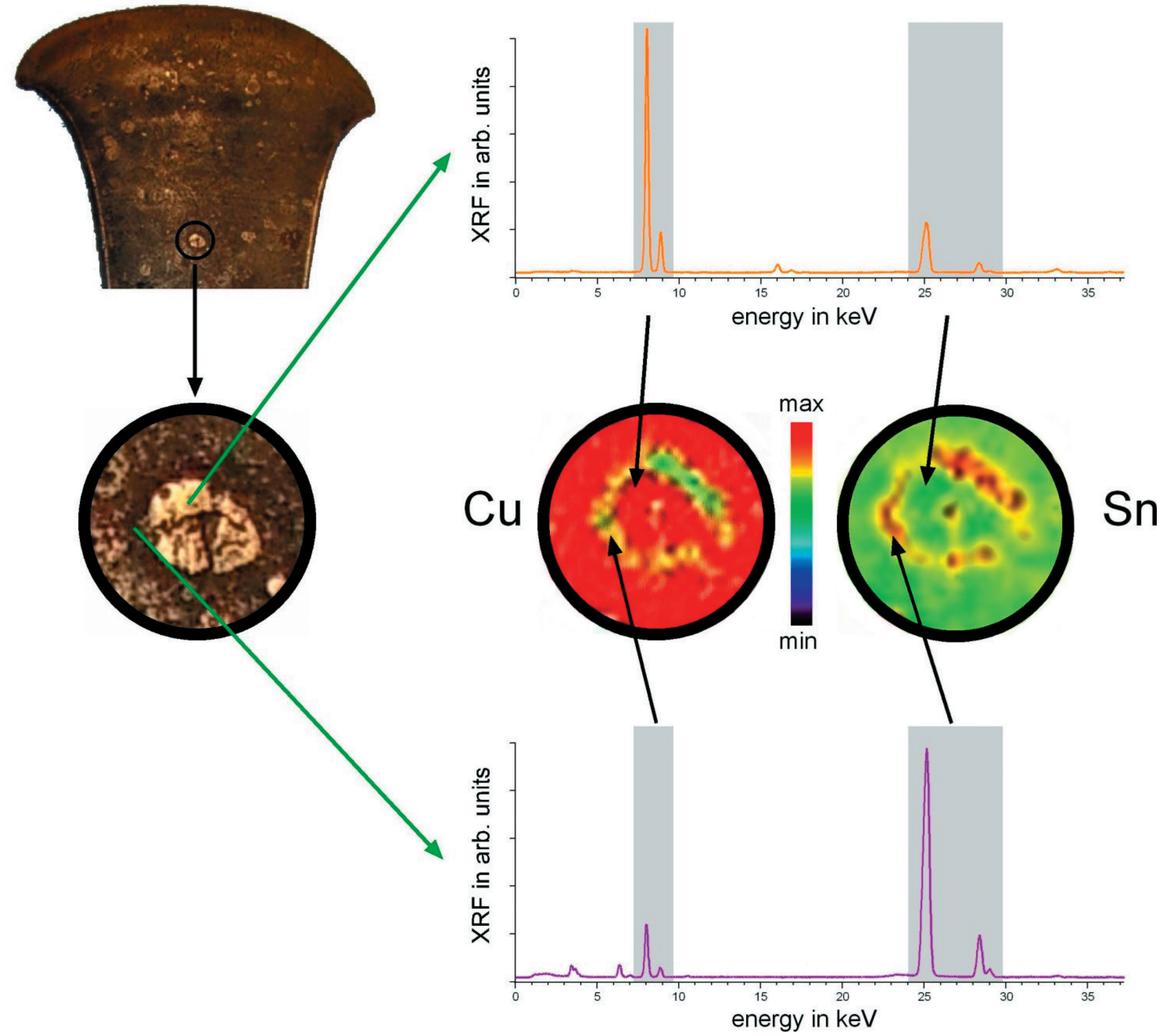

Fig. 5 The XRF mapping of the blowhole: on the left side, the area of the filled blowhole is pictured on the axe from Ahneby with a detail enhancement of the relevant region. The upper XRF spectrum on the right side is from an area mainly consisting of filling material, the lower spectrum from the rim region, containing mainly pure tin. By mapping the area, analysing each spectrum on its own, extracting the copper and tin contributions, separate intensity maps of copper (Cu) and tin (Sn) can be extracted, showing clearly a ring like depletion in the copper and the inverse for the tin.

