Gerhard Eggert & Britta Schmutzler (Eds.)

Bronze Conservation Colloquium 2012
Extended Abstracts

BRONZE CONSERVATION COLLOQUIUM 2012

State Academy of Art & Design
Stuttgart
June 22nd & 23rd, 2012

STAATLICHE AKADEMIE DER BILDENDEN KÜNSTE STUTTGART

in cooperation with

ICOM Committee for Conservation Metal WG

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Landesmuseum Württemberg
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CONFERENCE PROGRAMME

Friday, June 22nd — **State Academy of Art and Design, Vortragssaal, Neubau II**

09:00 am	Registration open
09:30 am	Welcome Address *Petra von Olschowski*, President of the Academy *John Scott*, New York Conservation Foundation and ICOM-CC DB *Gerhard Eggert*, Head, Study Programme 'Objects' Conservation'

Session I: Bronzes of the Old World

Chair: *Katharina Schmidt-Ott*, Zurich (CH)

09:45 am	*Frank Willer*, Bonn Small Fragments of Large Statues: the Limes Project
10:15 am	*Uwe Peltz* , Berlin The Etruscan 'Tomb of the Warrior' from Tarquinia and the Conservation of Bronzes in the 1960s on the Museum Island in Berlin
10:45 am	**Poster Session / Coffee Break**
11:15 am	*Janet Schramm*, Stuttgart *Lorica Squamata* - Investigation of a Roman Copper Alloy Scale Armour
11:45 am	*Nicole Ebinger-Rist*, Esslingen Virtual Reconstruction of Shadows - Corroded Celtic Copper Investigated with X-ray CT
12:15 pm	*Roland Schwab*, Mannheim Brasses are not Bronzes: History, Metallurgy and Corrosion of Archaeological and Historical Brass Alloys
12:45 pm	**Lunch Break**

Session II: Bronze Corrosion

Chair: *Gerhard Eggert*, Stuttgart

02:00 pm	*Amalia Siatou*, Athens (GR) Corrosion of Archaeological Bronze in Non-Hostile Burial Environment
02:30 pm	*Martina Grießer*, Vienna (A) Analysis of Corrosion Phenomena and Optimisation of the Storage Conditions for High Leaded Antique Bronze Coins

03:00 pm	*Andrea Fischer*, Stuttgart Whodunit: Glass Corrosion or Cleaning? A Survey of Corroded 18th Century Enamel Boxes in the Landesmuseum Württemberg
03:30 pm	**Poster Session / Coffee Break**
04:00 pm	*Brigitte Brühl*, Stuttgart Copper Soaps on Ethnographic Objects
04:30 pm	*Edith Joseph*, Zurich (CH) Development and Evaluation of an Innovative Biological Treatment for the Protection of Metal Artifacts
05:00 pm	**Tour** A Short Walk into Architectural History: The Weißenhof Estate
06:00 pm	**Get-together**

Poster Session

Kati Bott	Gilding Techniques on Roman Life Size Bronze Statues from UNESCO-World Heritage Limes – Investigations on Diffusion-gilding of Bronze Statues
Ines Frontzek	“When the eye is delighted by the art of these metals…” Brown Varnish on the Romanesque Comburg Wheel Chandelier
Jörg Stelzner	Decalcifying Archaeological Bronzes: a Comparison of Different Chelating Agents
ICOM-CC Metal WG	Call for Papers: Metal 2013, Edinburgh

Saturday, June 23rd **Landesmuseum Württemberg, Vortragssaal**

09:00 am	Welcome Address *Andrea Funck,* Chief Conservator, Landesmuseum Württemberg

Session III: Conservation of Outdoor Bronzes

Chair: *Britta Schmutzler*, Stuttgart

09:15 am	*Jörg Freitag*, Potsdam Restoration and Conservation of Freely Weathered Bronzes in Germany –the Last 15 Years
09:45 am	*Martin Mach*, Munich The Restoration of the Bavaria (Bronze) Memorial in Munich
10:15 am	**Coffee Break**

10:45 am	*Rolf-Dieter Blumer*, Esslingen Composition and Corrosion-Behaviour of Differently Old Patinas on Copper Plates for Roofing and on Some Parts of a Bronze Statue in South-West Germany
11:15 am	*John Scott*, New York (USA) A New Method for Conserving Weathered Surfaces of Copper and Bronze
11:45 am	*Christa Scheiblauer,* St. Pölten (A) Conservation of Cast Bronze Sculptures by Daniel Spoerri
12:15 pm	**Pretzel Break**
12:45 pm	**Guided Tour** by *Rolf-Dieter Blumer*, Esslingen A Short Walk to Recently Conserved Bronze Statues
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Introduction: The Making (?) of a Tradition

GERHARD EGGERT

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I could tell you of the grand design, the master plan for the creation of a series of annual international conferences on objects' conservation in Stuttgart. It would certainly be a nice story – but a plain lie.

It just happened by chance: In 2005, we had funds from the Academy to invite Christian Degrigny (Germolles, F) for a lecture on 'Modern Electrochemical Methods in Metals Conservation'. But why not share it with our colleagues in Germany who support our students in many ways? To be more attractive (and help our friends to get travel allowances from their museums) we added lectures on recent diploma theses, e.g. Britta Schmutzler on 'Tin and Pewter in the Decorative Arts'. All in English, so that also Christian can understand what we are talking about. And the baby needed a name: I found 'colloquium' would sound, hm, academic - and, therefore, fit nicely to us. And as I love alliterations 'Metals Conservation Colloquium 2005' was the choice. Christian was coordinator of the ICOM-CC Metal WG, so we collaborated with them even at our first event. Some photocopied pages with the programme and abstracts of half a page per presentation were stapled and handed out. Value for money: A fee of 10 € / 5 € (paid cash, no pre-registration) was all we needed to cover copies, coffee, and cookies.

Participants apparently loved the format, so why not repeat it with another theme next year? As we were planning a students' ceramics project in 2006, we continued with the 'Ceramics Conservation Colloquium' (wow, a triple alliteration!). External German (Tanja Kress, Elena Agnini) and English speakers from the UK (Norman Tennent, Victoria Oakley) formed the core of a bilingual programme. On Saturday, we visited the famous Ludwigsburg castle and its ceramics museum. The first conference devoted to ceramics conservation in Germany in decades!

What next? There is a saying in German: 'What you do thrice is a tradition'. A combination of work on ancient bronze statues and organic remains on metal finds gave the first 'Antike Bronzen Kolloquium' in 2007. All the external speakers on life-size statues (Frank Willer, Uwe Peltz, Roland Schwab) did not hesitate to come back 2012 which we might take as a compliment. With all speakers being native Germans, no English lectures and a German conference title this time.

In 2008, a number of prestigious speakers from abroad for our 'Glass Conservation Colloquium' (Sandra Davison, UK; Kate van Lookeren Campagne, Univ. Amsterdam; Luc Megens, ICN; Gorazd Lemajič, Ljubljana) let us switch back to English. In the night, we proudly presented the glass workshops of the Academy. The Ernesto Wolf Glass Collection in the Landesmuseum Württemberg was the obvious choice for the social programme on Saturday.

As I had a sabbatical in 2008/9, the colloquium series also took a break in 2009. The first two PhD projects in the Objects' Conservation Course (Katharina Schmidt-Ott on plasma applications; Britta Schmutzler on the desalination of iron finds) gave the idea for the 'Archaeological Iron Conservation Colloquium 2010'. A long neglected, but now internationally hot topic! Invited speakers and our 'Call for Papers' (new!) brought together 2 full days of lectures. We could acquire external funds (new!) and cooperation from Deutsche Bundesstiftung Umwelt, Landesamt für Denkmalpflege BW, and Landesmuseum Sachsen-Anhalt (KUR-Project). As we have a limited lecture hall capacity, Britta and I asked for pre-registration of participants (new!) - and had to stop the registration soon thereafter as we were totally booked. A preprinted brochure with extended abstracts (3 pages) of all contributions and a website (www.iron-colloquium.abk-stuttgart.de) set the standard for the following colloquia. David Scott's keynote lecture on metallography, the conference dinner in the Salemer Pfleghof and the excursion on Saturday (both organized by Nicole Ebinger-Rist) will be unforgettable to all who were so happy to register early.

To be representative for the whole field of objects' conservation, organic materials formed the core of the Ethnographic Conservation Colloquium 'The Life of Things' in the Academy's 250th jubilee year 2011. Senior lecturer in objects' conservation Andrea Fischer used her contacts as chair of the VDR's Ethnographic Objects Group to invite a number of speakers from Germany and abroad to Stuttgart and created the conference website (www.ethnographic-objects.abk-stuttgart.de). The date was chosen to allow also for a visit of the Lindenmuseum's special exhibition 'World Views – Looking Beyond the Cultural Horizon'. Some students could proudly present displayed objects preserved by them to our guests.

The 'Bronze Conservation Colloquium 2012' stays with the tradition of English as only conference language. A private sponsor (new!), the bronze casting company Ernst Strassacker GmbH (www.strassacker.de), helped us with their generous support to keep the fees reasonable and affordable. On Saturday, the Landesmuseum Württemberg invites you to coffee and the 'pretzel break' (yes, I love alliterations!). As for 2010, the organization is again (another tradition?) in the proven hands of Britta Schmutzler.

We do not know about the future, its chances and developments and where they will lead us. If we started a tradition, it stays somewhat unpredictable. We'll possibly take a break again in 2013 due to another sabbatical. But new research projects on **G**lass **I**nduced **M**etal-corrosion on **M**useum **E**xhibits (GIMME, funded by Friede Springer Stiftung, Andrea Fischer) and the freeze drying of organic finds (DFG funded, Ingrid Wiesner) just started in the Objects' Conservation Course. So do not be too surprised if they will inspire us to the next themes (but stay tuned!).

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SESSION I

BRONZES OF THE OLD WORLD

Small Fragments of Large Statues: The Limes Project

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Large bronze statues form one of the important object groups from the Roman provinces north of the Alps. Especially for the emperor and his family portraits and statues were put up in great numbers in the military camps and civil settlements along the Limes (fig. 2). But there must also have been bronze statues in considerable numbers in ritual contexts. Therefore, it is quite astonishing that these statues, which are still preserved in more than 4,300 fragments, have never been collected systematically and, to this day, have often been archived as "forgotten old stock" in the depots of museums and other collections.

Now a research project of the Archäologisches Landesmuseum Baden-Württemberg, the Institut für Archäologische Wissenschaften der Universität Frankfurt a. M. and the LVR-LandesMuseum Bonn is reappraising these important pieces and going to make them accessible to researchers, as well as a wider public. The research project is being supported by the Volkswagenstiftung, Germany, within the initiative „Research in Museums", and also by numerous project partners of museums, universities and specialized research institutes.

In addition, the project pursues an innovative approach that combines archaeological-historical, archaeometrical and production methods. Hence, apart from the interpretation of the bronze fragments, the reconstructions of the original statues, their locations and functions, as well as aspects of production techniques and material science form the foci of interest.

This approach will not only allow new statements on the complicated bronze industry of the Romans, but should also advance research into the statuary representation north of the Alps to a considerable degree.

There is some new discussion about similarities of particular statues and, therefore, about specialized workshops casting large bronze statues. It is most unlikely that heavy, larger-than-life bronze castings were transported several hundreds of kilometers over the Alps. It has to be assumed that, if Roman founders worked in the region of the Limes like medieval bell-founders, they could have left their traces within certain regions. The chemical compositions of Roman large statues from the Limes analysed by the Curt-Engelhorn-Zentrum Archäometrie Mannheim give a quite uniform impression concerning the alloy compositions and impurity patterns. There are marginal differences within the compositions from the individual find-spots. Technological features like repairs and founding do probably allow a more differentiated view and some specific techniques could be observed in certain regions so far. Discussing a chronological development is not possible at the moment, as work is still in progress. The quantitative estimation and chronological classification of the different gilding techniques employed, for example, is restricted in terms of the small number of gilded fragments investigated so far, but leaf-gilding seems to be the most popular type.

The destruction of the bronze statues and their post-Roman use as scrap metal is also important. The date and type of destruction can be examined on the fragments, as well as the handling of scrap by German looters or Roman scrap collectors, for example. Marks of hammers, levers or chisels, as well as scratches on the surface of gilded bronze are evidence of the demolition of the

Fig. 1 Fragments of bronze statues from Aalen.

Fig. 2 Head of the Emperor Gordian III from Niederbieber, LVR-LandesMuseum Bonn (left); computed tomography of the same bronze, with a view inside (right).

sculptures by probably post-antique looters greedy for metal. Numerous small-scale fragments indicate the preparation for remelting (see fig.1).

The project's aim to reappraise these important relics of ancient bronze casting and to make them available to research and the public comprises an archaeological-historical approach, as well as technological aspects. Casting techniques, alloy compositions and surface working, like gilding, chiselling, repairs and joining are investigated by different scientific methods.

A lot of the technological details like casting flaws, repairs, joints and the positions of chaplets can be revealed by careful optical surface observations and conventional radiography. Computed tomography (CT) provides 3-D information (fig. 2) of more complex casting techniques and makes it possible to investigate the interior surface.

With its interdisciplinary approach the project first aims at continuing the research on statuary representation north of the Alps to a considerable extent. Secondly, it offers the possibility to work out the similarities and differences between the military dominated provinces and the Italian or Mediterranean regions in the Graeco-Roman tradition.

For the conclusion of the research project, an international symposium is planned, after which the original finds and the research results will be presented to the public in 2014 in a joint exhibition of the LVR-LandesMuseum Bonn, the Limesmuseum Aalen and the Museum Het Valkhof, Nijmegen (NL). Last but not least the project offers a great opportunity to emphasize the importance of finds that are stored in museums for the UNESCO World Heritage Site of the Limes – exemplified by the outstanding group of Roman bronze statues. The paper will give an overview of the project and present the first research results.

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For further information see also

www.grossbronzenamlimes.de

The Etruscan 'Tomb of the Warrior' from Tarquinia and the Conservation of Bronzes in the 1960s on the Museum Island in Berlin

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The Tomb of the Warrior from Tarquinia, with its extremely rich grave goods (see fig. 1), has recently been studied under the direction of Andrea Babbi, in preparation for a new, comprehensive publication (Babbi et al.). For this, it was indispensable to investigate the conservation measures that in the 1960s permanently altered almost all the bronze grave goods.

From autumn 1869, the Marzi family had excavations carried out on their land at the southern edge of the town of Corneto (called Tarquinia from 1870 on). At the end of November 1869, the German archaeologist Wolfgang Helbig inspected the newly discovered grave goods of a burial and in the same year he published the spectacular new finds (Helbig 1869). A commission of experts recognised their importance and recommended that the Vatican Museums acquire the finds from the tomb. After the collapse of the Papal State, no-one was thinking about the Tomb of the Warrior, so the Königliche Museen in Berlin entered into negotiations in Spring 1873 to acquire the more than 120 objects of gold, silver, bronze, ceramics, textiles, wood and bone. In November of the same year, the *Assistent* at the Berlin Antiquarium recorded the new acquisitions in an extensive special inventory (Spezialverzeichnis 1973). The true significance of the 'Tomba del Guerriero' was recognised almost 40 years later (Montelius 1912): the Tomb of the Warrior is still accepted today as marking the change from the Villanovan period to the orientalising period of Etruscan culture. In the Second World War, the finds were packed into various cases that were taken to different bomb-shelters. After the war, the storage locations were secured by the Allied power responsible in each case. The Western occupying powers in 1958 handed over the works of art to the institution in West Berlin regarded by the Allies as the official legal successor in ownership. These included six small bronzes from the Tomb of the Warrior. The Soviet Union regarded the confiscated objects as reparation for its loss of cultural goods due to the National Socialist regime, however in 1958 the works of art of the East Berlin collections were in large part returned, including 54 of the 67 bronzes from the Tomb. The fate of eight bronze objects has not yet been fully clarified.

For the description of the condition of the objects when found, the depictions of the archaeologist Adriano Prachov are important; he was commissioned by Helbig to document the grave goods in drawings while they were still in Tarquinia (Helbig 1874). Heydemann's notes on surviving, missing and damaged items provide more extensive information. Negatives taken in the first third of the 20th century document the appearance of the most important finds. Short comments in the Soviet list of objects handed over in 1958 describe their condition at that time. Finally, in 1975 the restorer Ralf F. Voß made a note of the patina on the last bronze basin that at that point still remained unrestored: "teilweise ist sie metallisch blank, zum größten Teil aber mit Ausblühungen in verschiedenen Farben (weiß, grün, blau) besetzt" (Voß 1975). This was roughly how all the grave goods were corroded in the parts that were surrounded by air inside the stone sarcophagus. The areas in direct contact with the soil were often mineralised completely. In the basin mentioned above, fragments were therefore missing from the bottom when it was excavated.

