Colour Code:
RED: Application
BLACK: BM report
BlUE: RCE Report

STAATLICHE
AKADEMIE DER
BILDENDEN KÜNSTE
STUTTGART

Report:

Stuttgart, Sept.26th, 2016

ARCHLAB visit to the British Museum Lab

July 24th to 28th, 2016

Visiting researchers:
Gerhard Eggert &
Britta Schmutzler

ARCHLAB visit to the RCE

Sept. 12th to 16th, 2016

Visiting researchers:
Gerhard Eggert &
Andrea Fischer

BM: Our expectation in the RACOPHINO (**R**ARE **C**ORROSION **PH**ENOMENA OF **IN**ORGANIC **O**BJECTS) research were fully met: We could identify a number of reports with interesting details in the digitized files of the BM lab and could check some old Debye Scherrer films which considerably adds to the knowledge base on rare corrosion phenomena.
This will have direct impact on our future research in Stuttgart:

- Glass-induced metal corrosion: we will analyse two samples from BM enameled objects and exchange information.
- Zinc corrosion: We will focus on this in our new research project as the BM reports confirm that there are still unknown compounds.
- Black Spots grown in the lab will be analysed by modern XRPD to better identify the involved phases in our ‘Pech mit Schwefel’ PhD project.
- Curly malachite: future occurences will be analysed by Raman microscopy, we’ll watch out for azurite.
- Spertiniite: Results were included in our review paper.
- Oddy Test: New tests in Stuttgart will be set up to troubleshoot our experimental setup and to clarify the influence of variations and its possible impact on results.
- Calcium acetate: We will synthesize the calcium acetate formate hydrate detected by the BM on marble and try to determine the crystal structure.

Details can be found in the following where information from BM lab reports collected during our visit are inserted in black in the appropriate text passages from our application (in red).

RCE: we could not only check laboratory reports (mainly by Pieter Hallebeek and Luc Megens) but also discuss research with colleagues Inneke Joosten, Bart Ankersmit, and Matthijs de Keijzer. As the conservation programme of the University of Amsterdam and the conservation labs of Rijksmuseum are hosted in the same building ('Ateliergebouw') we also had very fruitful exchange of ideas with Kate van Lokeren Campagne & Tony Beetjes (both UvA) and Robert van Langh, Isabelle Garachon, Sarah Creange, & Chiara Gamarra (all Rijksmuseum). This all will have impact on our work in Stuttgart:

- Glass-induced metal corrosion: we will analyse two further samples from Rijksmuseum.
- Curly malachite: future occurences will be described using the metrics proposed by the RCE. An exchange of findings has been agreed upon.
- Spertiniite: A joint programme for investigation of pigment samples in the RCE collection (Bremen blue and green, Kalkblauw) and replication of old recipes will be set up.
- Calcium acetate: We will try to determine the structure and formula of an unknown compound where Guus Verhaar found also nitrate and formate.
- Research strategy: As the example of NICAS with integration of humanities, science, and conservation in research design forms an impressive example for Germany, we will invite Robert van Langh to present the Dutch experience in Stuttgart.