Strain measurements at G3 were done in reflectance geometry (**Fig.** 7 [a]) with a primary X-ray beam of 5.9 keV, illuminating a square centimetre of the object, while data was recorded using the MAXIM camera or a scintillation detector.

Results and Discussion

XRF analysis of the axe from Ahneby confirmed previous measurements of the University of Kiel, but allowed additional mapping of specific regions, showing that the blowhole filling was done probably using small spilled pearls from the cast, adding some tin for better fitting, which is reflected by the circle of pure tin on the blowhole circumference, while most of the filled region consists of stoichiometric bronze similar to the cast part of the blade of the axe (**Fig. 5**).

The most likely method leading to this result with no residual open pores is the filling of the hole by using a small piece of bronze from the cast, imbedding the piece on a small amount of tin in the blowhole and then coldworking the area. This would create a fully closed surface, with only a small ring of high tin content on the original rim of the opening.

Surface diffraction scans show well-defined changes in the intensity of the diffraction peaks in the order of 30 %, but not in the position when comparing cast and coldworked

Fig. 6 Forging the cutting edge of one of the replicated axes.

bronze (**Fig. 7**). The surface strain analysis using the (220) reflex proved a tool one order of magnitude more sensitive to differentiate cast, coldworked and retempered material. This spatial resolving method applied for the first time on objects of cultural heritage worked fine on the axe from Ahneby and the replicated objects. We can conclude that for the blade region of the axe the final surface treatment procedure was coldworking. Additional measurements show no signs of final coldworking in regions not close to the cutting edge. The results there are comparable with the tempered state of the replicas. Due to the visible imprint marks on the surface of the axe from Ahneby from coldworking on those regions too, it is our conclusion that the axe was at least in some parts once coldworked and tempered before the blade was finally hardened for use by forging.

This conclusion is in agreement with our transmission diffraction measurements, where we observed strongly deformed grains in the blade region of the axe and much less deformation already 2 cm away from the edge.

Conclusion

In this paper we presented a brief overview of non-destructive methods and their application during our investigations performed on the axe from Ahneby. XRF allowed stoichiometric analysis of the bronze of the axe. In addition the mapping of highly inhomogeneous regions of the axe surface as well as the filled blowhole was discussed. With surface reflectance and transmission XRD, the grain structure and stress in the sample could be addressed. With the axe from Ahneby we could show the strong residual stress in the blade region with both methods and the tempered state in the rest of the axe's body. The methods applied can in principle also be used on any metallic object and XRF on any inorganic surface. XRD allows generally the determination of the final surface treatment of any metal objects made of, for example, iron, silver or gold.

All our samples had clean metallic surfaces. If a thick (several 100 µm) layer of patina covers the object, the results of surface reflectance XRD measurements would not, in most cases, be expected to be as useful as in our case. Also the XRF would then primarily analyse the chemical composition of the patina. In cases of fake patina made of a burnt carbon-based substance, like the one we encountered in the hoard find from Kappeln (District of Schleswig-Flensburg, Schleswig-Holstein, Germany; Freudenberg/Glaser 2016), the XRF did nicely measure the bronze stoichiometry of the axes, since it is blind to very light elements like carbon, oxygen or nitrogen.

