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'Copper and Bronze in Art' and the search for rare corrosion products

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Abstract

Information taken from David A. Scott's book "Copper and Bronze in Art" was crucial for research on copper corrosion products in Stuttgart. Examples discussed are

- the nature and variability of 'Black Spots' (aka 'Brown Fuzzies'),
- cupric hydroxide by cleaning, patination, and pigment synthesis,
- the wondrous phenomenon of curly malachite,
- chalconatronite formed by contact to soda glass,
- the formation of copper formates by glass-induced metal corrosion,
- and synthesis and X-ray diffraction of basic copper acetates ('verdigris').

Keywords

basic copper(II) formate, 'Black Spots', chalconatronite, copper(II) hydroxide, copper sulfide, curly malachite, namuwite, sodium copper(II) formate, verdigris

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Introduction

"The book is a mine of information" commented the British Museum's Keeper of Conservation, William Andrew Oddy (2002), in his review of David A. Scott's highly prized and praised work 'Copper and Bronze in Art: Corrosion, Colorants, Conservation' (in the following referred to as SCOTT). One can rarely find a book which so deeply fulfills both the need of students new to the field for a comprehensible introduction and of researchers to identify the frontiers of knowledge. And there is also an extra hidden in the text and the appendix: Hitherto unpublished data of original research.

No wonder, whenever I encountered unusual copper corrosion, the first thing to do was looking up what David reports. Black Spots on Bronzes? I learned that they might also be brown and contain sulfates. Copper hydroxide in brass patina? Yes, that must be rare. Malachite curls on an Alamannic fibula? David had already investigated curls on Roman bronze figures. Chalconatronite? There are various sources for the sodium it contains. Unmatched diffraction data? SCOTT's Appendix D is full of them for comparison, including his intensive work on verdigris.

This review of two decades of copper corrosion research at the Stuttgart State Academy of Art and Design (ABK) reports how this book worked as fruitful starting point for the author's and his co-workers own investigations and their outcome.[1]

Black Spots, Brown Fuzzies

"A spectre is haunting Europe". This was the impression when conservators first heard from Helge Brinch Madsen at the ADR conference in Schleswig 1976 (Brinch Madsen 1978) and the SSCR conference in Edinburgh 1979 (Brinch Madsen and Hjelm-Hansen 1979) about 'Blacks Spots on Bronzes' identified in European museums (Fig. 1). As the spots looked like black mould (while containing copper sulfide) and a copper tolerant *cladosporium* fungus was detectable Brinch Madsen discussed a 'microbiological attack'. "The impression was clearly given that there is an epidemic of 'black spot disease' sweeping through European museums" (Oddy and Meeks 1982). Colleagues went home, took a closer look at their collections - and found them themselves! Some conservators were even fearing that they might spread the 'infection' from case to case. A kind of a scientific *déjà vu* experience: a *cladosporium* species had already been thought to be the cause for bronze 'disease' as early as 1893 (SCOTT 126), recommended 'therapy': sterilisation at 120 °C.!

It needed Oddy and Meeks (1982) to exorcise the revenant spectre by showing that the formation of copper sulfides can be explained with chemistry alone.

At about the same time, the New World developed another term (SCOTT 232): 'Brown Fuzzies', then unknown in Europe. Such 'fuzzies' were (first?) mentioned in writing by Tom Chase as 'brown-to-black mossy-looking substance which forms on some bronzes in the Walters Collection (the renowned Walters Brown Fuzzies)' (Brown et al 1977: 228/9). They occurred together with silver sulfide whiskers, rubber mats were seen as the source of volatile sulfur. Rarely, the necessary reduced sulfur sources emitting e. g. hydrogen or carbonyl sulfide for the occurrence of 'Black Spots' were identified at all, rubber, wool, and objects from anaerobic sites being the main culprits (Eggert

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[1] An updated version of this contribution will be submitted to the Festschrift David A. Scott (*Materiality of Metals, Pigments and Dyes*, L. Dodd and I. Kakoulli (eds.), Cotsen Institute of Archaeology Press, LA, in preparation).

et al 2004). Elemental sulfur can also cause ‘Black Spots’ as Eggert and Sobottka-Braun (1999) demonstrated when discussing a bronze nail from the Mahdia shipwreck. They speculated on the presence of elemental sulfur in sea-logged wood; shortly after that more than a tonne was discovered in the *Vasa* timbers (Sandström et al 2002). Another (unexpected) material sometimes containing elemental sulfur as ingredient and causing ‘Black Spots’ is plasticine (Eggert 2006, see also SCOTT 396, note 2).