As could be expected, the Tomb of the Warrior dropped right out of scholarly attention as the National Socialists consolidated their power, and it was only in the mid-1960s that it regained interest. While preparing extensive publications on early Etruscan culture, from 1966 to 1967, Hugh Hencken corresponded with the curator of bronzes on the Museum Island, Gerald Heres. Heres was the successor of Ursula Blaschke, who left East Germany in 1966. Hencken made the finds from the Tomb of the Warrior central to his study (Hencken 1968). The attentions given to the grave goods beforehand on the Museum Island were correspondingly intensive. In the summer of 1966, Blaschke acknowledged receipt of numerous antiquities that were handed over by the Museum für Ur- und Frühgeschichte in Weimar. These included 23 small bronzes from the Tomb of the Warrior. Thanks to an administrative cooperation, Blaschke had the finds brought safely into a lab in the still young state of East Germany that had been making important new contributions in restoration science since the 1950s.

The restoration measures undertaken on the Berlin pieces were documented by the staff in Weimar in the store-room card-index ('Magazinkartei') that was usual there. For the bronzes from the Tomb of the Warrior, index cards on 19 objects give a picture of the methods of conservation of archaeological bronzes then in use both nationally and internationally. Eleven or twelve pieces were treated with the so-called Thouvenin Method. The French restorer Aimé Thouvenin (Thouvenin 1958) recommended that salinised objects be exposed to the gases of ammoniac, through which insoluble, corrosive copper salts convert into water-soluble, blue compounds and are washed out. Remaining copper chlorides and ammonium salts were stabilised by acetone vapours or formaldehyde. Four bronzes were partly or completely freed from their corrosion using Komplexon III, in a cleaning method modified in Weimar for the purpose of restoration (Emmerling 1965; Emmerling 1967). For two objects, the Weimar 'Magazinkartei' records that coatings of corrosion were removed by electrochemical means.

The Danish chemical scientist Axel Krefting in 1892 published a method (Krefting 1892; Applegren 1897) that was soon afterwards adopted by Friedrich Rathgen, the first director of the Berlin Chemical Laboratory, for the treatment of bronzes (Rathgen 1897). This electrochemical reduction, still known today as the Krefting Method, was very popular throughout the Museum Island in the 1960s for the restoration of bronzes. In this process, archaeological bronzes are completely wrapped in strips of zinc foil. In a 5% soda lye, the copper minerals are reduced by the electrochemical reaction. The coatings, once reduced, can be brushed off in water during the leaching. The treatment was finished as soon as the bronzes were free from corrosion and the surface of the metal was covered by a more or less transparent brown layer. This colour suited the aesthetic impression of an aged ancient artefact, and the surface was understood as its ancient appearance. Rudolf Kuhn, restorer at the Berlin Egyptian Museum, had promoted this process from when he first took up his position in 1925. When the works of art were returned from the Soviet Union, Wolfgang Rakel was taken on as bronze restorer at the Antikensammlung, whom Kuhn had trained in the use of Krefting's Method. It is recorded that the larger bronzes from the Tomb of the Warrior were not restored by the museum staff in Weimar. The electrochemical reduction of these objects, and further treatment of some objects already restored in Weimar, was undertaken by Rakel. No documentation of the restoration work undertaken by Rakel has been found, but numerous archive documents leave no doubt that he carried out the reduction not only on the bronzes of the Tomb of the Warrior. Using this method, which was initially valued for its effectiveness by restorers and archaeologists alike, Rakel treated several hundred bronzes in the Berlin collection from 1958 to well into the 1960s with Krefting's original recipe.

Fig. 1 Some important finds from the 'Tomb of the Warrior'.

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Acknowledgement

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Lorica Squamata – Investigation of a Roman Copper Alloy Scale Armour

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Introduction

In the summer term of 2012 fragments of a Roman scale armour from the 2th-3th Century AD currently form the subject of a diploma thesis at the State Academy of Art and Design, Stuttgart. They are part of the research in the DressID project (Clothing and Identities).

The armour is a stray find from Baumgarten an der March in Lower Austria. About 900 scales are partially complete, partially fragmented, single or affiliated with other scales. Noteworthy is the good state of preservation of the base fabric on which the scales are sewn. The fragments were recovered 10 years ago from the plough layer of a field in Baumgarten which is just 30 kilometres from the Roman legionary camp at Carnuntum. In Roman times Baumgarten lay north of the Roman Limes (the Danube), consequently in the Barbarian countries free of Roman domination. Carnuntum was for almost 500 years an important hub between Western and Eastern Europe, and the peoples North of the Danube and the Roman Empire itself (Jobst et al. 1992).

Scale armours are body armours and belong to the class of defensive weapons. In the Middle East they are confirmed as early as the 16th-15th Century BC (Černenko 2006; Gamber 1978; Garbsch 1978). The armour consists of individual pieces of iron or copper alloy sheets. The shape of the scales is

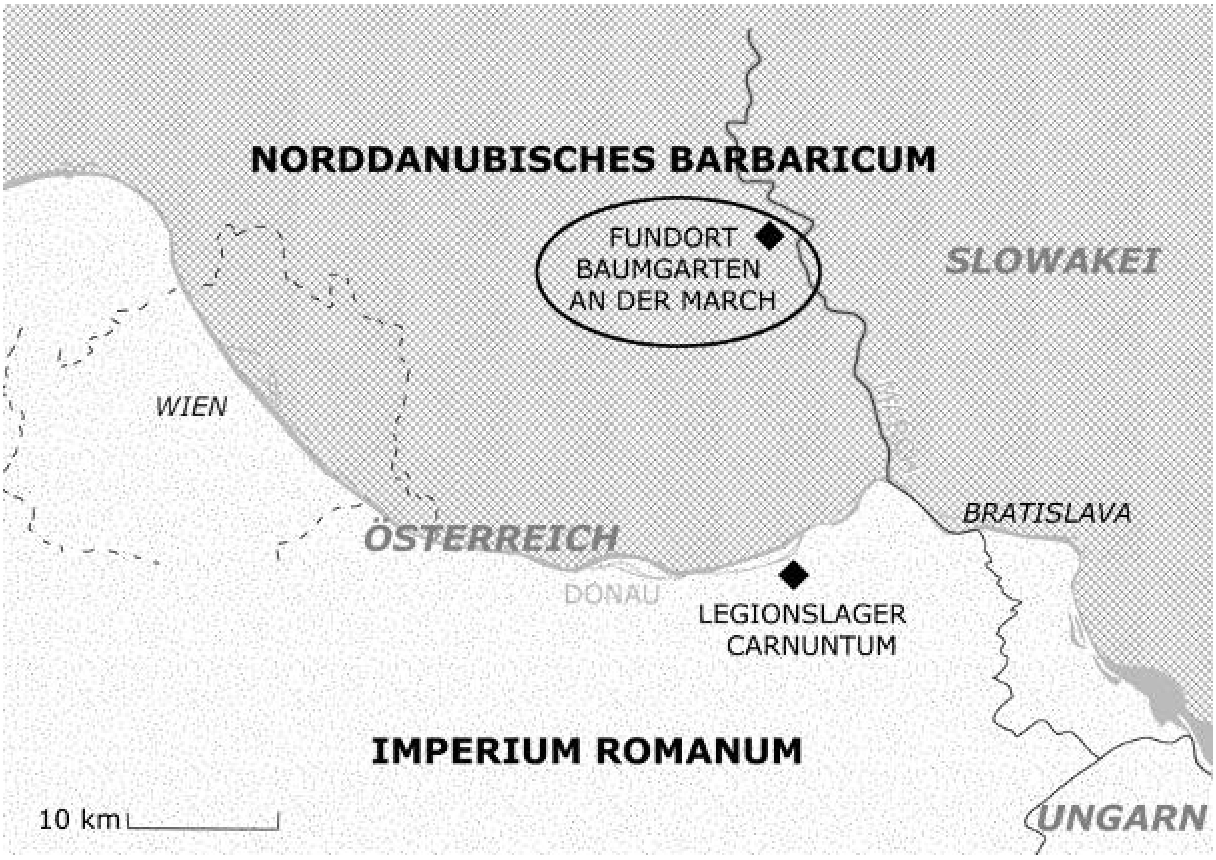

Fig. 1 Site of the scale armour.

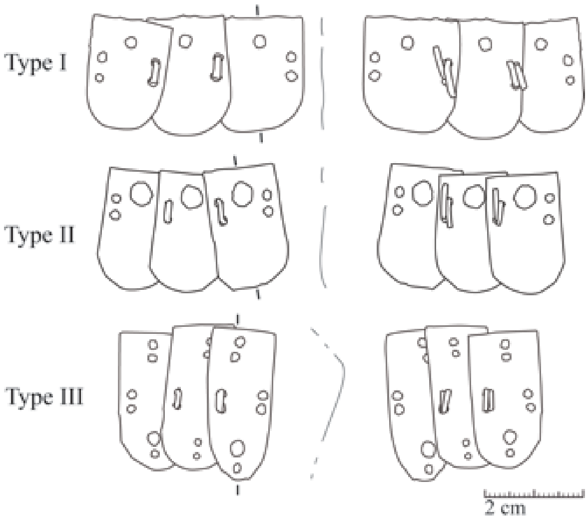

Fig. 2 Different types of scales.

almost rectangular; one narrow side is rounded or pinnacled. Because of the similarity to fish scales the armour is often called *Lorica (armour) Squamata (scaled)*.

Description of the Object

The scale armour from Baumgarten is made of a copper alloy with zinc content and consists of three different types of scales. The use of several types of scales for armoured equipment is not uncommon (Alfs 1941; James 2004). The majority of the scales have five holes for the fixing. This corresponds with the majority of scale findings from Carnuntum (Alfs 1941).

Type I has a rounded narrow side and five holes. A pair of holes is located on both longitudinal sides. To connect the scales with each other, they are lined up side by side until the holes overlap. The left side of the scale lies under the right side of the previous scale. A thin metal strip, which is bent on the back, connects the scales with each other. In this way, rows of scale are constructed. The fifth hole serves to attach the scales onto a backing fabric. Using two opposing running stitches the scales were sewn with a thread on to the ground fabric. Therefore two threads pass through the hole. The base fabric is a coarse basket weave (0.8 mm yarn, 10-12 yarns/cm). Attachment to the base fabric starts with the bottom row. The following row covers about the half of the previous row. This protects the fragile and injury-prone seam.

Scales of type II are slightly thinner than those of type I. They also have a much larger central hole. Moreover, the arrangement of the scales is different: The right side of the scale is under the left side of the previous scale, which is the inverse arrangement of Type I. Probably, the rows where connected with leather straps. This assumption is supported by similar finds from Straubing and Dura Europos (Robinson 1975).

The smallest group is Type III, with 18 elongated scales. These are fragments of a lamellar armour. Unlike Type I and Type II these scales have holes on both narrow sides. Large holes alternate with hole pairs. They were used to connect the individual scale rows, therefore there is no need for a backing fabric.

Beside the scales two breastplates were found. Originally they were embellished with twisted tin-lead decorations. The ornaments, however, had already fallen off. A rotary knob secured with a cotter pin was used to open and close the breastplates (Humer 1999). Breastplates were used primarily to minimize the neckline. With their rich ornamentation, they also had a decorative character.

Preservation of Organic Remains

The preservation of the leather is very bad. At this stage of investigation it is suspected that scales of type II were associated with leather strips. From these, only a few remains are preserved. Also the neck reinforcement of leather is in a very poor condition, only a few fibres are evidence of its existence. The find has very good textile preservation. The bast fibres were preserved by the antibacterial effect of copper ions and are more or less present in organic form.

Scale Armour: Protection or Parade?

In the literature there is a discussion as to whether scale armours were used during cavalry sports or served as combat armour. Through historical sources cavalry sports wear is known and one assumes today, that scale armours were destined for combat. For the tournament manoeuvres of cavalry Kimmerian robes were worn. These are colourful clothes and tight-fitting trousers. This is stated in the rider's treatise of the governor and military commander Flavius Arrian who wrote in the year 136 AD, and lived at the time of the Emperor Hadrian (Junkelmann 1995).

Furthermore the theory of scale armours for combat is supported by a citation of Herodotus. He reported that at the battle of Erythrai in the early 5th Century BC, the Persian Masistios wore a golden scale armour and fell in battle. The sword thrusts against the armour were without effect. But finally, he was killed with a deadly strike into his eye (Herodotus IV: in Černenko 2006).

Also the thinness of the scales (0.4 mm) raises questions about the usage. But due to the overlapping imbricate arrangement of scales, the material thickness is increased by up to four metal layers, so that the armour is more stable and robust (Černenko 2006). In addition, padded cloths provide additional cushioning against the blows of combat. In Carnuntum it was found that the padding was made of straw-filled linen pillows. Leather was used less frequently (Alfs 1941).

Copper alloyed with zinc is less resistant than bronze, a copper-tin alloy, and seems to be less suitable as a material for armour. Maybe there were aesthetic reasons to use this alloy, since it is golden-yellow in colour (Černenko 2006). The scales would have been polished and the splendour of the weapons is designed to cause the enemy additional fright (old Roman military theorist Vegetius, in Černenko 2006).

The advantage of scale armours is the quick and cheap production, together with ease of repair. For the manufacture no specific manual skills were required, in contrast to the production of chain mail or other iron devices (Robinson 1975). The soldiers themselves could repair the armour any time. That is confirmed by many finds of scales in forts.

Future Treatment

Due to the good preservation of the find, the conservation should be kept to a minimum. The fabric protection is going to be achieved mainly by mounting. Treatments of the metal parts might be necessary only to a small extent.

The reconstruction of the appearance is made more difficult since the find was not recovered in situ. By adding information from similar findings the appearance and the production techniques can be reconstructed in a graphic representation. In addition, a catalogue will document the find.

During 2013 the fragments will be displayed at the exhibition *Dress Code im Alten Rom* in Mannheim.

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Virtual Reconstruction of Shadows – Corroded Celtic Copper Investigated with X-ray CT

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Introduction

Since 2007 the Landesamt für Denkmalpflege Baden-Württemberg (LAD) has gathered extensive experience in the use of 3D computed X-Ray tomography (XCT) for investigation and documentation of archaeological finds, with very good results. Having standardised the application of this method the LAD is now able to draw on XCT in many research questions, investigating objects of a wide variety of materials, mostly from block excavation, prior to or even instead of their conventional manual extraction (for analysis a Phoenix XRAY Vtomex 450® is used in combination with the software VGStudio MAX 2.1®, see Stelzner et al. 2010). Currently the LAD utilizes its great experience in this method for the investigation of the largest block excavation project ever conducted in Baden-Württemberg, the princess tomb of Heuneburg. Discovered in 2010 around 2.5 km southeast of Heuneburg in the Danube valley the tomb has been excavated as a single block weighing 80 tons.

Block Lifts as a Conventional Strategy

The preferred method of securing personal burial gifts from tombs or burial chambers in present-day archaeology is block excavation, since the primary regions of interest around the head, chest and hips often present extremely intricate find complexes that call for systematic excavation under laboratory conditions. This holds particularly for finds made of metal or organic materials such as textile or leather. The common procedure is to excavate sub-blocks from the most exposed parts of the site and clear them layer by layer in the laboratory (e.g. one block for the hip sector, a second for the head, etc.).

In the case of the princess tomb working with sub-blocks was impossible because the site was wet-preserved, making it difficult to discern boundaries for safe excavation. Furthermore, some finds in the scanned areas were located only a few centimetres or even millimetres above the heavy oakboard floor of the burial chamber. It was therefore decided to excavate the complete burial chamber as a single block and to bring it into a temporary lab for systematic excavation with all advantages like e.g. microscopy and high-tech documentation facilities (Krausse and Ebinger-Rist 2011).