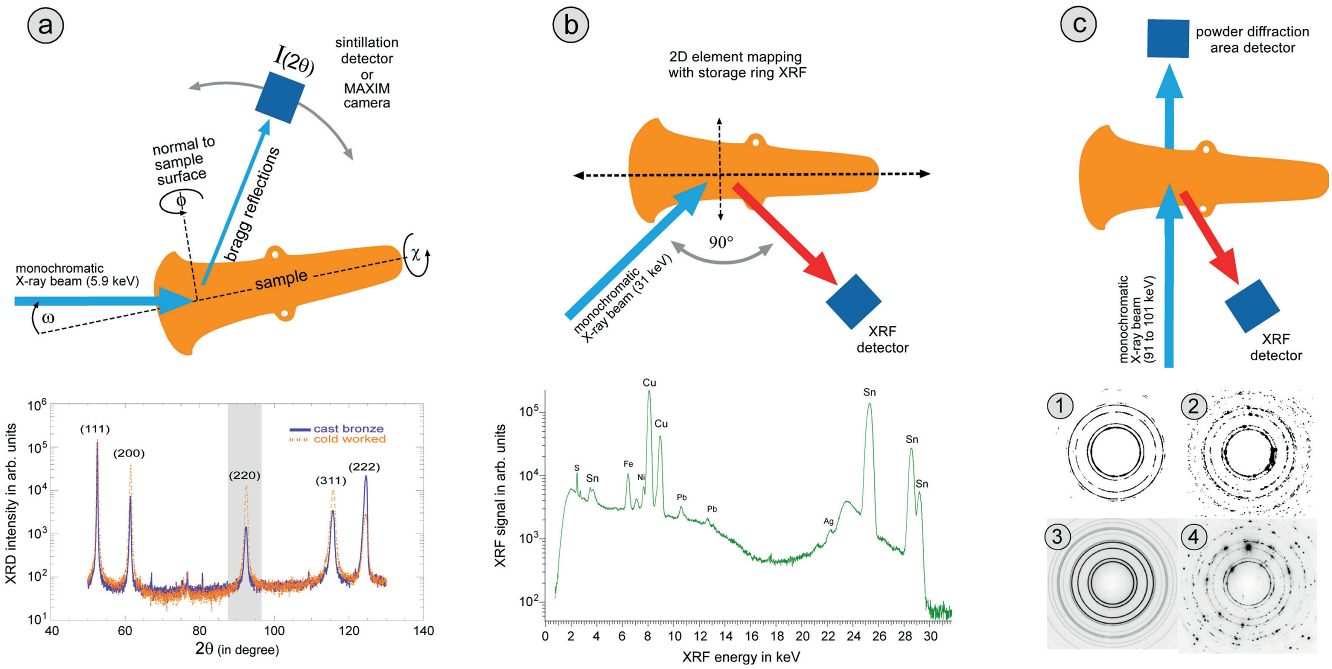

Fig. 7 The different experimental setups for the applied methods are depicted together with a typical measurement. **a** For strain analysis with surface reflectance XRD, the object is illuminated with X-rays (5.9 keV) in gracing incidence (angle ω) and can be rotated around its surface normal (angle ϕ), as well as along its own symmetry axis (angle χ). The detector can be moved on a semicircle (angle 2θ), measuring, for example, the intensity of the diffracted X-rays as shown in graph for cast and coldworked bronze. **b** For XRF element mapping, the sample is mounted in 45° geometry to the beam and the detector in 90° to the beam to minimize scattered X-rays reaching the detector. The object is moved on a 2-D stage, while X-ray source and detector stay fixed. A single XRF spectrum is shown in logarithmic scale, with the symbols of the elements at the respective peaks. Here the main contributions are copper and tin with traces of iron, nickel, lead and silver. **c** Grain and chemical analysis can be measured in parallel, by hitting the sample normal with the X-rays and placing an area detector behind the object, while collecting the XRF signal from the surface. The pattern of the strongly coldworked blade (1) with strongly deformed grains and of the less strained more central region (2) of the axe from Ahneby measured with a 10-µm beam. The central region of the axe from Ahneby (3) measured with a 1-mm beam in comparison with the image of one of our replicated axes (4) shows immediately that the Neolithic bronze has much smaller grains.

Acknowledgements

The authors would like to acknowledge the indispensable help we received in reproducing bronze axes from Armin Leppert and the team at the Howaldtsche Metallgießerei Kiel, as well as the excellent assistance of the Experimental Archaeologist Harm Paulsen formerly at Gottorf Palace. We are most grateful for the splendid support during the measurements at DESY from Jörn Donges at beamline G3, Karen Appel at beamline L, Thomas Lippman at beamline W2 and Norbert Schell at beamline P07. L. G. thanks DESY Photon Science for financial support.

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