SCOTT (232/3) described problems with diffraction because of the poor crystallinity of samples. Some spots are indeed amorphous (Lee 1996, Eggert et al 2004) and, therefore, hard to characterise. SCOTT (233) analysed samples from brass mounts, clocks, and other items in the Wallace Collection in London. He could not match them with any known copper sulfide although a number of copper sulfides of stoichiometries ranging from covellite (CuS) to chalcocite (Cu_2S) have been identified on objects. But his compound contained zinc and was identified instead as the sulfate namuwite, $(Zn,Cu)_4SO_4(OH)_6{\cdot}4H_2O$, a zinc substituted brochantite (SCOTT 445). Following this lead, Eggert et al (2004) also reported the sulfates chalcanthite, brochantite, and schulenbergite ($(Cu,Zn)_7(SO_4)_2(OH)_{10}{\cdot}3H_2O$, on brass) in connection with ‘Black Spots’. As sulfides (S^{2-}) are known to get oxidised in humid air to their thermodynamic stable state (sulfate, SO_4^{2-}), the occurrence of sulfates on heritage objects must not always be related to air pollution by sulfur dioxide (SO_2), the usual explanation for sulfates (e.g., brochantite) which had been adopted by Seeley also for namuwite (SCOTT 234).

Observations on samples from Weichert´ et al (2004) ten years later and new results from laboratory experiments by Charlotte Kuhn-Wawrzinek (2020) show that 'Black Spots' on copper objects are indeed not stable, especially when exposed to a high RH. She was able to synthesise different types of corrosion (‘Trees, bunches, cauliflower’: Weichert et al 2004) ranging from typical ‘Blacks Spots’ to ’Brown Fuzzies’ in reproducible experiments for the first time. Copper sulfides can undergo further reactions and hereby cause damage to the metal surface of the object when covellite is involved. Kuhn-Wawrzinek’s (2020) experiments could not prove a corrosive effect of copper sulfides to copper without direct contact. However, there are hints from mineralogical collections (Waller et al 2000) where the degradation of disulfide minerals resulted in increased levels of sulfurous gases and hereby caused the corrosion of copper (and other metals). 'Black Spots' should therefore be removed from objects for long term conservation. Until then, the storage at low RH can decelerate ongoing reactions.

However, in most cases only small amounts of the 'Black Spot' corrosion products can be observed on objects and the immediate challenge is to find and remove the original source of sulfur when 'Black Spots' are discovered in a collection.

Fig. 1: 'Black Spots' and 'Brown Fuzzies' in the eye of a classical Zeus figure, photo: C. Kuhn-Wawrzinek, ABK

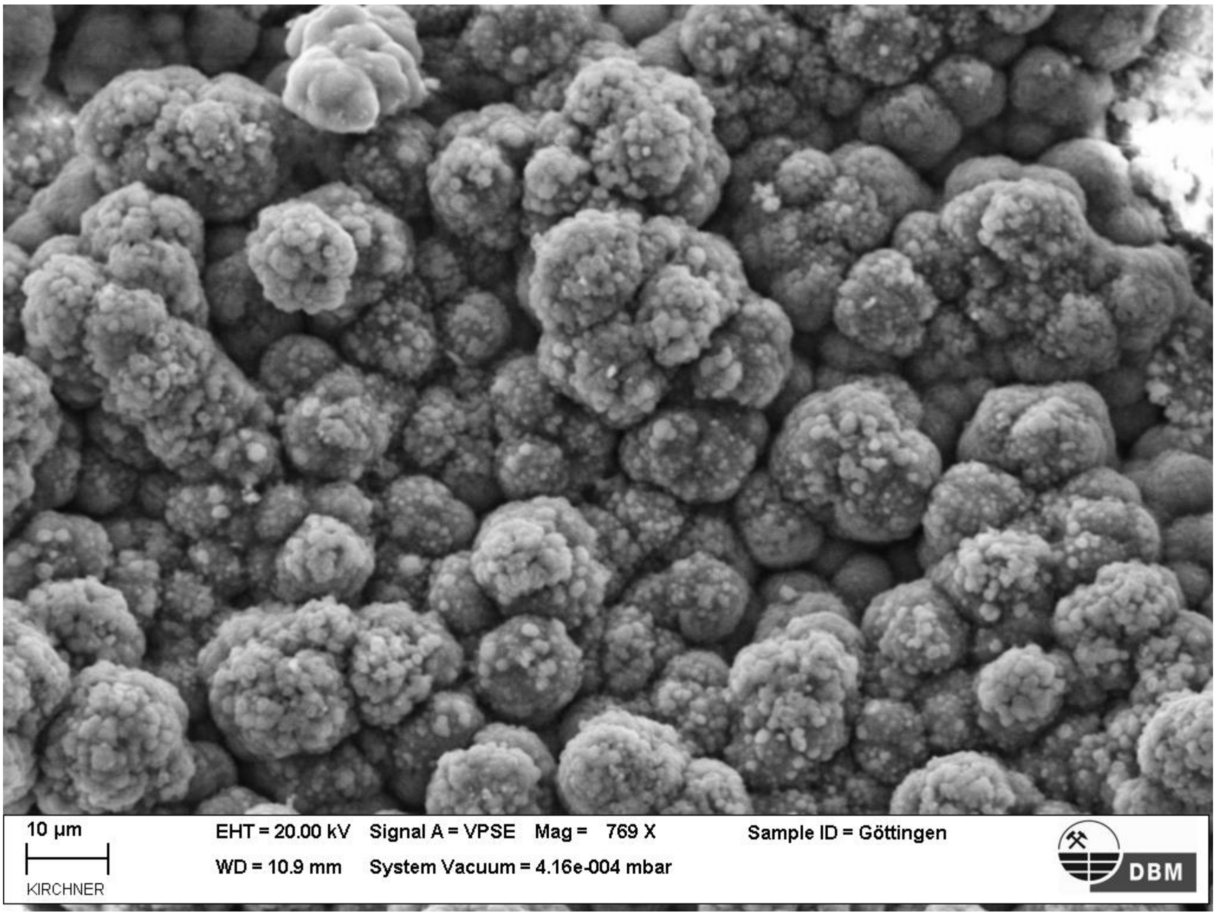

Fig. 2: 'Cauliflower' type of 'Black Spots' as seen in the FE-SEM, photo: D. Kirchner, DBM