State of Preservation of Different Materials

The initial stages of excavation yielded gold finds and finds of amber. The amber was in an exceptional good state of preservation, whereas the bronze finds were in a very poor state, often only manifest as a shadow on the soil surface. Iron had not lasted at all in the burial chamber. After months of excavation work over the entire area the burial chamber itself exhibited different degrees of preservation. Its north wall showed a better state of wet preservation than the south wall, permitting identification of a piece of wickerwork as well as animal fur. The princess' burial gifts also show differing preservation states. Bronze/ Copper alloy finds from the hips downward are better preserved than elsewhere in the chamber. This is attributable to an oakboard which was

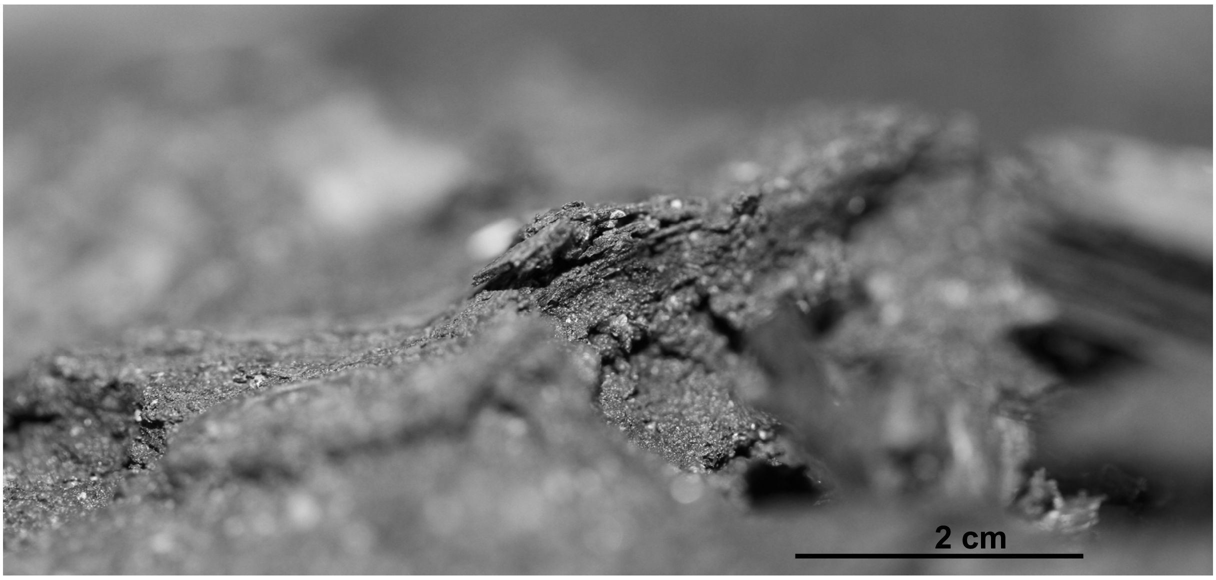

Fig. 1 Side view of a heavily corroded bronze plate flaked into “puff-pastry-like” layers.

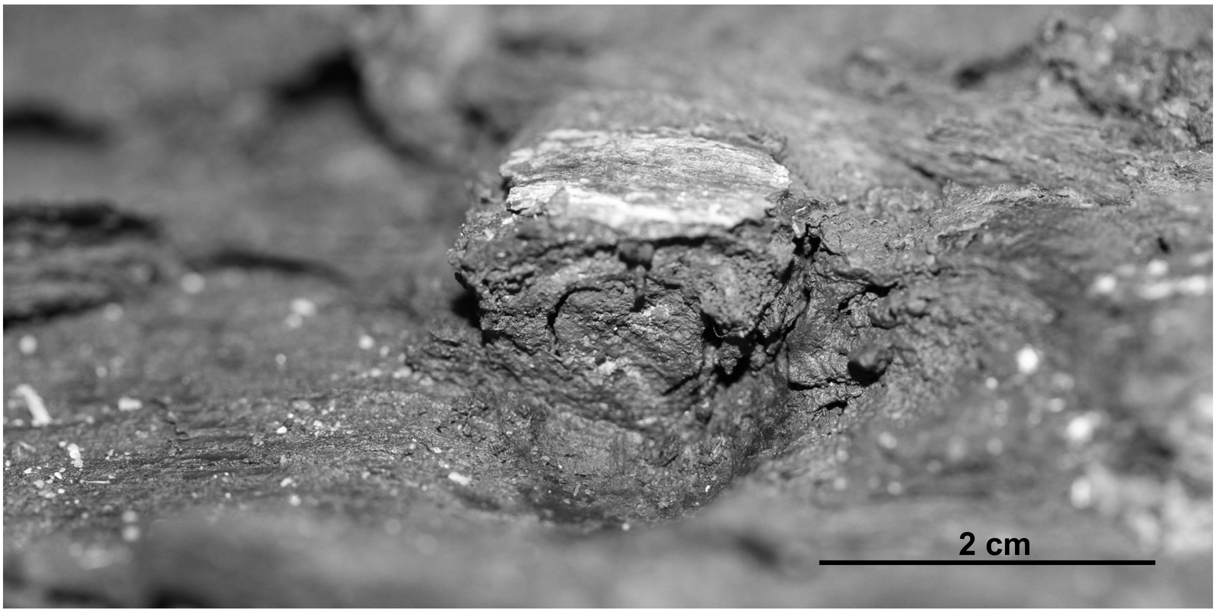

Fig. 2 Fractured ankle bracelet, the fractured face showing dissociation of the outer layers from the metal core.

found extending from the hips to the feet on the upside of the body, possibly soil conditions were more constant here, i.e. permanently water-logged. It appears as though the wet board lay over the lower body for protection, but at present it is not clear, if this deposition was made intentionally. In the hip area is a bronze belt plate showing corrosion into “puff-pastry-like” layers in side view (figure 1). Four bronze bracelets have been found in the ankle region, some still covered with organic matter. A fracture in one of these bracelets reveals a round cross-section with metal core (figure 2).

Due to the complexity of the main burial area with its diversity of materials such as gold, amber, jet, and bronze in the hip region and the overlying organic matter it was decided to remove the princess from her resting place on three oakboards as a sub-block and to analyse her together with the oakboards by XCT.

Advantages of XCT

A major asset of XCT is the possibility of conserving finds in their original context permanently, which will always suffer a degree of damage during conventional archaeological excavation. The method has also proved valuable in the case of heavily decayed materials, where it can serve to generate a virtual 3D image of the original three-dimensional shape of objects even when these are heavily fragmented or are merely discernible by their impression in the soil (Ebinger-Rist et al. 2011).

In the case of the belt plate it was even possible to bring the ornamentation of this find into view. The belt was found to be composed of several plates, which, while only partially restorable by conventional means, permit complete virtual reconstruction.

Conclusion

Although the measurements' evaluation has just started, XCT has already proved an extremely rewarding method in studying the princess tomb. The initial results show that it facilitates the interpretation also of poorly preserved find complexes. In the case of finds as outstanding as that of the Celtic princess of Heuneburg which must be swiftly presented to the public, there is still no way around manual excavation. At the same time however, XCT is unsurpassed in terms of how fast it allows one to work and to document finds in three dimensions. Work on the princess tomb is currently still in progress, and further results will be presented in due course.

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For further information see our website:
www.keltenblock.de

Brasses are not Bronzes: History, Metallurgy and Corrosion of Archaeological and Historical Brass Alloys

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Introduction

Art historians, archaeologists and even conservators are generally used to call all copper alloys bronzes. There is considerable confusion in the use of the term bronze, but in our archaeological and historical context, bronze is essentially an alloy of copper with tin, whereas brass is an alloy of copper with zinc. Modern bronzes can be alloys of copper with tin, or aluminium, or silicon, or beryllium, or nickel, or manganese, or many others. Actually the copper alloys used from prehistory up to modern times are also much more multifarious than the simple term bronze could describe. There are arsenical coppers as well as arsenical bronzes, leaded bronzes, antimony bronzes, iron-copper alloys and the large family of copper-zinc alloys which can be separated into nickel silvers and brass (see Northover 1998). Brass is essentially of copper and zinc, but due to their specific compositions and uses a variety of names is common.

History and Metallurgy

Today, the most widely used copper alloys are based on copper with zinc. In Europe, brasses have already been established as the prevalent alloy since Roman times. Indeed, most Roman, medieval and post-medieval so called bronze objects are in fact brasses. Earlier brasses are rare and there is still confusion by published data of prehistoric brass objects that are modern copies (Craddock 2009). Indeed zinc bearing alloys can occur sporadically in nearly all periods and regions.

In Europe brass was exclusively produced by the so called calamine or cementation process until the end of the 18th century when the industrial production of metallic zinc became possible. This is a process in which the components zinc ore, copper and charcoal are heated in a lidded crucible or furnace, to reduce the ore to a zinc vapour, which diffuses into the copper, because the boiling point of zinc is below the melting point of copper. Several modern experiments have shown that alloys with 40 wt % of zinc and more can be produced by this process, but actually most of the European brasses contain less than 32 wt % of zinc, which is the normal limit for α-brass. From the 16th century in Europe, higher zinc contents are found (Northover 1998; Craddock 2009). Different to modern brasses, all ancient and most historical European brasses are usually single-phased α-brasses, which is essential for understanding their physical properties and their corrosion behaviour (see Hoffmann-Schimpf et al. 2011). Contrary to tin bronzes, their tensile properties increase with increasing zinc content and all α-brasses maintain good cold-working properties and are not susceptible of hardening by heat-treatment. Early Roman brasses usually do not have any additional alloying elements, but brasses have higher iron contents than bronzes in general, which is due to the high reduction atmospheres in the lidded crucibles. Beneficial impurities like tin or arsenic usually come from the copper. Up to the end of the 1st century AD, the Zn-Sn-Pb contents start to vary to a wide range through the ages, but zinc bearing alloys kept the most prevalent copper alloys. Major developments in the compositions of brasses appear at the end of the 19th century, but most of all at the beginning of the 20th century. Some alloying additions have a large effect on the structure of brass, because most of them enter into solid solution and the simple binary copper-zinc equilibrium diagram is no longer valid. By altering the proportion of alpha and beta or forming intermetallic compounds, the presences of modern additives are usually good indicators for modern fakes.

Corrosion

The corrosion behaviour of archaeological and historical brasses is little investigated and relevant literature usually adopts modern corrosion handbooks describing the well-studied corrosion mechanism of modern brasses (see Hoffmann-Schimpf et al. 2011). Stress corrosion cracking and dezincification are the most familiar forms of brass corrosion, which have been the subject of much study since the failure of condenser tubes in battleships became a serious matter during World War I (Evans 1951).

Dezincification is one type of dealloying, which causes the selective removal of zinc from the alloy by the corrosion of the solid-solution and the redeposition of copper as a porous layer. The zinc bearing corrosion products usually are swept away and indeed they are hardly reported from archaeological contexts, due to their high solubility. Two types of dezincification are common: the plug and the layer type. The layer type is a uniform attack over the surfaces and will hardly be documented for ancient single phased brasses. The plug type can occasionally be observed, but it is different to the intensive dezincification of modern yellow brasses. The intensity of dezincification of brass is very closely related to the structure and single phased α-brasses are less prone to dezincification than high zinc brasses. Brasses containing less than 15% of zinc have the same oxidation resistance as copper, therefore they are relatively immune to dezincification and impurities like tin or arsenic increase the dealloying resistance.

Selective corrosion and dealloying in ancient and historic brasses usually is metallurgically influenced and takes place in localized areas after cold work without sufficient annealing. This kind of corrosion can also be observed in ancient bronzes, whereas the mechanism is still in dispute (Bosi et al. 2002). However it should be noted, that all kinds of dezincification described in modern corrosion literature can be perfectly studied in “antique” objects coming from the art market.

Stress corrosion cracking is a result of the combined interaction of mechanical stress and the attack of a corrosive species. All copper alloys can crack in an ammoniacal environment, but the effective corrosion behaviour is due to their compositions. Single phased α-brasses crack usually intergranular, while α/β-brasses are more affected by transgranular stress corrosion cracking. Therefore stress corrosion cracking should hardly be distinguishable from “normal” intercrystalline corrosion of ancient brasses, but it has recently been observed during the restoration of a Roman gladiator helmet (see Hoffmann-Schimpf et al. 2011).

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SESSION II

BRONZE CORROSION

Corrosion of Archaeological Bronze in Non-Hostile Burial Environment

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The present work is focused on the investigation of the corrosion mechanisms of archaeological bronze artefacts found in non-hostile burial environment. An attempt to associate the corrosion formation with the burial/soil environments is made through electrochemical corrosion simulation in samples of the excavation soil.

Six archeological bronze fragments, found in two excavations of the 12th Ephorate of Prehistoric and Classical Antiquities (prefecture of Ioannina-Greece) were studied. Artefacts that belong to the same period (1st c. BC-1st c. AD) and follow the same typology were selected. Additionally, soil samples from the excavation areas (location and depth of the artefacts) were collected for analysis. Finally, a three (solid state) electrode corrosion cell, connected with a potentiostat-galvanostat, was employed for the electrochemical corrosion simulation. As electrolyte, samples of the excavation soils were used.

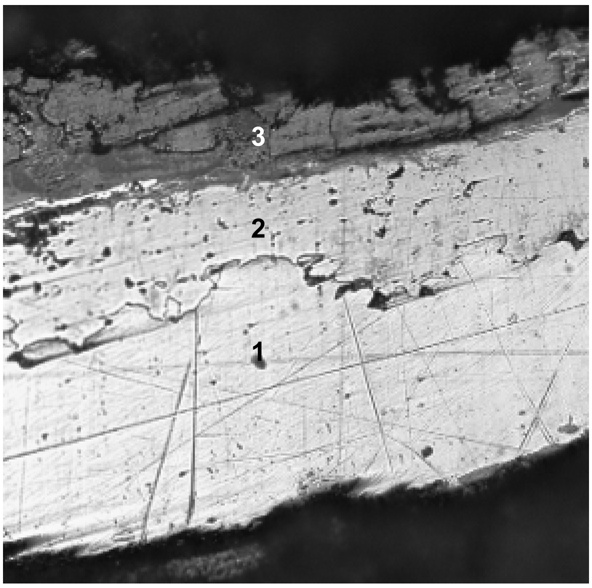

Fig. 1 Corrosion stratigraphy on a cross section of an archaeological bronze sheathing.

Archaeological Bronze Samples

All samples are fragmented pieces, usually parts of sheathing foils, of thickness less than 0.5 cm. The preservation state is similar for all samples. Extended uniform corrosion surrounding the entire sample with three distinct layers is observed in most cases, shown in Fig. 1:

Layer 1: The remaining metal core

In most cases, the metal core is preserved; no holes or inclusions are observed. SEM-EDS showed a tin-bronze alloy with an average tin content 8-10 wt%, whilst, in most cases, no additional trace elements were detected. Metallographic observations after etching with ferric chloride revealed a single α-phase, binary alloy with twinning and recrystallization, evidence of their manufacturing technique by cold forging and annealing.

Layer 2: of uniform appearance and variable thickness, surrounding the metal core

SEM-EDS analysis showed high tin (Sn) and oxygen (O) contents, attributed to the decuprification phenomenon. XRD was only able to identify cuprite, however, a mixture of cupreous and stannic oxides and/or hydroxides was identified by Raman.

Layer 3: of non-uniform appearance and variable thickness surrounding layer 2.

SEM-EDS analysis reveals the simultaneous presence of corrosion products (O, Cu, Sn) and soil elements (Si, Ca, Al, Fe). XRD and Raman spectroscopy were able to identified malachite in few samples.

Decuprification seems to be the main corrosion mechanism. Intergranular corrosion is rarely observed, starting at the surface and proceeding into the bulk alloy through cracks and imperfections. Only, in few samples has corrosion led to complete mineralization. The presence of chlorides is negligible, since the samples originate from a plain area, away from the sea.

Burial Environment

The two excavation soils are chemically and mineralogically similar and are characterized as sandy clay ones. Their main constituent minerals are hornstone and quartz. As secondary constituents, different oxides and a small percentage of calcite were identified. The trace elements are also similar for both types of soils and they bear similar amounts of chloride ions (80-90 ppm). However, their acidities are rather different (pH(SC1)=5.34, pH(SC2)=6.73).

Electrochemical Corrosion on "mimicking bronze" Samples

Cyclic polarization curves (10 mV/min scan rate) of "mimicking bronze" samples (Cu8Sn) in the two excavation soils are presented in Fig. 2. The insignificant areas of the negative hysteresis loop (i.e. higher reverse polarization currents than the forward polarization ones) and the repassivation occurrence upon reverse polarization, classifies the two soils as very mild localized corrosion inducers. However, SC2 presents better passivation ability than SC1, based on the lower values of passive current density (i_p) and (E_{cp}-E_{corr}), as well as the higher values of (E_{rep}-E_{corr}) and ($E_{a/c\ tr}$-E_{corr}). This can also be associated with the lower pH of the SC1 soil. It should be noted that SC1 soil does not present a clear E_{cp} potential but a decrease in the increasing i_{corr}, therefore current stabilization does not occur.