1.2 Glass Induced Metal-corrosion on Museum Exhibits (GIMME)

Humidity can cause hydrolysis of historic glasses resulting in alkaline surface films. These take up carbon dioxide from the air (forming carbonate anions) and – if present – carbonyl pollutants (e.g. from wood or adhesives, forming formate or acetate). If metal is in contact to glass and oxygen around, these liquid films are ideal electrolytes to cause metal corrosion. This has only recently been noticed [2, 6] and studied systematically by us in the GIMME project 2012-2015.
Copper and its alloys (including historic silver) mainly form a sodium copper formate [3, 4, 8, 10], whose formula and crystal structure could now be determined by us from powder diffraction data [1]: $Cu_4Na_4O(HCOO)_8(OH)_2 \cdot 4H_2O$ (no acetate as proposed by Trentelman et al. 2002). Indeed, RCE most likely detected it on a Limoges enamel 'The judgement of Paris' of Rijksmuseum (BK-NM-7323) by XRD [2014-037_Megens]. This corrosion product was also found in the BM on a silver kantharos (GR 1962,1212.1) that contains very little copper (Wang 2007) and possibly on some Saqquara bronzes (Wang et al. 2009) and other objects (Robinet & Thickett 2005). In these cases, the sodium in the compound does not originate from glass hydrolysis but from the soil or conservation treatments. The second most frequent GIMME compound is a basic copper formate, $Cu_2(OH)_3HCOO$ [5, 7], which was also reported from a BM pair of Egyptian eyes EA 6895/6 (no glass present, Robinet & Thickett 2005; more details in [AR-2001-10]).
An unidentified (in 1996) copper corrosion product reported from an enamelled hat badge occurring together with sodium and lead formate [AR-1997-30; Debye Scherrer film c1883] could now clearly be identified by us as $Cu_2(OH)_3HCOO$.
Often, both products occur together as in the case of a Limoges painter's enamel from the Rijksmuseum Amsterdam (RMA-BK17210), jointly investigated by us (Raman) and the RCE (XRD). In fact, our evaluation of the just measured diffraction data [AR-2016-16] of green corrosion from a BM procession cross (Sienna, ca 1320) proved that both products occur together with at least one other hitherto unidentified phase. The procession cross is a classical GIMME case with metal corrosion occurring only in contact to enamel. A sample will be taken for Stuttgart with the aim to identify all

phases with high precision XRPD and Raman. Another sample (courtesy: Dora Thornton) will be taken from an enamel object from climatized storage with the same goal.

According to Raman analyses, other products contain carbonates, e.g. chalconatronite [11], and acetates, e.g. the sodium copper carbonate acetate reported (without glass context) from the BM by Thickett & Odlyha (2000; more details in [FR-1998-18]), Robinet & Thickett (2005), and Quanyu Wang et al. (2009). Lead corrosion (e.g. in mirrored glass balls) precipitates basic sodium lead carbonate [9]. Zinc (from brass) forms zinc formate dihydrate (10 cases, unpublished), a product hitherto only reported from the British Museum (Oddy 1993, Robinet & Thickett 2005). Other occurring zinc compounds are yet unidentified

BM reports confirm our impression that there are still a number of unidentified zinc corrosion phases. Zinc corrosion products could only be fully characterized in one case (AR-2007-79: gilt brass Buddha with mixed zinc sulphate phases). Zinc formate dihydrate occurred on a Swiss zinc token (AR-1995-53: together with simonkollite, and other not identified phases) and on metal mirrors on a dance necklace (AR-2002-15: with unidentified corrosion product). In two other reports no zinc formate was identified (AR-1997-9: white crystals on brass spur - simonkollite and unknown phase; AR-2000-16: Somali necklace with zinc plated copper and stable glass beads [FTIR: no gel layer] - white undetermined zinc corrosion product and blue copper acetate [?, in the vicinity (!) of glass]). Except the last unclear case, no glass was involved. The BM experience encourages us to actively search for brass and zinc cases in our just started project on glass-induced metal corrosion (funded by DBU). The RCE also found zinc formate on a printing plate [D2000-031_Hallebeek].

as are compounds in contact to potash glass containing potassium. –

[AR-2003-2] found a potassium copper carbonate formate but the diffraction data c2259 are different from the unknown potassium compound published by Scott (2002: 447). We found the latter compound on a gold ruby cup with silver mounting from the Green Vault Dresden (EDX-SEM: K, Cu; Raman: CO_3^{2-}, CH_3COO^-).

The prevalence of formates is most likely due to the alkaline pH which allows direct formation of formate from formaldehyde via the Cannizzarro reaction.

Interestingly, ion chromatographic analysis of glass ‘weeping’ [AR 2006-51; Bohemian glass; FR-2003-10; enamel and glass] already found formate as prevalent anion, not carbonate as is common wisdom in textbooks on glass corrosion. This confirms later research by Robinet (PhD) and current measurements by Verhaar and Tennent (2015, 2016). Guus Verhaar (UvA/Rijksmuseum) presented his updated results.