Fig. 3a displays the electrochemical behavior of the "mimicking bronze" in SC1 soil during 36 Consecutive forward potentiodynamic Polarizations (CP) in SC1. The polarization curves corresponding to cycles 2-36, present similar characteristics, suggesting that:

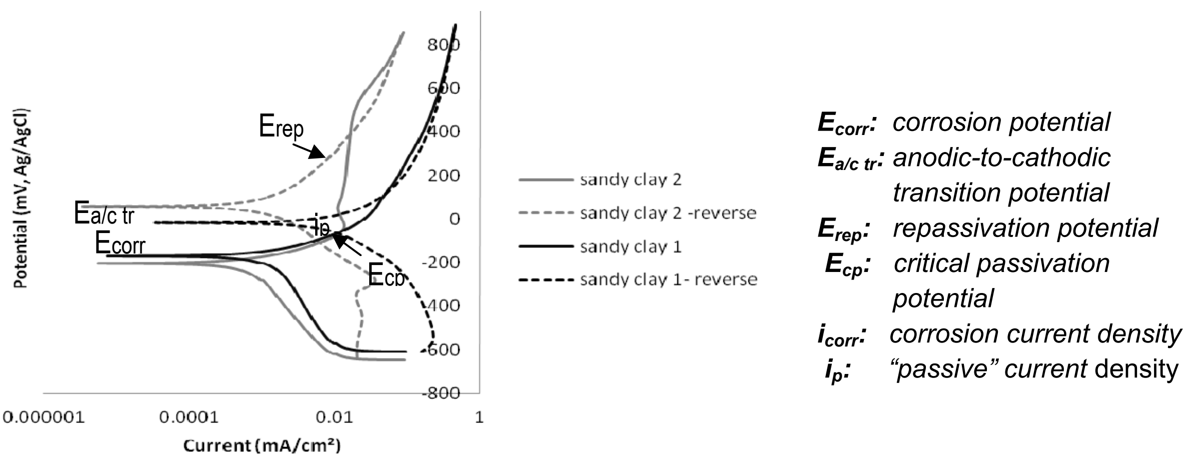

Fig. 2 Cyclic potentiodynamic behavior of a "mimicking bronze" specimen during immersion in the two excavation soils.

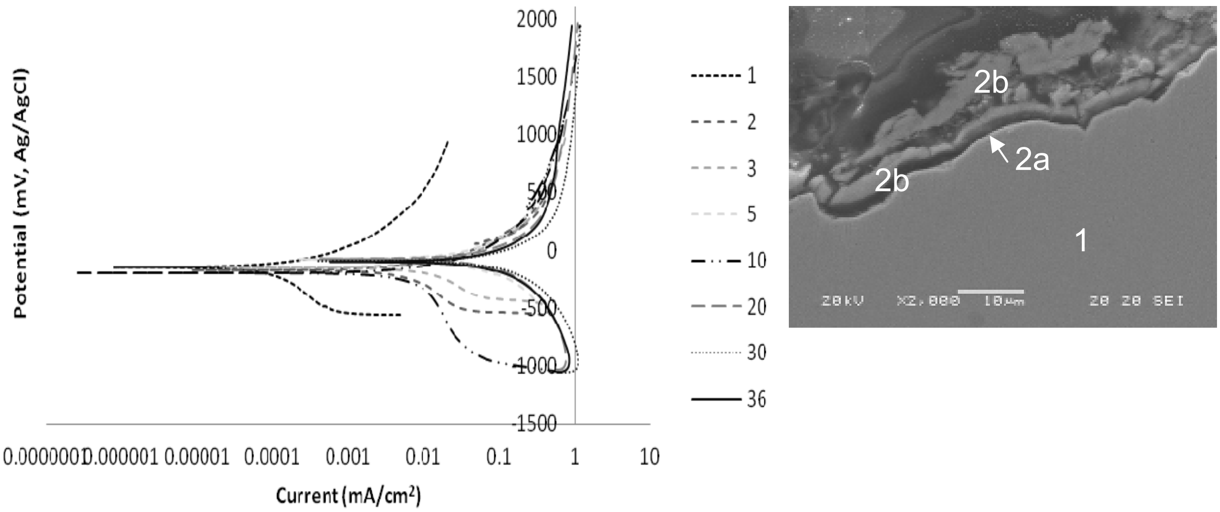

Fig. 3 (a) Consecutive forward polarization (CP) behavior of a “mimicking bronze” specimen during immersion in SC1 soil (b) Cross section of the same specimen after 48 CPs showing the corrosion stratigraphy.

a) The corrosion mechanisms are similar, governed by a behavior typical of uniform corrosion in the overpotential range Ecorr up to Ecorr +600 mV; at overpotentials greater than Ecorr +600 mV, the stabilization trends of current density vs. potential, suggest formation of surface layers.
b) The stability of the passive layers is only slightly reduced during the 2-36 cycles. Indeed, SEM/EDS analysis on a cross-section of the “mimicking bronze” after 48 CP showed the formation of tin and copper oxide based compositions (Fig.3b-layer2). Especially, the gradually decreasing copper concentration from the boundaries of the metal core (Fig.3b-layer2a) towards the periphery of the external layer (Fig.3b-layer2b), suggests that the decuprification phenomenon seems to also characterize the accelerated corrosion of the “mimicking bronze”. However, additional elements due to chemical interaction of the soil with the alloy surface, as in the case of the archaeological samples were not detected. Nevertheless, the presence of carbon in the oxide layers is evidence of the strong chemical interaction between the soil/electrolyte and the buried/immersed metal.

Therefore, CPs of commercial bronze of composition and thermomechanical treatment resembling those of the genuine objects, in a preliminary attempt to somewhat mimic the burial conditions of the archaeological artefacts, confirmed that decuprification accompanied by tin passivation is the main corrosion mechanism, in compatibility with the observations on the archaeological samples. Furthermore, the “mimicking bronze” demonstrates an excellent performance in the two soils, in terms of high passivation ability and low susceptibility to localized forms of corrosion, in accordance to the adequately preserved state of the majority of the examined artefacts.

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Analysis of Corrosion Phenomena and Optimisation of the Storage Conditions for High Leaded Antique Bronze Coins

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Introduction

The Coin Cabinet of the Kunsthistorisches Museum (KHM), Vienna, holds a large collection of ancient Greek bronze coins minted during the Roman imperial time. These so-called Greek imperials were produced in the eastern provinces of the empire between 50 - 280 AD, often using highly leaded bronze alloys. As normally they were used as currencies in quite local areas, the images shown pass down unique historic information and documents – otherwise unknown – of their area of circulation. Most of them are, therefore, important witnesses of the eastern part of the ancient world.

The coins not shown in the permanent exhibition at the KHM are stored within wooden storage cabinets. Due to the release of organic acid pollutions from the wood and together with other air pollutants (i.e. SO_2, NO_x, O_3) severe corrosion develops on the antique bronze coins showing a high lead and/or tin content (Tennent 1995; Tétrault et al. 1998). The coins start to show some points of whitish, powdery corrosion products on the surface. 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 (Linke et al. 2000).

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.

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 by UV-fluorescence microscopy. Scanning Electron Microscopy (SEM-EDX) proved the presence of mainly lead containing corrosion products.

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.

In addition, for the same group of objects X-ray and thermal neutron tomography investigations were performed at the NEUTRA beam line, neutron spallation source SINQ, of the Paul Scherrer Institute (PSI). To get a first overview of the inhomogeneity of the coins X-ray and neutron radiographies were taken from all objects showing very different results. For some of the coins nearly the same image could be detected using either X-rays or neutrons, for others the images looked quite different.

Following these first investigations the coins were divided in three stacks of six to seven coins. These stacks were investigated by neutron tomography overnight, enabling the 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. The Pb containing inclusions of varying size are inhomogeneously distributed over the width and depth of the coins (typical thickness about 3 mm).

During the evaluation of the neutron tomography data it got 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 (Pilon 2003; Elayi and Elayi 1995; Moesta and Franke 1995) – the Pb containing phase can be found in different parts of the object. For the vertically cast blanks a clear enrichment of the Pb rich phase at one end of the coins is visible. 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 in the future.

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Whodunit: Glass Corrosion or Cleaning? A Survey of Corroded 18th Century Enamel Boxes in the Landesmuseum Württemberg

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Introduction

In recent years an unusual and so far unknown metal corrosion phenomenon has increasingly been detected on museum objects. Among those affected are historic glasses and enamels with deterioration problems which harm neighbouring copper alloys. Alkaline surface films, formed by hydration of the glass, cause special forms of metal corrosion in the contact area. So far, two different copper formates have been identified as corrosion products. Sodium copper formate acetate (´socoformacite`) is the most common copper/glass corrosion product (for more details see Eggert et. al. 2008, 2010, 2011). Carbonyl pollutants, emitted from wood, glues or cleaning agents are the major source of the formation of the formates.

The GIMME Project (**G**lass **I**nduced **M**etal-corrosion on **M**useum **E**xhibits, funded by Friede Springer Stiftung) has been set up to investigate in detail this corrosion phenomenon and its causes. How common is this phenomenon in collections and what is the context in which it appears? The identification of the corrosion products is important, as their composition contains a great deal of information about the object and its history. Corrosion products are comparable to a dosimeter: they measure an object's exposure to adverse influences in the environment, particularly those risks which inflict a cumulative impact over long periods of time.

A survey of 18th-century enamel boxes in the Landesmuseum Württemberg will show the approach and the objectives of the GIMME Project. The analyses of corrosion products were hitherto mainly carried out by X-ray diffraction (XRD). In this study, µ-Raman spectroscopy will be used for identification. The ability to focus on individual particles under the microscope has proved most advantageous, due to the small quantity of corrosion products taken by sampling.

The Collection

Most of the small boxes in the collection of the Landesmuseum Württemberg were probably used to store snuff. Particularly in the 18th century, snuff boxes were very popular and were valuable accessories, mostly with a personal character. The museum owns a huge collection of these small decorative boxes, 62 of them are enamelled. The painted enamels are rich in detail; lids and bases are mounted onto gilded brass frames which are joined by means of hinges. Copper has been used as a substrate for the opaque white enamel. In some cases the white enamel is overlaid by coloured enamel. The lids are often adorned with portraits, classical vignettes or floral ornaments. One of the boxes was decorated by Johann Andreas Bechdolff. He was employed in Ellwangen, in about 1760, to produce porcelain and later worked as a house painter and as a painter of boxes. He died in 1817.

Visual examination

The survey was carried out in the storage area of the museum. As basic equipment a camera and a binocular (x 10) was available. Corrosion phenomena were detected in 11 out of 62 boxes. The corrosion could be observed in spallings in the enamel (figure

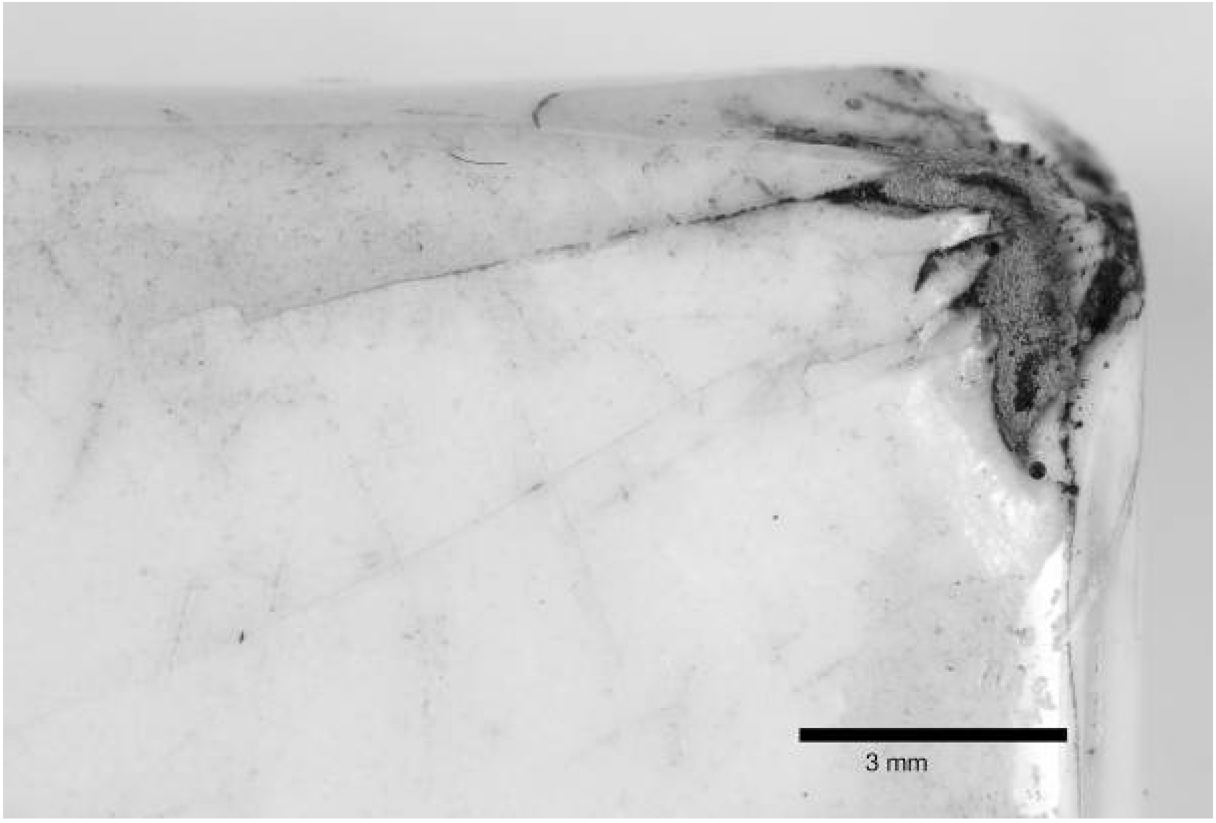

Fig. 1 Turquoise corrosion products at spallings in the enamel (box no. G 8,360).

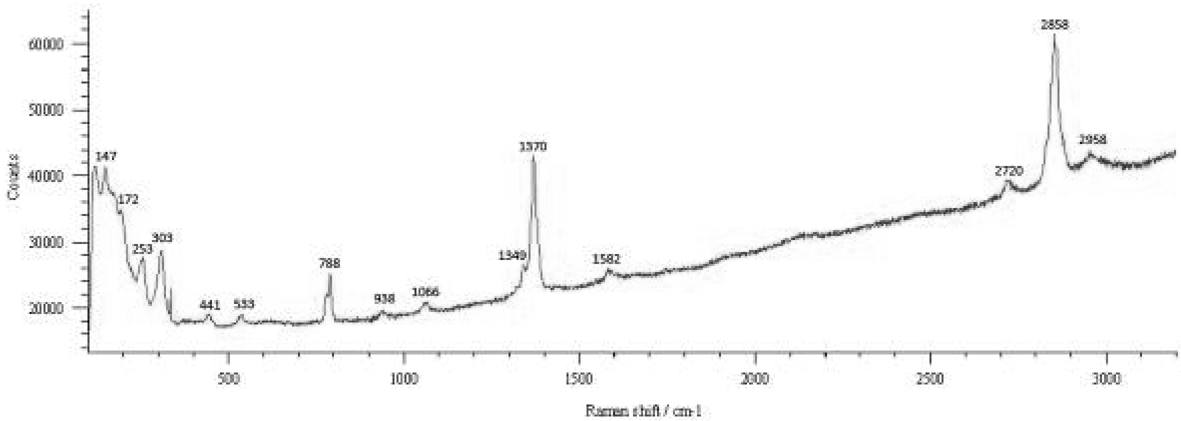

Fig. 2 Raman spectrum of socoformacite.

1), on exposed edges of the copper plate and on the gilded brass frames. The surface of most of the opaque white enamel appears semi-glossy. A few of the boxes show localized areas of a dulled appearance. Several enamels have suffered damage by fractures, probably caused by mechanical stress. Some boxes have been repaired in the past.

Experimental

In analysing corrosion products, the size of samples is a challenging factor, as it is often limited to a few particles on the surface of the object. For this reason, using XRD was not considered suitable. μ-Raman spectroscopy is becoming increasingly available in conservation science and has proved to be an appropriate method for examination. The instrument used was a Renishaw inVia Raman spectrometer, equipped with a He-Ne laser operating at 632.8 nm and with power kept below 800 μW on the sample surface. SEM-EDX was used as a complementary technique to characterise the corrosion products. To gain some information about the enamel, two spalled opaque white particles were analysed using SEM-EDX.

Results and Discussion

The examination by Raman spectroscopy identified ´socoformacite` as the most significant corrosion product. It was detected on four snuff boxes and was found in all the turquoise corrosion products on box no. G 8,360; in the corrosion products on the gilded brass frame in the inside of box no. 5744; in the corrosion on the copper plate of box no. 1309 and on the lid of box 5433. The Raman spectra of all samples showed almost identical Raman shifts and relative intensities (figure 2), corresponding to those published by Trentelman et.al. (2002: 221) and Robinet & Thickett (2005: 331). The homogeneity of the samples varied, some appeared pure and others contained particles which have not yet been clarified in detail.

Most of the samples gathered from the gilded brass frames have been determined as chloride, sulphuric and carbonate containing corrosion products.

The opaque white enamel samples were found to be a sodium-lead-silica glass, comprising tin as an opacifier.

The presence of ´socoformacite` suggested that the exposure to organic pollutant gases, containing carbonyl groups, is involved in the deterioration of the snuff boxes. Since the boxes are kept in wooden cabinets, wood is the obvious source of the pollutants. Conservation materials like polyvinyl acetate adhesives, which emit organic acids during deterioration, were not found. Furthermore, it can be assumed that the enamel has provided the sodium ions for the formation of ´socoformacite`, although the enamel does not appear conspicuously instable.

However, this corrosion phenomenon is only found in 4 out of 62 boxes. This raises the question as to whether this explanatory approach is appropriate. The snuff-boxes have been in use as prestigious objects; most likely they were frequently cleaned. Most of the corrosion products were detected in comparatively inaccessible parts of the boxes, in gaps between enamel and metal. Residues of a cleaning agent can accumulate here. Several traditional cleaning agents for brass and glass contain vinegar, or other organic acids as well as soda. In this case it is conceivable, that the source of the ions of ´socoformacite` can be found here as well. This option has not been considered in the previously published cases of metal/glass join corrosion on historic objects, as the corrosion always occurred exactly at the join between glass and metal. As ´socoformacite` has been observed on bronze objects without glass (Trentelman et al. 2002) due to exposure to sodium solutions (either in the soil or during conservation) future research on glass/metal objects has to address the following questions:

1. Whether there is evidence (e.g. documentation, water stains, etc.) or at least the possibility of cleaning treatment with alkali(ne) solutions. This can be ruled out for some objects, e.g. the Black Forest *Schäppel* (Eggert et al. 2010)
2. Whether the glass phase is likely to release alkali (e.g. from alkali lead enamels). If the glass shows no visual signs of deterioration quantitative electron beam microprobe analyses of the composition might be needed.

Conclusion and Prospects

The present case-study is part of the recently started GIMME Project. It shows that copper formates can be detected frequently on historic enamel objects. Further studies will include surveys in collections of decorative arts and archaeological artefacts, in order to obtain more information about metal/glass joint corrosion products. The use of µ-Raman spectroscopy for the analysis of copper corrosion products has proved to be very successful. Most of the samples generate strong Raman signals. Systematic examinations of affected objects will allow us to extend the collection of reference spectra. The results of various case studies will provide a strong basis for the interpretation of the analyses. At this point it is not possible to determine the exact reason for the formation of ´socoformacite` on the snuff boxes.

To study the phenomenon on a broader base, the authors would appreciate any relevant information and samples.

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Copper Soaps on Ethnographic Objects

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Introduction

Copper soaps are metal salts caused by the reaction of copper ions with particular organic acids, especially with free fatty acids. They are usually a kind of corrosion occurring on objects due to a close contact of the metal with fatty acids containing material.

The copper ions can be formed by copper alloys or copper-based pigments. Free fatty acids can stem from organic materials, for example oils, fats, waxes or leather, by the manufacturing or the use and care of an object. Furthermore, fatty acids can be caused by agents used for conservation treatments. Due to degradation of organic materials fatty acids can be released from the compounds (Selwyn 2004).

Examination of Copper Soaps on Ethnographic Objects

Based on the observation of turquoise-greenish efflorescences on several ethnographic objects, a study on copper soaps was carried out.

The efflorescence was mainly found on objects made of copper alloys associated with leather and in a few cases with wood. Most of the objects had a greasy appearance and some a rancid smell of degraded fats.

The efflorescence occurred directly at the contact between the metal and organic material as a waxy mass or in form of drops. Frequently, it looked like extruded and had the shape of thin bands or fine threads, partly also in form of curls.

Experimental

The efflorescence of different ethnographic objects was examined using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope / energy-dispersive X-ray spectroscopy (SEM/EDX) analysis. A few of them were analysed by gas chromatography with mass spectrometry (GC/MS) to identify the involved fatty acids. Samples of the efflorescence in form of curls and bands were examined by SEM to scrutinize the structure of their surface.

Results

The efflorescence could be identified as copper and zinc soaps by the FTIR analysis according to the reference data given by Robinet and Corbeil (2003). The SEM/EDX analysis confirmed the involved metallic compounds (copper and zinc). The GC/MS analysis gave indications of the involved fatty acids.

Formation of Copper Soaps on Reference Materials

Two test series were carried out in order to study the formation of copper soaps on reference copper alloys with fatty acids of oils and waxes.

In the first series, types of oils and waxes were brought together with different copper, bronze and brass coupons. They were chosen regarding the materials often used for care and conservation purposes on objects and due to their high ratios of fatty acids. For the group of oils, the technical oil Ballistol®, neat's-foot oil and olive oil were taken. As waxes lanolin, beeswax and stearin wax were tested. Furthermore, paraffin wax was included as fatty acid free reference material for comparison. A few samples were additionally combined with leather and wood intending to imitate the common manufacturing of metals and organic materials on ethnographic objects. Moreover, the effect of the surface properties was examined by testing coupons with differently treated surfaces.

The samples were exposed using the "Oddy-Test" (Lee and Thickett 1996) in order to form copper soaps under conditions of accelerated aging. All test specimens were stored in an atmosphere of high temperature and humidity for 28 days. Over the course of the test the samples were observed and alterations were documented focusing on the formation of efflorescence as well as colour changes on the surface of the coupons or of the oils and waxes.

After four weeks newly occurred green efflorescence and samples of oils and waxes turned to green were examined by FTIR analysis to detect if copper soaps had potentially formed.

In the second test series, wax from beeswax and stearin wax candles was dripped on coupons of copper, bronze and brass with a polished or oxidised surface. These types of candles were chosen due to their high ratio of fatty acids. Furthermore, they are most often used in candlesticks. In addition, a paraffin wax candle was included as fatty acid free reference material.

The samples were stored for eight weeks under natural conditions, which means room temperature and humidity. The observations during that time were focused on colour changes of the waxes.

At the end of the test period the wax coatings were partly lifted and removed to examine if any alteration had taken place between wax and metal coupon. Samples of coloured wax were analysed by FTIR to detect if copper soaps had potentially formed under this conditions.

Conclusions

In the first test series, greenish coloured efflorescences occurred with lanolin, beeswax and stearin wax under conditions of accelerated aging. They were identified as copper soaps, on brass coupons also as zinc soaps (except with lanolin). The oils had turned to turquoise-green (Ballistol®) or yellow-green (neat's foot oil, olive oil), but no metal soaps could be detected by FTIR. However, due to the results none of these organic materials can be recommended for conservation treatments because of their corrosive character towards copper alloys.

In the second series, copper and zinc soaps were identified with beeswax and stearin wax candles on both the polished and the oxidised coupons. This demonstrated that copper and zinc soaps can be formed on different treated surfaces under natural conditions in a relatively short period of time.

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Development and Evaluation of an Innovative Biological Treatment for the Protection of Metal Artefacts

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Introduction

There is a growing interest for the production of inorganic materials by biological synthesis because those are more environmental friendly processes. Novel applications of this are the use of microorganisms for corrosion control or protection of stone monuments, which were recently illustrated in literature (Cappitelli et al. 2007; Zuo, 2007). In the case of outdoor bronze monuments, copper oxalates, which are not associated with the phenomenon of cyclic corrosion, have been observed (Nassau et al. 1987, Mazzeo et al. 1989). The copper oxalates can form compact patinas of an attractive green color on the bronze surface. Moreover, with high insolubility and chemical stability even in acid atmospheres (pH 3), copper oxalates provide the surface with good protection (Marabelli and Mazzeo 1993). In the literature, some species of fungi have been reported for their ability to transform metal-bearing minerals into metal oxalates (Sayer and Gadd 1997, Gharieb et al. 2004). In this study, this potential is exploited for the transformation of existing corrosion patinas into metal oxalates' patinas. Within the framework of the Biological patinA for arcHaeological and Artistic Metal ArtefactS (BAHAMAS) project, alternative possibilities offered by a fungal treatment are envisaged for the protection of copper, iron and silver artworks. The research activities foreseen aim at creating protective fungal patinas by the conversion of existing corrosion products into more stable and less soluble compounds while maintaining the surface's physical appearance. As part of this project, we evaluated the ability of *Beauveria bassiana* to produce copper oxalates. *B. bassiana* was isolated from vineyard soils highly contaminated with copper and is a well-known cosmopolite fungi used as biopesticide for more than 100 years (Längle 2006).

Experiments in Petri dishes

The performance of *B. bassiana* was compared with eight other fungal species selected for their ability to produce oxalate crystals: *Aspergillus niger*, *Aspergillus alliaceae*, *Penicillium* sp., *Fusarium* sp., *Trichophyton mentagrophytes*, *Trichophyton rubrum*, *Arthroderma quadrifidum* and *Geomyces pannorum*. All MA-based (MA: 15 $g.L^{-1}$ agar and 12 $g.L^{-1}$ malt in distilled water) media were autoclaved at 120 °C, 25 $min.L^{-1}$. In the four respective MABRO, MATA, MACUP, and MABC media, powders (5 $g.L^{-1}$) of (a) brochantite, (b) atacamite, (c) cuprite, and (d) a 50:50 mixture of cuprite and brochantite were added after autoclaving.

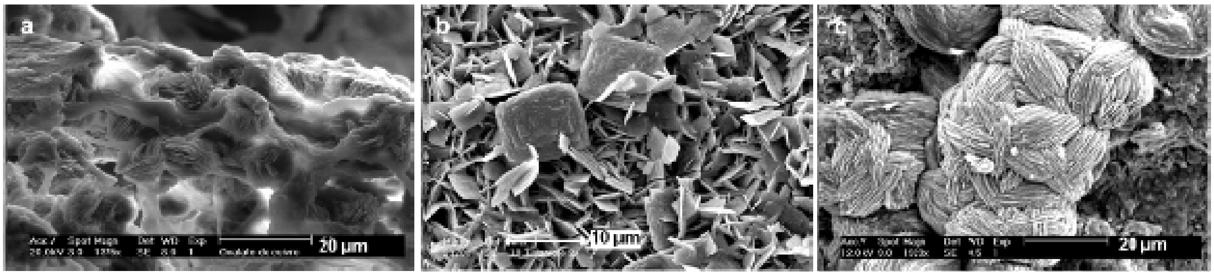

Fig. 1 SEM observations of a) culture of *B. bassiana* on a copper-enriched media with copper hydroxysulfates showing the embedded copper oxalates crystals. The same crystals are formed on corroded coupons with b) a copper hydroxysulfates patina and c) a copper hydrochlorides patina.

These minerals were sterilized by exposure to UV light for 30 min. The different strains were inoculated on three replicates of each medium under laminar flow. The growth performance was determined measuring the radial growth diameters of the mycelium each 3–4 days in two directions at 90° angles during 18 days. MA medium was used as a control. The formation of copper oxalates was confirmed by SEM observations and XRD and FTIR measurements. *B. bassiana* showed the best performance with almost 100% of conversion from copper hydroxysulphates and hydroxychlorides (fig. 1). Among the different fungi species tested, this strain was the most suitable for growing in a copper-enriched environment and precipitating copper oxalates.

Experiments on Copper and Bronze Coupons

First experiments were done on urban natural copper coupons in order to optimize the application procedure. The fungal strain was inoculated on different media which had previously been poured on the coupons. Tests with MA, MACUP, MABRO and MABC media led us to conclude that the strain *B. bassiana* grew more efficiently with this latter medium. The results also showed that the original patina is gradually transformed into copper oxalates and that, after one month, the conversion is all but complete on the surface areas where *B. bassiana* had grown (figure 1). As highlighted several times, protective treatments efficacy is dependent on the underlying patina. Attention has thus been paid to test the same treatment on several kinds of coupons. Different copper and bronze coupons with either urban or marine patinas were prepared and characterized with a complement of analytical techniques: XRD, SEM-EDS, optical, FTIR and Raman microscopies, colorimetry and electron impedance spectroscopy (EIS). The optimized fungal treatment was then applied on the coupons and the newly formed metal oxalates were investigated using the same analytical techniques as for the untreated patina. The different coupons treated with *B. bassiana* or reference materials (e.g. wax: Cosmoloid H80; silane: Dynasylan® F8263 …) have been exposed in a corrosion site (class 5, Genoa Harbor) in December 2011. Their long-term behavior and performance will be compared and monitored over a one-year period. Different application procedures are also being investigated on real artworks (archaeological finds, outdoor monuments). The procedure is adapted to better fit with the three-dimensionality of the objects.

Conclusions and Perspectives

Biopatinas created are expected to be stable and insoluble, providing a very high protection and allowing the inhibition of the corrosion processes. They are an eco-friendly strategy with which maintenance costs may be reduced to minimum. The treatments may also have no side-effect on health and environment as non-toxic and naturally occurring microorganisms are used. For more details, please see references (Mazzeo et al. 2008, Joseph et al. 2011, Joseph et al. 2012a, Joseph et al. 2012b) below.

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SESSION III

OUTDOOR BRONZES

Restoration and Conservation of Freely Weathered Bronzes in Germany – a Retrospect of the Methods of Work and the Decision-Making Processes over the Last 15 Years.

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A few hundred freely weathered bronzes were restored in Germany over the last fifteen years. In the last ten years, the most frequently applied method was to develop a concept based on preliminary examinations. Then the restorers were contracted based on these preparations. Usually, conservators who have academic training and experience with the restoration of bronzes were selected for the job. Contracting craftsmen or inexperienced restorers have become rare. The results of restorations essentially depend on the quality of the prepared concept, which again depends on the level of expertise of the planners. Concepts that are problematic from the conservatory perspective have been created when architect or engineers prepared the concepts without consulting conservators. The standard requirements from the monument conservation offices were not harmonized. It was usual practice to prepare sample surfaces before starting the restoration. The following standard variations of work steps on the objects were applied most frequently:

1. Pre-Cleaning

Pre-cleaning with steam jets has been found to be expensive in relation to the observed benefit. Over the last ten years, the technology was applied less frequently. Mainly, the bronzes were washed with water.

2. Surface Treatment

Surface treatment consists of a complex of activities for further cleaning (removal of foreign substance) and dismantling (processing of the attached products of corrosion, partly with foreign substance included). A dry-mechanical work method was most frequently used. Chemicals were very rarely applied. Scalpels and scrapers were the standard tools. Grinding fleece was also frequently used. Wire brushes were used in special, problematic cases only. In the nineties, ultrasonic fine-tip chisels were used frequently. In recent years however, they have been used only for removal of calcified crusts. Blasting technologies (micro-abrasive blasting) were not successful for differentiated processes of surfaces layers, and they were applied in certain exceptions only.

The first tests for processing bronzes with lasers were performed in Dresden in 1995/96. More tests followed. Extensive and systematic tests took place in the years 2002-2007 under a research project (DBU-AZ 18843-45). It turned out that the possibilities of removing foreign substances with the laser or differentiated processing of surface layers are very limited. Therefore laser technology was never routinely applied other than on test objects and test surfaces.

The method of dry ice blasting has been available since approximately 2000. Several smaller tests were performed on bronze objects. The work results did not lead to wider application of this technology. As with laser technology, the initial expectations to the work results were high. However, it showed once more that this technology gives reason to expect good and effective results for certain problematic issues only.

While the requirements and targets of restoration defined by the monument conservation offices often seem to be very similar, the work results are different. Opinions about the role the substances on the bronze surfaces are playing in the corrosion process differ. This leads to different ratings of which of the layers attached on the surface have to be considered a document worthy of conservation. Obviously, the term “patina” which is frequently used in this context is too subjective and not precise enough to define the work targets and work results through it. The value of the different surface-attached substances as a document worthy or unworthy of conservation is rated differently and hence the handling of these substances also differs. In the restoration of bronzes this especially affects the dismantling. Different opinions about the necessary degree of dismantling have come up. The restoration of the monument of Friedrich II. in Berlin (1997-2000) essentially stimulated the discussion. While the conservators in charge emphasized that only hazardous substances had been removed, other peers thought too much of the surface-attached layers had been reduced. In their opinion, the historic surface had not been sufficiently acknowledged as a document. Some planners favour the processing strategy of removing surface-attached layers partly down to the copper oxide layer. A certain number of bronzes were processed in this manner. The alternative strategy is much more moderate. With this strategy, after cleaning the layers will be levelled and removed moderately. More of the layers are removed only if they are porous and have a high proportion of foreign substances (crusts). All other surface-attached layers on the copper oxide layer are considered to be of high documentary value. It is assumed that (other than the layers with high contents of foreign substance) normal layers presently have a rather low damage potential. Hence they would have to be conserved as a historic document regardless of their colouring (green or black). There were only very few cases were all layers were removed right down to the base metal by sandblasting. This was not, or hardly, due to conservatory reasons.