Until now, some 240 (!) corrosion cases in many types of combined metal/glass objects were documented during the GIMME project: mounted hollow glasses, enameled metals (e.g. from Limoges, Japanese cloisonné), glass gems in betzels, glass balls and beads on metal wires, Christmas tree ornaments, glass buttons, watches, glass framed miniatures and daguerreotypes, optical instruments and spectacles.

There is no doubt that this corrosion process also occurs in the Netherlands and the British Museum and some cases might have already been investigated. Indeed, PR00784 describes the removal of green corrosion from a 16th cent Limoges enamel triptych (in 1956, no analysis), PR01155 treatment of a Chinese cloisonné bowl. [AR-2008-49] investigated Bulgarian silver jewellery with glass (hatpin and ring).

To better understand the formation of the observed products, cases were no glass was present (alkaline pH and/or sodium from other sources) are also highly interesting for us. We expect a number of relevant observations.

Sodium copper formate was identified:

[AR-2007-61] blue corrosion on a silver head vase,
[AR-1996-35] most likely also on a Nimrud copper alloy roundel and knob
[AR-2009-44] Ganesa metal figure, together with chalconatronite
RCE [D1999-09 Ankersmit] found copper acetate and formate and lead formate on objects from Scheepvart Museum Amsterdam due to the use of an unsuited paint for the display case. A similar find was made on African bronzes [A1992-192_Hallebeek]

1.3 Other Corrosion Processes

Besides Glass/Metal corrosion, other decay phenomena (1.3.1-1.3.6) shall be studied as well.

1.3.1 ‘Black Spots’

Brinch Madsen (1977) was the first to report black spots of copper sulphide on bronze finds in a number of museums and thought of a microbiological attack. Oddy and Meeks (1982) showed that their formation can be explained chemically with no need for microorganisms. In “black spots” or “brown fuzzies”, Eggert, Weichert, et al. (2004) found different copper sulphide phases, but also sulphates and amorphous phases on all kind of copper containing materials: metal alloys, minerals, corrosion products, pigments etc. Rarely, the sulphur sources in the environment (wool, rubber, sulphur containing cements or modelling clays, finds from anaerobic sites…) could be identified.

Research Questions:

What phases were detected in the RCE and the BM? On which materials? Sulphur source?
The BM has executed a number of analytical studies with very interesting details. Additionally to copper sulphides (covellite, chalcocite, digenite, djurleite, geerite, and possibly spionkopite [LR-1996-16] and yarrowite [AR-1997-44]), they also found amorphous phases [LR-1996-16, AR-1992-68] and sulphates [AR-2007-58]. As sulphur sources, objects from anaerobic site (black spots on ceramics [AR-1994-37; LR-1992-14]), velvet [AR-2007-58], a stone base containing pyrite [AR-1996-5] and possibly tortoiseshell [AR-1992-19] were identified. The appearance of the spots resembled cauliflower [AR-1992-68; AR-1992-19] or broccoli [AR-2007-58] or was described as soot-like [LR-1992-8; LR-1981-II-20]. Spots are not always black, but can look yellow-brown [AR-1992-68] or brown [LR-1982-II57] with less sulphur than black ones [LR-1996-16].
These findings confirm our own observations and publications (Metal 2004) with some new important details (e.g. pyritic stone, tortoiseshell, geerite, spionkopite).
The RCE report has no analytical reports.

1.3.2 Curly Malachite

As a natural phenomenon, sometimes malachite in the form of microscopic curls develops on copper alloy finds (e.g. tin bronze, brass, historic silver) from all periods. It has nothing to do with hair or textile fibres. Cases have also been observed in the Netherlands.

Research Questions:

Has this also been observed and analysed in the British Museum? Further observations in the Netherlands? Any hints to the (unknown) necessary conditions for their formation?