3. Corrosion Protection

The most frequently used material for corrosion protection today is microcrystalline wax. In 1996/97 few monuments were conserved with acrylic coatings containing polyurethane. The use of the coating was initiated by a monument conservation office. It was guided by the need of obtaining corrosion protection that would last longer than that of protective wax. Based on similar considerations, a new coating for bronze conservation was developed from 1995-97 at the Fraunhofer-Institut (ISC). This coating, consisting of organic-inorganic hybrid polymers (ORMOCER®, trademark of the Fraunhofer-Gesellschaft), was meant to combine stability against environmental impact with good reversibility. Although the product showed good corrosion protection characteristics in tests, it was never applied on a bigger object. The problems of application technology were opposed by the good and safe results of wax conservation. Ever since, coatings have been applied only in special individual cases. Cosmoloid® H80 and different TeCero®-types have been applied for standard conservation with wax. As comparably good results can be achieved with all products, the monument conservation offices rarely define compulsory product standards. Products are mainly selected by the restorers in charge based on their individual experience with application technology. In a few cases in the 1990ies an inhibitor (BTA) was added to the wax.

Regular care and upkeep are beneficial considering the limited standing time of wax conservations. Unfortunately, in practice these activities often cannot be realized or cannot be completed due to lack of funding. The consequences are partial wear-off of the wax by weathering and formation of differently conserved surface areas. The appearance of visible spots further impairs the aesthetics of the objects. Since the SO_2-concentration has gone down drastically, there have been frequent considerations to give up wax conservation, and hence to concentrate once more on the aesthetics of natural surface colouring. Considering the present environmental conditions it seems not to be irresponsible to do without wax conservation in upkeep and monitoring. Unfortunately, so far there has been no cross-disciplinary discussion of this matter. The restorers are confronted with the fact that restoration of bronzes has little public acceptance if it is not followed by finishing conservation.

4. Documentation

Detailed documentation of the works in word and image, with mapping of findings and activities, is standard proceeding. The first 3-dimensional documentations with laser scanners were created in 1994. The first big bronze object was recorded in 3-D with a strip scanner in individual images (monument Friedrich II., Berlin). Other 3-D-models of big monuments were recorded in 2002 (Freiherr v. Stein, Berlin) and 2005 (Bavaria, Munich). This technology is still expensive and so far has been limited to certain individual objects.

The Restoration of the Bavaria (Bronze) Memorial in Munich

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The Bavaria Memorial

The giant "Bavaria" statue in Munich was modelled by the sculptor Ludwig von Schwanthaler, cast in bronze by the famous Bavarian Royal Foundry (later Ferdinand von Miller Foundry) and unveiled in 1850. Even today it is ranking among the biggest bronze memorials worldwide. With the stone base its height is 27 m, the bronze statue alone makes up 17 m.

The inside of the statue is open to the public. An iron winding staircase allows the visitors to climb up into the head, sit down on cast bronze cushions inside the head and look down through a small window onto the vast area where the annual Munich "Oktoberfest" takes place. Due to this accessibility of the inner surface some interesting bronze casting and bronze finishing specialities can be studied from outside *and* inside. So, when preparing your visit, choose a torch in order to look out for mirror-inverted core component numberings!

The Most Recent Restoration (in the Years after 2001) Was Unavoidable

The main reasons for this restoration were static concerns due to a large crack in the bronze wall of the left arm. Furthermore, mineral debris filling material within the bronze statue had been soaked by condensation water running down along the inner sides of the bronze walls, thus causing additional corrosion problems. In parallel various other, sometimes minor damages to the bronze, e.g. those caused by high visitor frequences and vandalism, had to be cured. It was clear from the very beginning that everything would have to be done with appropriate respect for the original craftswork.

Restoration Work

The recent restoration of the Bavaria Memorial was performed by the Bavarian Department of State-Owned Palaces, Gardens and Lakes (i.e. Bayerische Verwaltung

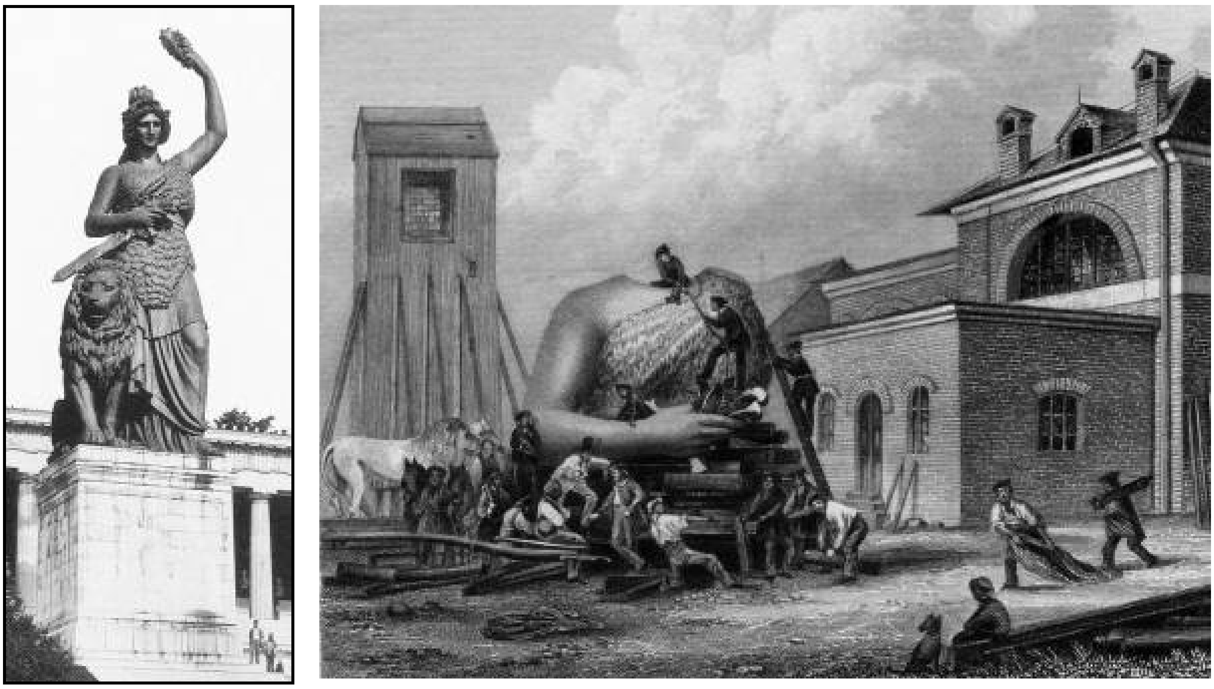

Fig. 1 The Bavaria statue: historical photograph (1892) and engraving depicting its making (~ 1850)

Fig. 2 New bronze reinforcements within the left arm of the Bavaria statue.

der staatlichen Schlösser, Gärten und Seen) and supervised by Claus Haller, a free-lance metal restorer from Munich. One of the most difficult tasks was the reinforcement of the left arm which had to be performed by specialists in situ, inside the arm, under very difficult working conditions. The reinforcement was designed by a spezialized structural engineer. Its main function is to preserve the circular cross section of the arm. Without the reinforcement the arm was considered to be in danger of denting and sinking down in a kind of twisting spiral movement.

Scientific Investigation

It was found that virtually all literature alloy analysis data were wrong. The Bavaria bronze is basically a CuSn6, with negligible amounts of zinc and lead. Its elemental composition is very similar in all main components of the Bavaria statue. Furthermore this type of alloy is found to be in perfect accordance with the analyses of other, earlier bronze works by the Bavarian Royal foundry. It does make sense to assume that the foundry intentionally chose this already well-proven alloy type in order to minimize the casting risks, well keeping in mind the huge portions of liquid bronze (up to 20 metric tons per individual item).

Surface corrosion phenomena are very similar to those of other 19th century bronzes in Munich – but due to the enormous size of the statue they were classified as minor threats.

3D Computer Model

Last but not least a photorealistic, very detailed 3D computer model of the memorial was established in order to document the findings and restorations tasks.

DIY

The bronze lady is awaiting your visit from April to mid-October, every day (9:00 – 18:00)! Just keep in mind that the entrance fee of € 3.50 is really low and that the interior inspection of a 19th century bronze lady might be a thrilling experience not only for you but also for your family and friends!

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Composition and Corrosion-Behaviour of Differently Old Patinas on Copper Plates for Roofing and on Some Parts of a Bronze Statue in South-West Germany

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Patinas on copper plates for roofing of older buildings (Figs. 1 and 2) being time-dependent differently produced and patinas on a bronze statue (Fig. 3) have been examined by the Research Institute for Precious Metals & Metal Chemistry (**fem**) in Schwäbisch Gmünd and by MPA in Stuttgart. Several destructive and non-destructive examination techniques have been used. Besides by XRD and SEM all specimens were examined metallographically and analysed chemically. Additionally, the parts from the statue were examined by 3D-CT whereas the copper plates were chemically analysed by GDOS specific to the depth of the patinas. All specimens passed electrochemical tests by potentiostatic and potentiodynamic measurements.

The patinas on the copper plates and on the different parts of the statue are all built up rather complex but surprisingly their differences are relatively small instead of the fact, that they have grown on different base materials (i.e. copper plates for roofing of different age and different production processes, cast bronze parts from the statue and a wrought brass part from the statue). Typically, an intermediate layer of cuprite could be observed on every kind of base material. This layer is covered usually by a mixture of different Cu-containing phases mainly like antlerite and brochantite. Also other Cu-containing phases and where applicable Sn- or Zn-containing phases could be observed. Quite often dust particles being incorporated in the patinas were found and by this, giving at least a hint about the different environments of the patinas during their growth. The SEM examinations of all patinas regularly revealed fractured and porous plus some really spongy appearances. Occasionally, remains of a former gilding of the statue

Fig. 1 Old town-house in Esslingen

Fig. 2 Basilica in Weingarten

Fig. 3 Statue of Wilhelm I., King of Württemberg

were observed on its patinas. The dust particles being incorporated in the patinas could be revealed by XRD and by EDS/SEM often to be quartz and gypsum. Frequently, also between the green patina layers white gypsum layers could be ascertained. Better against rain protected dark grey parts of the patinas of the statue showed more particle inclusions than the more freely weathered greenish patinas.

The patinas on the copper roofing plates may be differentiated by their different ages i.e. whether their age is about 400 years as in Esslingen or about 300 years as well as 140 years after an intermediate repair as in Weingarten, and by this by their more or less different thickness. The compositional differences of these patinas i.e. the predominance of brochantite in Esslingen and the predominance of antlerite in Weingarten may mainly be attributed to the place of their origin. The patina on the roofing plates of the old town-hall in the city of Esslingen with its typical atmospheric pollution obviously was formed under other conditions than the patinas on the roofing plates of the old basilica in the more agricultural environment of Weingarten being quite far away from any city.

For the copper plates a dependence of the patinas' build-up upon the local weathering condition could not be observed of course due to their two-dimensional geometry. But the different parts of the bronze statue showed a pronounced dependence due to their exposition with respect to the weathering conditions. Patina surfaces being oriented freely to the particular weathering showed the typical greenish colours whereas their better against rain protected backsides frequently showed a dark grey colour. Because of high carbon contents detected by EDX in the SEM and because of its optical and morphological appearance this dark grey layer is expected to have at least partially biological origin (→ biofilm).

Even if the electrochemical measurements on the different parts of the patinas were somewhat tricky because of their rather high electrical resistance all patinas showed quite noble characteristics during potentiostatic measurements without any breakthrough behaviour up to a voltage of +2.0 V in the course of the potentiodynamic measurements. The dark-grey patinas on the different parts of the statue seemed at first to show a slightly less noble character if compared to the green patinas but after a little while the electrochemical differences between both surfaces vanished. The overall best corrosion resistance was observed for patinas having a high content of brochantite with respect to antlerite. Especially for the oldest copper plates the first build-up of a cuprite layer as the result of the old smithing technique using an open hearth for the plate production seems to promote and to assure the build-up of a more corrosion-resistant patina. This means that the complex patinas are providing an electrochemical equilibrium mainly between the phases brochantite, antlerite, and cuprite. To maintain such kind of electrochemical equilibrium during ongoing weathering the cracks and pores in the patinas are obviously necessary for the electrolytes in such electrochemical processes. This should be taken into account for example if patinas are waxed. In its freshly applied state the waxing will of course close all cracks and pores and this will stop at first any kind of ongoing corrosion virtually by inhibiting the approach to an electrochemical equilibrium in the waxed patina. This positive effect has been unequivocally proven by Krätschmer et al. (2000) after waxing patinas on copper roofing plates. But usually, copper roofing plates are not waxed at all, and surprisingly the oldest copper plates from Esslingen with its urban atmospheric pollution could withstand ongoing corrosion much better than new ones which is thought to be due to the thick cuprite layer in the course of the original plate production by smithing. Contrariwise, especially when waxes on patinas are not renewed periodically, the weathering of the patinas led to losses of their greenish components (Kolmanitsch 2009). Under certain circumstances this effect continued until only cuprite remained visible which can actually be observed in Mannheim on the Grupello's fountain pyramid. At least in these cases the inhibition of the system's approach to a stable electrochemical equilibrium in the patinas seems to be disadvantageous and the detrimental effect of a singular waxing without any further maintenance may be even intensified by the organic waxes themselves. Organic materials are well known to act as an optimal feed for microorganisms thereby leading to additional bio corrosion. Additionally, it is a fact that the atmospheric sulphur content usually as sulphur dioxide nowadays is strongly decreased due to environmental protection measures. This inhibits the build-up of new sulphates like antlerite and brochantite and the build-up of a new greenish patina is thereby pretty much reduced. Obviously, more scientific work is needed for a complete understanding of the interaction between the different phases in the patinas.

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A New Method for Conserving Weathered Surfaces of Copper and Bronze

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Conservators often need to mitigate unsightly patina on bronze or copper forms. Most conservation of weathered outdoor sculpture blocks up hues of weather patina by washing and waxing, or removes some metal during repatination. Textures change as we erode or reform metallic surfaces, and if corrosion products have psuedomorphically replaced metal surface, their removal is loss. With a new method developed using bioactive media which can be independently produced but are readily available, unsightly mottled greenish to black patinas give way to more pleasing reddish browns, with minimal or no loss of form.

The Method in Practice

1. Apply gel or immerse in liquid treatment medium, allow time for action (time based on pretests and observation). 2. Remove medium and rinse well. 3. Keep surface wet while removing softened matter. 4. Rinse well and allow to dry. 5. After treatment, apply coating(s) as needed. Greenish to black colors are replaced by reddish browns (fig. 1 - 6).

Weather Patina on Bronze and Copper

Weather patina covering bronze and copper corroded over time in outdoor moisture and air, generally at first comprises only metal oxides such as cuprite (oxidized copper), in a dense reddish stratum directly integrated with underlying metal at an interpenetrating interface. Over long periods these patinas usually also comprise copper hydroxysulfates such as brochantite, in a less dense greenish outer layer directly interfaced with the underlying oxides (fig. 7). Weather patinas always entrain diverse matter deposited from air. Many investigators over many years have studied outdoor corrosion of cultural heritage and other metal surfaces, often with some attention to patinas.

Experimental

Hypothesis: Treatment removes greenish sulfates strata, exposes reddish oxides strata, without exposing metallic surface. Experimental: Our treatment method was applied to part of the surface of a coupon cut from weathered copper flashing (fig. 8), while adjacent surface was protected from treatment by waterproof adhesive tape masking, which was removed after treatment. Finally, the surface's resulting adjacent untreated and treated areas were imaged using SEM, and analyzed using EDS. Results support the hypothesis (see fig. 10 a & 10 b).

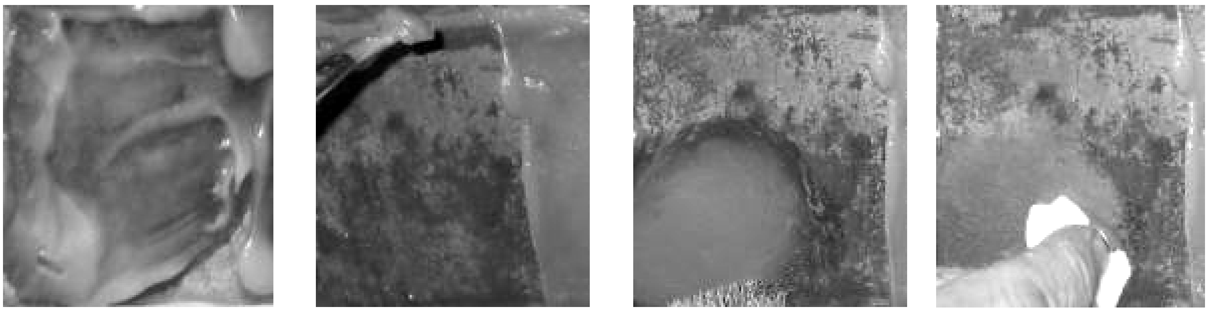
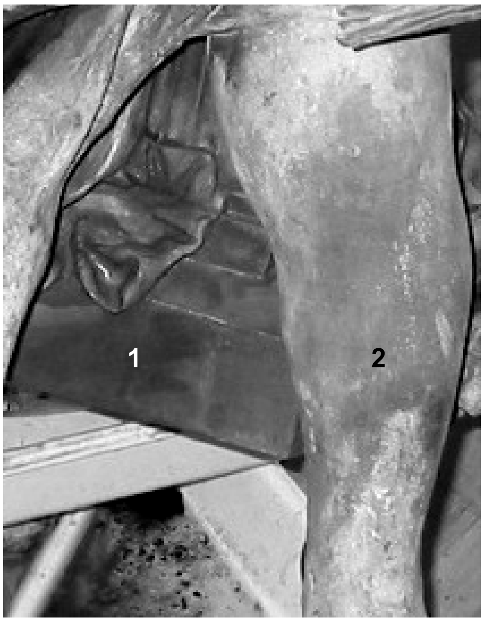


Fig. 1-4 Steps in treatment method.
Photos: J. Heinonen & J. Scott, at NYCF, NYC, USA



1 before

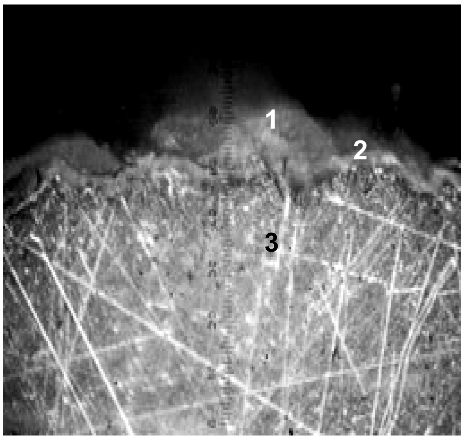
2 after

Fig. 5 Before/after, detail of Figure.
Photo: J. H. & J. S., at NYCF

1 after

2 before

Fig 6 Before/after, close detail of plaque
Photos: J. H. & J. S., at NYCF

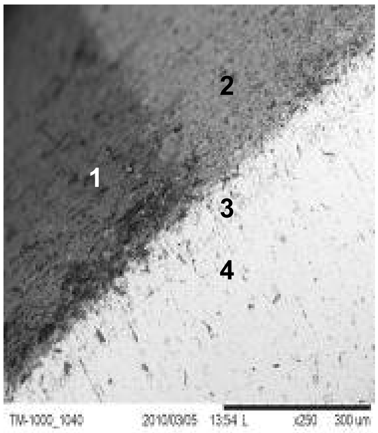


1 sulfates

2 oxides

3 bronze

Fig. 7 Weather patina structure magnified cross section. Photo: R. Lodge, Oberlin, OH, USA



1 untreated

2 treated

3 *CuO_2&Cu*

4 Cu

Fig. 8 Patina coupon surface.
Photo: J. Scott

Biochemical process

Literature and observation indicate a sulfates-oxidizing biochemistry enables our treatment, with treatment media adapted from biohydrometallurgy. In bioleaching and biomining, metals are recovered from leach solutions, after ore minerals have been digested via aqueous redox reactions catalyzed metabolically by bacteria such as Acidithiobacillus *ferrooxidans* (fig. 9).

Biooxidation is already used in removing corrosion products from objects made from silver, copper, iron, aluminum and their alloys. Our biooxidative treatment works too quickly for the acidic treatment medium to erode the patina's oxides layer or underlying metal, and under acidic conditions *A. ferrooxidans*' respiration does not engage copper oxides. Weather patina’s layered structure, its layers' distinct compositions of reduced

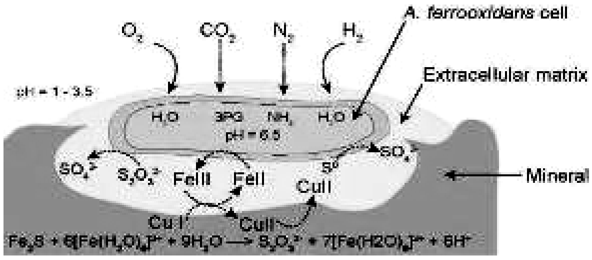


Fig. 9: *Acidithiobacillus ferrooxidans* catalysis of oxidation. Diagram: Valdes, et.al.

copper and oxidized copper, *A. Ferrooxidans*' oxidative respiration in aerobic acidic media, and conservator skill, are all key in this biooxidative treatment for outdoor patinas of copper and bronze. They allow us to soften and remove weather patina's outer sulfates layer, in order to exchange unsightly mottled greenish to black patinas for more pleasing reddish browns, with little or no alteration of texture.

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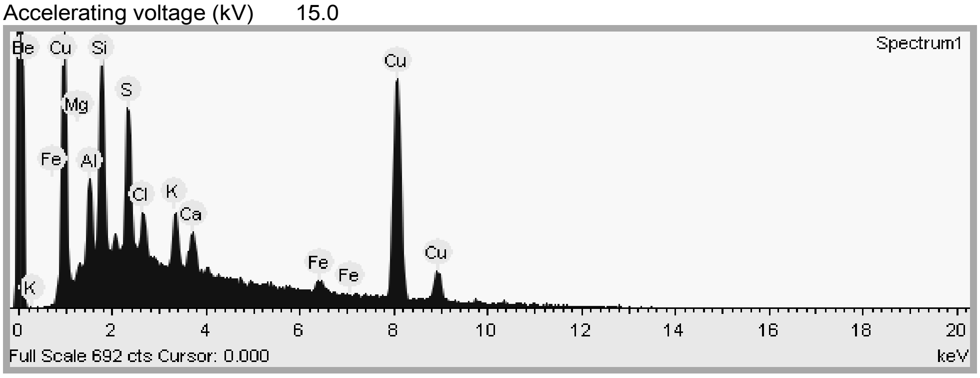
Spectrum name	**Spectrum1**	**outdoor weathered copper coupon**
Location	flat non-method-exposed surface very near transition 10000 b.ipj	
Acquisition time (s)	120.0	
Process time	4	
Accelerating voltage (kV)	15.0	



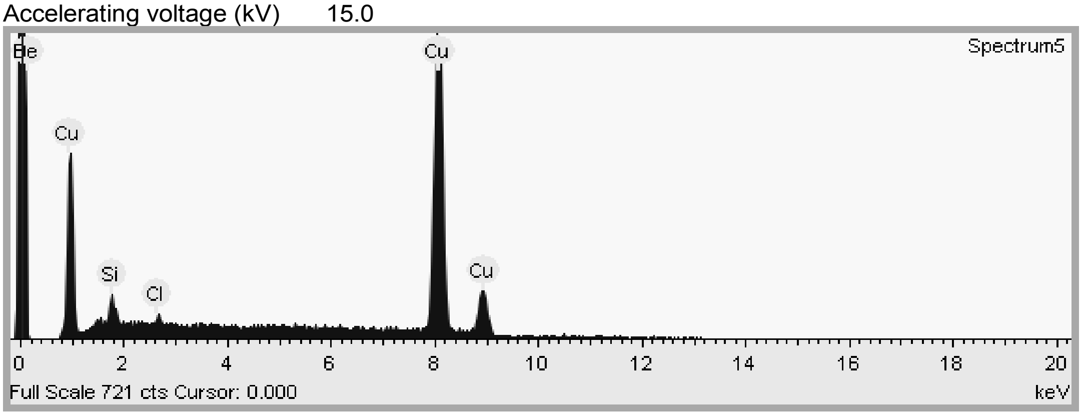
Quantification method All elements (normalised)

Summary results

Element	Weight %
Magnesium	1.4
Aluminum	5.2
Silicon	11.4
Sulfur	8.6
Chlorine	3.0
Potassium	3.9
Calcium	2.7
Iron	2.7
Copper	61.1

Fig. 10a EDS spectra of Fig. 5 patina surface: Spectrum 1 untreated. Spectra: J. Scott

Spectrum name	**Spectrum5**	**outdoor weathered copper coupon**
Location	flat method-exposed surface very near transition 10000 b.ipj	
Acquisition time (s)	120.0	
Process time	4	
Accelerating voltage (kV)	15.0	



Quantification method All elements (normalised)

Summary results

Element	Weight %
Silicon	5.1
Chlorine	1.5
Copper	93.4

Fig. 10b EDS spectra of Fig. 5 patina surface: Spectrum 5 treated. Spectra: J. Scott

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Thanks to Alicia F. Boan and Jari Heinonen.

Conservation of Cast Bronze Sculptures by Daniel Spoerri

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In 2010 the government of Lower Austria received a large donation from the famous artist Daniel Spoerri. The donation consists of 39 works, including a group of 36 smaller works of art. The sculptures are representative examples of the entire work of the artist. The donation was part of a deal between Spoerri and the Austrian government that also established a foundation and enabled the acquisition of two buildings for art projects.

Daniel Spoerri

Born in 1930, began his artistic career in the 1950s as a dancer and director. Later on he devoted himself to the visual arts. In 1960 Daniel Spoerri signed the Manifesto of “Nouveaux Réalisme” as a co-founder in Paris. He became world famous for his so called “Snare-Pictures” (“Tableaux piéges”). In these assemblages Spoerri presented remains of a meal or other situations encountered by chance. A segment of life was captured and frozen. The artist implemented not only the principle of chance, using everyday objects in visual arts, but also built on his literature work the “Topography of Chance”.

As a professor and lecturer, he organized exhibitions and banquets with students. The opening of the “Restaurant Spoerri” in 1968 and the associated “Eat Art Gallery” in Düsseldorf made Daniel Spoerri the founder of the so-called Eat Art. Daniel Spoerri also cooked in this restaurant. His definition of art includes not only Object-Art, but also performances and other projects. The frozen and glued moment belongs to his understanding of art, which also covers life and even death, decay and rebirth.

Also well known is Daniel Spoerri’s sculpture garden “Il Giardino di Daniel Spoerri” in Tuscany, Italy, which opened in 1997. In a large park numerous sculptures can be seen from the artist and also from his artist friends. The amount of sculptures in the park continues to grow. Since Daniel Spoerri has had this “Giardino” he has made his assemblages more frequently in bronze. In the year 2007 Daniel Spoerri returned to Vienna, where he taught in the 1980s at the University of Applied Art. Two years later, Spoerri acquired two houses which he named Eat Art & Ab Art on the main square in Hadersdorf am Kamp (Lower Austria). The artist also calls the house “Ab Art”, in which his works are permanently displayed, “Staulager” (depot). Special exhibitions with works by other artists will also be shown there. In the building “Eat Art” or “Esslokal” (eatery) culinary and cultural events take place. Visitors can also dine.

The Prillwitz Idols

The 16 objects that received conservation treatment are from the series of “The Prillwitz Idols”. In 1978, Daniel Spoerri discovered a book with the title “Liturgical Antiquities of the Obotrites” in Cologne. The engravings show figures of pre-Slavic divinities (Obothristic Antiquities) which reminded Daniel Spoerri on works of Art Brut. He was touched and fascinated by the figures. In 2005 he rediscovered this book and further research revealed the actual existence of those figures as sculptures also known as the “Prillwitz Idols”. His engagement with these figures can be seen in the series of large Cast Bronze Sculptures, the “Prillwitz Idols”, which were made in the years 2005–2008. In this edition the pieces were cast 12 times, but they are actually

Fig. 1 Daniel Spoerri, “Sensenmann”, 2006–2010; 240 cm, cast-bronze

“Originals in Series” because Daniel Spoerri designed each cast differently. The casting channels are kept and incorporated into the design like the Slavic deities. Therefore each cast is unique. In addition to these bronze figures Daniel Spoerri also made collages of the “Prillwitz Idols” from reproductions of the engravings in the aforementioned book. With the collages, the artist interprets the stitches by assigning small objects to them.

How to Find a Concept for the Conservation?

The process of creation of these sculptures starts with the assembling of objects like tailor’s dummies, coat stands, hats or more unusual objects such as anatomical models, animals’ sculls, African figures and masks chosen by Daniel Spoerri from his sprawling collection, from flea markets or elsewhere. Specialists in the foundry make a mold of the assemblages and make casts of bronze. When a cast is finished the artist decides on removing or leaving cast channels according to his creative ideas. Finally the surface of the bronze gets patination. Very often a so-called “Rostpatina” which is a rust-colored to brown patination is applied, sometimes the artist prefers a green to turquoise patination.

A number of sculptures are completed by welding a base of iron plate. As a rule these sculptures are created for outdoor exhibition. We could see some of them installed at Hadersdorf like for example the so-called “Sensenmann” in the courtyard of “Esslokal” where the sculpture was exhibited before it became part of the museum’s collection. This was the sculpture’s place for some time and so we could notice traces as a consequence of outdoor exhibition: the base had sunk into the ground, grass expanded above, the condition of the bronze surface must be correspondingly figured as follows: covered with green to black stained patina with considerable stripes from rain water, dirt and blotches of bird droppings.

All is corresponding to the intention of the artist. The possibility of the artworks changing is part of their creation. If one of these pieces of art enters a museum’s collection, the institution has to ask questions about how to deal with it.

Entry conditions to the collection were easily specified on the part of the conservators: to place the main focus on keeping away insects and animals living on the sculptures’ surfaces from storage areas. A second aspect was to think about the iron surfaces of the bases which are intensely rusty in many cases and also to think about the interaction of different metals – bronze and iron. Daniel Spoerri’s idea of the condition of his works and of their aging process is clear:

the surface and its patina has a blotchy appearance based on a technical process, changes of color or the development of other phenomena like stripes from rain water are welcome. Not even bird droppings seem to be a visual interference. The same goes for the iron bases for which he decided to use rusty material expecting the increase of rust after a while.

Following both aspects – the museum's interest and the artist's intention – the instructions for the operation were formed. Sculptures should be dry cleaned, insects and all their food sources must be removed, dirt such as spots of platter or bird droppings must be removed because of their heavily caustic impact. Also thick incrustations of earth (for example the adhesion of earth on the iron base of "Sensenmann" after its digging out) have to be removed. Furthermore we came to the decision to refrain from protecting the surfaces of neither bronze nor iron in accordance with the artist's intent to allow changes.

Questions in relation to exhibiting conditions appear particularly with regard to outdoor circumstances. Outdoor exhibiting means to consider explicit traces of change. From the conservator's point of view it is important to permit outdoor exhibition of these sculptures in accordance to the artist and to develop a concept of maintenance. It consists of recleaning the surfaces after outdoor exhibition, removing bird droppings and coating all sculptures for storage.

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POSTERS

Gilding Techniques on Roman Life Size Bronze Statues from UNESCO-World Heritage Limes – Investigations on Diffusion-Gilding of Bronze Statues

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How were Roman bronze statue fragments from the Limes region gilded? On a life size back fragment of a bronze statue found in Groß-Gerau near Mainz, surprisingly, a diffusion-bond between gold and substrate was detected (figure 1).

Diffusion-bonding on silver was an early applied gilding technique, especially in the Roman Empire in Germania. This gilding technique on silver by heating applied gold leaf has been successfully reconstructed. In connection with copper, especially copper alloys, however, there are only little finds and investigations (Drayman-Weisser 2000, Figuereido et al. 2010: 287, 288).

Within the project "Römische Großbronzen am UNESCO-Welterbe Limes" funded by VW-Stiftung (see Frank Willer, this volume) the gilding techniques of a few statue fragments could be analysed. The diffusion-bonding on the back fragment from Groß-Gerau was an exciting discovery (fig. 1).

Therefore reconstruction attempts on bronze coupons were undertaken within the framework of a diploma thesis in the Objects' Conservation Programme at the State Academy of Art and Design Stuttgart. Information from literature and observations on the original back fragment provided the basis for practical experiments. It was also interesting to investigate the possible meaning of lead in diffusion-bonded bronze.