One case [AR-2001-18] was observed called ‘filamentous malachite’. From the image [AR-2001-18a, see left] and the description (200x: ‘bundles of fibres’) it is clear that they are identical. Important details for us:

- Curls were first thought to be nematode worms.
- µ-Raman spectroscopy worked well for identification.
- Azurite is occurring not only as accompanying mineral lumps (known from heritage and mineral literature) but also as fibres (!). This new fact needs further study.

© BM AR-2001-18a

RCE arranged a meeting with Janneke Nienhuis for whom curly malachite is a topic in her PhD. She shared a manuscript where she investigated curls from 5 sites and proposed a standardized metric description for them. We discussed to add a measure for curvature (variable in ’clock spring’ spirals) and steepness (as in ‘corkscrew’ spirals). We reported on (unpublished) unsuccessful Stuttgart experiments to grow curls from ammoniacal malachite solutions in porous vessels (often used in crystallography for needle crystals). Proposal: More diluted solutions in glass filters with definite pore size.

1.3.3 Corrosion by Conservation: Spertiniite

Spertiniite, Copper(II)hydroxide $Cu(OH)_2$, forms only when copper containing materials are exposed to caustic solutions and no sufficient amount of other anions or its precursors (e.g., carbon or sulphur dioxide) is present. A classical brass centerpiece from Ludwigsburg castle showed it in a gap with limited access to air with carbon dioxide. Tests proved that common cleaning of brass with ammonia may result in spertiniite formation, the dark blue copper tetraamine complex decomposes on evaporation (Schmutzler et al forthc.).

Research Questions:

Has spertiniite ever been observed in the RCE or the BM? On which materials? After which treatments?

Spertiniite was detected once on a 1st cent. AD bronze bull [AR-1999-15], which later [AR-2006-17] also developed chalconatronite (from sesquicarbonate treatment?). Ammonium could be extracted from the surface with a paper poultice, therefore a cleaning treatment with an ammonium compound was assumed. As agreed by Quanyu Wang, we included this in the proofs of a review article (Schmutzler et al., Copper hydroxide on Artefacts, already published online first at Studies in Conservation, DOI: 10.1186/s40494-016-0092-3) acknowledging the British Museum and IPERION CH.

RCE detected copper hydroxide together with malachite on a bronze mirror [D2000-031 Hallebeek] of Tropenmuseum (MAK 1293) and below and above gold leaf of a Roman bronze laurel wreath

[D1977-019_Moll&Hallebeek] from Allard Pierson Museum (Z81). This adds two reports to the lists of this rarely reported corrosion product.
Besides corrosion, copper hydroxide can occur also in pigments (e.g., Bremen blue and green, Lime blue) and RCE has some samples (which are very rare!) in its reference collection. Only one RCE sample of Bremen blue was analysed so far (XRD), a mixture of copper hydroxide and blue verditer. The only published analysis in the whole literature so far is from a sample in the Stuttgart collection just published in our review. Therefore, we agreed upon a joint analytical programme of the RCE specimen. Stuttgart will also collect recipes for pigment production and will try to replicate them. Often mixtures of compounds might be formed which will give a clue to their production.

1.3.4 Metal Corrosion on Oddy Test Coupons Exposed to Cellulose Nitrate

Recently, we established in replicated test series with controls that cellulose nitrate products used in conservation (including HMG) cause severe corrosion on all Oddy test coupons of copper, lead, and silver (Ziegler et al. 2014, Fig. 4). In opposite to that, the actual list of materials tested in the British Museum (2015) has HMG as safe to use permanently. This needs further clarification.

Research Questions:
Are the BM tests replicable in a joint test? Did any corrosion occur in the BM tests, which products?

The coupons in the BM indeed showed no corrosion. This also holds true for a currently running replication test. Capucine Korenberg provided us with a sample of the adhesive film she tested and the adhesive itself. In discussions, slight differences in running the test were noted. The BM tests after 3 d drying, we use 1 month or more because fear of solvent retention. We tested blocks of adhesive cast in a mould, the BM uses films on mylar. Our metals are 99.99%, not 99%. It is hard to believe that such differences can cause a drastic change in results but we will look into that with new replication tests in Stuttgart.
Relevant to BM only.