For the tests different copper and bronze coupons were cast and gilded with a thick gold leaf (3 µm) which complies with ancient gold leaf. First, the metal surface was roughened with sandpaper. Secondly, one or two gold leafs where burnished and heated in the furnace by different temperatures. Mostly the coupons were heated under oxidizing conditions. Then, metallographic sections were made from gilded samples in order to find out if diffusion-bonding was generated. In the scanning electron microscope a few samples showed little diffusion-bonding on some points, mostly those heated under reducing conditions. For example, copper heated to 450 °C

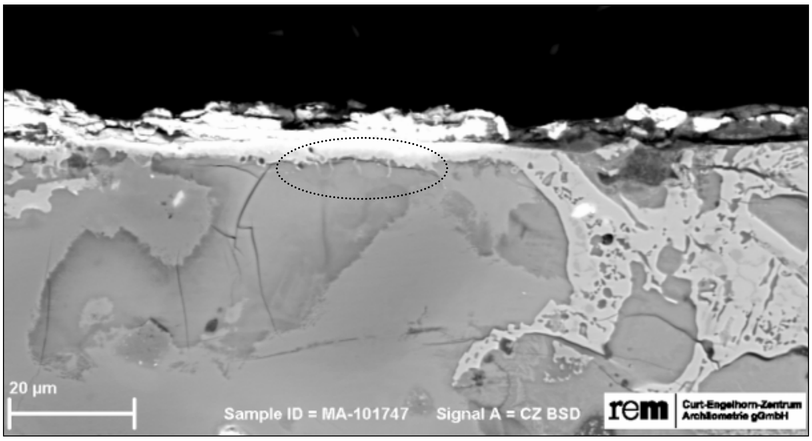

Fig. 1 Metallographic section: "Diffusion fingers" on back fragment (Schwab: 10.08.2010)

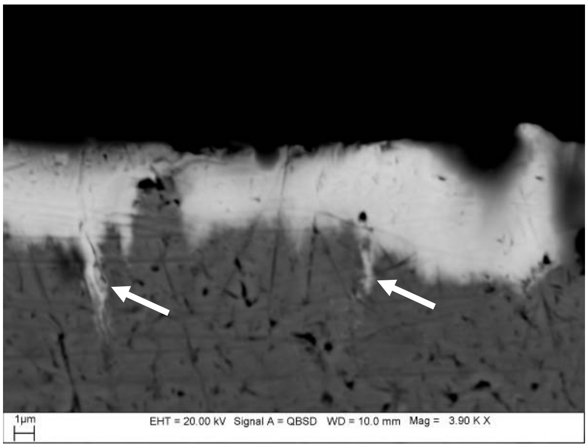

Fig. 2 "Diffusion-fingers" (arrows) on Copper in reducing atmosphere heated to 450 °C (Fischer: 05.07.2011)

at the air showed some copper accumulations in the gold layer. In reducing atmosphere, so called diffusion fingers from gold drew into the copper substrate. Diffusion between gold- and copper-atoms was also clearly visible by using an EDX-Line- or Spotscan. With tin bronze (7% Sn), only those heated (450 °C) under reducing atmosphere showed a substitution from gold to bronze substrate, which was clearly visible (fig. 2), also with EDX-Mapping.

By heating a high leaded bronze (7% Sn, 20% Pb) to about 200 °C, a problem occurred. Molten lead globules from bronze destroyed the gold layer by forming dark-grey colored spots at the surface. Therefore, it was not possible to reconstruct the diffusion bonding observed on the original back fragment from Groß-Gerau of high leaded bronze. There were no references to diffusion between gold and substrate and mostly there was a gap between the bronze and the gold layer.

Conclusion

In principle, the experiments for reconstruction shows that it is possible to reproduce diffusion-gilding on copper and bronze if the lead globules are not near the bronze surface. Twelve out of thirteen gilded original fragments inspected were leaf gilded. Only one fragment shows diffusion-bonding. Thus there were doubts about intentional diffusion gilding on the back fragment from Groß-Gerau. An explanation could be that diffusion-bonding resulted from secondary fire, charcoal adherence indicates this assumption.

As a result, diffusion-bonding for gilding life size bronzes in the Limes region seems highly unlikely: almost all examined fragments were leaf gilded – which is an easier method for gilding.

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“When the eye is delighted by the art of these metals…” Brown Varnish on the Romanesque Comburg Wheel Chandelier

INES FRONTZEK

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The mediaeval Hertwig wheel chandelier from Comburg / Steinbach (Schwäbisch Hall) in south Germany is an impressive, but not well-known work of Romanesque metal art. Its manufacture, conservation history and preservation was studied for a Stuttgart diploma thesis (Frontzek 2011) in objects' conservation. The chandelier was created in the 12th cent. to give worshippers an impression of the heavenly Jerusalem “when the eye is delighted by the art of these metals” as its inscription says. It has a darkened brown varnish on its copper alloy surface, a little-known decoration technique. Such objects all date from the beginning of the 11th century to the first half of the 14th century.

There are many names for this type of varnish including *aufgebrannter brauner Firnis, Braunfirnismalerei, Braunmalerei, brown varnish, Firnisbrand, Leinölfirnis, Ölbräune, émail brun* etc. Behind these names is a mediaeval metal decoration technique for copper alloys (bronze and brass), pure copper or, in rare cases, iron. Only since the 19th century has brown been the final colour achieved by this technique. Brown varnish is predominantly used on objects used in sacred services and churches. In modern times, it is known that the goldsmith Amberg from Würzburg applied the technique on his own works as well as for restorations.

Fig. 1 Hertwig wheel chandelier

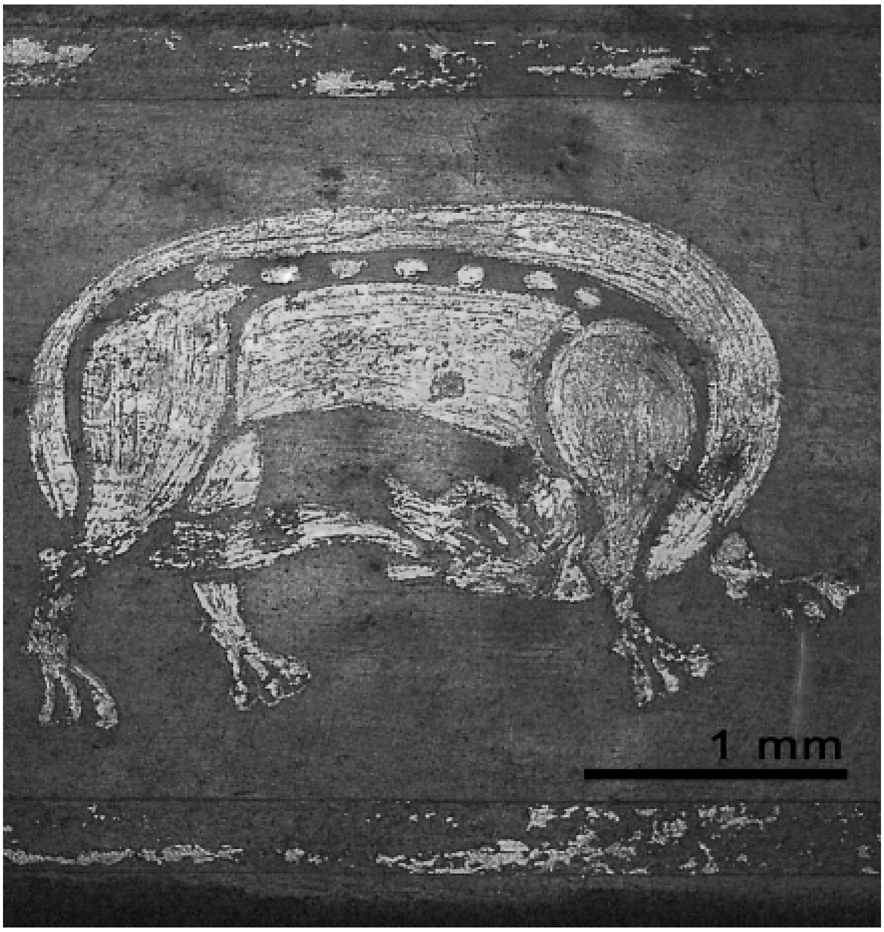

Fig. 2 The brown varnish: gold on brown background

Area of Distribution

According to Wolters (1997: 153ff.), the “Brown Varnish” decorative technique can be found in Lower Saxony, the Rhineland, the Weser area/Westphalia, Northern Hesse and Denmark, about 1130 AD in the Rhine-Maas area, as well as in Russia. The golden age of the technique was achieved in objects from the Rhine-Maas area.

Method of Production á la Theophilus

Together with gilding, the varnish forms part of polychrome metal decoration. The varnish is an organic coating of slightly viscous linseed oil, natural asphalt, wood resin, or a kind of a wax, which forms after the heating and cooling process. This produces a hard coating on the treated surface. The colour depends on the material used for metal and for the coating, the number of layers, the oxygen available during the work, the temperature, and the duration of heating. The production of linseed oil brown varnish starts with a metal sheet painted with oil and then heated slowly. At the same time the linseed oil gets hard and elastic, forming a resin-like polymer by oxidation and polymerization, based on linoxyn. The colour changes from transparent to brown or black and the number of layers influences the final colour. It is due to copper oxide, yellow to red from cuprite (Cu_2O), and brown to black from tenorite (CuO). The ornament is scraped out of the varnish and the surface is plated with gold (fire gilding). The areas still covered with varnish resist the gilding. After the treatment the ornament is seen as being brown and gold on the metal surface. The gold can be polished to a bright finish.

The most important ancient source on this technique is the „Diversarium artium schedula“ written by Theophilus in the 12th century. Theophilus describes the process in

Fig. 3 Inscription: The part with the name Hertwig; brown on golden background

the third book, chapter 71, under the title „Quomodo denigretur cuprum“ (”How To Put a Black Coating on Copper“) (Brepohl, 1999:198) step by step:

1. A sheet of copper
2. Draw the decorative ornament
3. Apply linseed oil with the finger or with a goose feather
4. Hold the sheet with pliers about glowing coals
5. As soon as the linseed oil is warm and liquid – distribute again with the goose feather or the finger.
6. If it is plain, bring it about burning coals long enough that the linseed oil doesn´t smoke any longer.
7. Once the colour is good, then it should cool down at the air
8. When the colour isn`t good the sheet needs another treatment with linseed oil.
9. With a scraper create the ornament in the brown varnish
10. You can choose between gold on brown or brown on golden background.
11. After this step amalgamate the surface with a mix of tartar & mercury then gild the copper sheet.
12. Cool down slowly at the air
13. The last step is polishing the surface.

The Hertwig Wheel Chandelier

The chandelier shows the brown varnish on the band of inscription, around the medaillions and in few areas of the tower. Inside one can also find bands decorated with brown varnish. They show animals and mythical creatures. In which way the brown varnish is created on this wheel chandelier is unknown but at least it dates from the times of Theophilus. Much of what we see today might have been done indeed following the recipe of him, but some of it is certainly due to later renovation and restoration work. Nevertheless, extensive analyses were beyond the scope of the thesis.

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Decalcifying Archaeological Bronzes: a Comparison of Different Chelating Agents

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Introduction

After excavation the surface of archaeological copper alloy objects can be covered by hard accretions of calcium carbonate. They are usually removed by mechanical methods, but this can be arduous, time consuming and may harm the surface of the object. An alternative is the use of sequestering agents, which may remove the calcareous accretions satisfactorily. But this may occur at the cost of altering the composition of the patina or etching the surface. The surface of archaeological bronzes usually consists of the corrosion products cuprite, Cu_2O, and the basic copper carbonate malachite, $Cu_2CO_3(OH)_2$. Especially in calcareous soils, malachite forms in contact with calcium carbonate over the initial cuprite layer (Scott 2002).

Selected Chelating Agents

The use of four chelating agents were examined to determine whether they are effective in discriminating between calcium carbonate and copper patina, and non-corrosive to copper alloys in the presence of air. Citric acid (in this study the trisodium salt Na_3-Citrate), sodium tripolyphosphate (STPP) and disodium ethylenediamine-tetra-acetate (Na_2-EDTA) are chelating agents that are proposed in the literature for the removal of calcareous accretions on archaeological bronzes (Sharma and Kharbade 1994, North 1987, Emmerling 1969). Another aminopolycarbonacid analysed in this study is cyclohexanediamine-tetraacetate (CDTA).

Experimental

The effectiveness of the chelating agents was investigated by immersing synthetic malachite and calcium carbonate in solutions of the chelating agents at different pH values. After one hour, the solutions were filtered and the dissolved copper and calcium concentrations were analysed by atomic absorption spectral analysis (AAS). To investigate whether cuprite is dissolved by the chelating agents, cuprite was treated for one hour with the chelating agents at pH 9. The solutions were also filtered after one hour and the copper concentration quantified by AAS. To analyse the reactions with the base metal of copper alloy objects, polished bronze (92% Cu, 8% Sn) and brass (80% Cu, 20% Zn) sheets were immersed in solutions of the chelating agents at pH 9. The dissolved copper and zinc concentrations were quantified by AAS. The surfaces were also analysed by scanning electron microscopy–energy dispersive X-ray analysis (SEM-EDX) and inspected visually (SEM, reflected light microscopy).

Results and Discussion

Despite higher stability constants of the chelating agents with copper than with calcium much more calcium carbonate than malachite was dissolved (Table 1). This can be explained by the higher solubility of calcium carbonate compared with malachite (Stelzner and Eggert 2008). At lower pH values the chelating agents except Na_3-Citrate dissolved more calcium carbonate

	Na_3-Citrate		STPP		Na_2-EDTA		CDTA	
pH	Cu (%)	Ca (%)	Cu (%)	Ca (%)	Cu (%)	Ca (%)	Cu (%)	Ca (%)
6	0.11	1.60	0.51	14.0	0.59	29.8	0.67	33.3
7	0.05	2.50	0.34	13.4	0.29	25.3	0.24	25.2
9	0.16	7.60	0.23	6.25	0.18	23.7	0.12	23.9

Tab. 1 Dissolved calcium carbonate and malachite in % (by weight) after one hour of immersion of 0.2 g calcium carbonate and 0.2 g malachite in 25 mL of 0.02 mol·L^{-1} Na_3-Citrate, STPP, Na_2-EDTA or CDTA at different pH values.

	Na_3-Citrate	STPP	Na_2-EDTA	CDTA
Cu (%w)	0.17	0.21	0.79	0.13

Tab. 2 Dissolved cuprite after one hour of immersion of 0.2 g cuprite in 25 mL of 0.02 mol·L^{-1} Na_3-Citrate, STPP, Na2-EDTA or CDTA at pH 9.

Chelating agent	Bronze Dissolved copper (ppm)		Brass Dissolved copper (ppm)		Brass Dissolved zinc (ppm)	
	1 h	24 h	1 h	24 h	1 h	24 h
Na_3-Citrate	4.09	36.77	1.26	15.36	0.57	3.85
STPP	4.19	34.25	3.65	17.32	1.77	8.55
Na_2-EDTA	5.81	47.23	7.07	36.85	1.83	8.50
CDTA	6.63	43.12	6.51	39.00	1.75	9.01

Tab. 3 Dissolved copper and zinc from polished metal coupons (3 × 2 cm) immersed in 25 mL of 0.02 mol·L^{-1} Na_3-Citrate, STPP, Na_2-EDTA or CDTA at pH 9.

and malachite. This can be explained by the solubility of the salts, which is higher under acidic conditions and STPP, Na_2-EDTA and CDTA are able to build stable complexes even under low pH conditions (table 1).

The best balance between dissolved calcium to copper was obtained in alkaline conditions at pH 9 and especially CDTA showed the best result. A possible explanation could be the structure of CDTA molecule with its organised functional groups (Umland 1971).

That cuprite is also attacked to some extent by the chelating agents was revealed by the experiment on synthetic cuprite (see table 2).

The experiment on brass and bronze sheets showed that the chelating agents dissolve parts of the metal. The amount of dissolved copper and zinc is listed in table 3. Na_3-Citrate and STPP are less corrosive than Na_2-EDTA and CDTA.

Etched metallographic structures could be observed by SEM after 24 hours immersion on all bronze and brass sheets. The bronze sheet treated with Na_3-Citrate and the brass sheet treated with STPP showed a colourful etched surface. The bronze turned dark red and brass black. Small amounts of phosphate could be detected by SEM-EDX on the brass sheet treated with STPP. No patination was observed on the sheets immersed in Na_2-EDTA or CDTA.

Conclusion

The comparative experiments on synthesized malachite and calcium carbonate showed that all chelating agents dissolve a measurable amount of malachite. The chelating agents are also able to dissolve cuprite to a small extent. The best results were obtained at pH 9 and especially with CDTA. Nevertheless it also may harm the base metal of bronze or brass like the other chelating agents. In particular Na_3-Citrate and STPP lead to patination of the metal.

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