1.3.5 Magnesium Phosphates on Ivory

Ivory from elephant or mammoth tusks contains more magnesium (ca 4% w/w !) than any other bone or teeth. In contact with humidity Mg is more easily extracted than Ca, on drying various Mg-phosphates (struvite, newberyite, bobierrite,…) form crystalline precipitates.

Research Questions:
Has this also been observed in the RCE or the BM? Which phase(s)? Any connection with bleaching treatments or (humid) storage conditions?

A mediaeval ivory comb showed white crystals identified as newberyite [AR-2008-51], but there is no hint to former storage conditions or any bleaching treatment.

RCE has no reports on ivory investigations.

1.3.6 Acetate Deposits on Calcareous Objects

Salt contaminated calcareous objects (e.g. snails, shells, corals, limestone, calcium carbonate deposits on ceramics or other finds) develop acetate containing crystals (often in needle shape) when stored e.g. in oak cabinets. Already in the 1920s, Alexander Scott (1926) illustrated a case from the British Museum. Calcium acetate phases with known structure are calclacite ($Ca(CH_3COO)Cl$) and thecotrichite. The crystal structure of the latter could recently be determined by us from powder (!) data (Wahlberg et al. 2015) and the formula corrected to $Ca_3(CH_3COO)_3Cl(NO_3)_2{\cdot}6H_2O$. The structure of other occurring compounds like calcium acetate formates (Tennent and Baird 1985) is unknown. They are hard to identify as reference datasets are missing in the Powder Diffraction File (PDF).

Research Questions:

Have Ca-phases unknown at the time of measurement been found in the RCE or the British Museum by Debye-Scherrer diffraction? Do data match with phases determined in the meantime?

Thecotrichite was found on Greek and Roman ceramics [AR-2006-77], two mediaeval tiles [AR-2006-83], and cuneiform tablets [FR-2003-23]. Calcium acetate formate hydrate occured on a marble relief [AR-1995-41] and on samples from Greek and Roman ceramics. Hitherto, this phase was never described on artefacts, but only on mollusca. As Tennent and Baird (1985) described a synthesis, we will use this in an attempt to determine the crystal structure and confirm the formula in our “In Search of Structure”-project (partner: R. Dinnebier, MPI for Solid State Research) funded by DFG and starting in 1/2017.
An unknown (!) phase (ion chromatography: calcium chloride nitrate **formate**) occurred on an Egyptian limestone fish mould [AR-1995-50]. We will use the Debye-Scherrer diffraction data as reference in our investigation (XRD, Raman) of calcium efflorescence on calcium carbonate heritage objects from the Natural History Museum Stuttgart (eggs, shell, etc.), the Landesmuseum Württemberg (tiles), the Allard Pierson Museum Amsterdam (Greek Ceramics) and the Rijksmuseum Leiden (Greek ceramics). In case a pure sample can be obtained, crystal structure and, including, the chemical formula determination are possible, even from powders.
Despite the long standing cooperation with the principal researcher Norman Tennent , RCE had no reports in its files but Kate van Lookeren (glass & ceramics lecturer at UvA) informed about needle crystals on objects currently in treatment). Guus Verhaar (UvA/Rijksmuseum) investigated an unknown Stuttgart sample with ion chromatography and found formate(!) and nitrate besides acetate, no chloride. We will try to determine now its cyrystal stucture and formula from the existing powder diffraction data.

Other corrosion

An interesting report [D1976-005_Hallebeek] found golden looking chalcopyrite on a Late Roman bronze and mentioned patination or corrosion as possible explanation. Oddy (BM) 1981 published a similar case as patination [‘pseudo-gilding’) citing recipes in the Leiden Papyrus X and Mappae Clavicula. We argued for corrosion (ICOM-CC Rio 2002). The report identifies another object with such a layer.

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