Cupric Hydroxide: Corrosion, Colourant, Conservation

Copper(II) hydroxide has rarely been reported as mineral (spertiniite) and in conservation science as the very short reviews in the book (just six sentences, SCOTT: 98) and the preceding article (Scott 1997) prove. The more surprised we were when detecting it by X-ray powder diffraction (XRPD) in a blue patina on a classical French centrepiece (c. 1800 AD) made of brass with a polished surface. The patina was hidden in gaps, only recovered during demounting (Fig. 3, Schmutzler et al 2017).

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Fig. 3: Blue cupric hydroxide under the base of a brass column, photo: L. Albrecht, ABK

Fig. 4: Brass test sheets after 46 d with a drop of ammonia between them, photo: B. Schmutzler, ABK

But can this be intentional patination, inside only on an invisible spot? The formation of $Cu(OH)_2$ needs an alkaline medium - and there is a volatile base traditionally used for the household cleaning of brass: ammonia. Ammonia is corrosive to copper alloys, long time exposure dissolves a considerable amount of Cu^{2+} as the well-known dark blue $Cu[NH_3]_4^{2+}$ complex. But when ammonia evaporates on drying this complex decomposes again and leaves a residue of $Cu(OH)_2$. Since evaporation proceeds quickly there is not enough time to form visible amounts of copper salts on the outside of the cleaned surface by atmospheric corrosion on cleaning. However, ammonia trapped in gaps has enough time to corrode the alloy The result is (amongst some Zn compounds) $Cu(OH)_2$, as yielded by a demonstration experiment with a drop of ammonia between two brass sheets (Fig. 4). SCOTT emphasises the double role of many compounds as both pigment and corrosion product. But even he missed the role of the duck-egg blue copper hydroxide in patination when objects are intentionally exposed to fumes of ammonia (for recipes, see Hughes and Rowe 1991). And there is also a rare pigment which many (but not all) colour chemists since the 19th cent. identify as copper(II) hydroxide: Bremen blue (Schmutzler et al 2017: 65f.). It was not directly precipitated from copper(II) solutions (which yields an unstable compound), but formed indirectly by 'blueing' solid green basic copper(II) salts (sulfate, chloride, nitrate) with caustic solutions. Nevertheless, first measurements came as a surprise: The sample in the historic collection of the Stuttgart Institute of Painting Technology consisted mainly of permanent white ($BaSO_4$). Raman microscopy gave evidence for an organic dye, possibly copper phtalocyanine; SCOTT 315). $BaSO_4$ was already reported from a copper-free Bremen blue sample (no. 136) from Vienna (Hochleitner et al 2003: Fig. 3-5). Apparently, the term Bremen blue was not only used as label for a kind of material, but also for imitations with a similar colour. More analyses of samples and source texts of the 19th century are needed.

A Wonder: Curly Malachite

On search for traces of organic remains, microscopic inspection of metal finds has become routine in the last decades. And the more you look, the more you see. In 2001, bundles of curved green fibres ('curls') on an Alamannic bronze fibula were detected at the ABK (Eggert 2007). Till then, this phenomenon has only been mentioned before on Roman bronzes by Scott (1994, Fig. 8; SCOTT: 106, Plate 21) as a form of malachite, not to be mistaken as textile. But what do they tell us?

Fig. 5: Malachite curls on a Frankish brass fragment, image width: 6 mm, photo: A. Stäbler, ABK

We could confirm the identification as malachite by qualitative spot tests, XRPD, and Fourier Transform Infrared Spectroscopy (FTIR). Curls seem to contain a little zinc (mostly close to the detection limit). They occurred on brass, bronze, and copper-containing silver alloys objects and there are reports from Bronze Age finds. While most curls formed only part of a circle (radius some tenth of a mm), some looked like a corkscrew (helix), others like a clock spring under the microscope. In the electron microscope, no structure of any organic material, to be expected for negative or positive casts of them in corrosion products ('pseudomorphs'), could be detected. A Field Emission-Scanning Electron Microscope (FE-SEM) image (Fig. 6) of a curl cross section shows that the individual fibres of sub-µm diameter are polygonal, as to be expected with minerals. An intensive search in the mineralogical literature brought some curl reports from mines to light, excluding any human involvement in their growth (Eggert 2007). Giving no clue to Ages or alloys, even to human involvement at all, therefore, malachite curls are somewhat disappointing as historic information source.

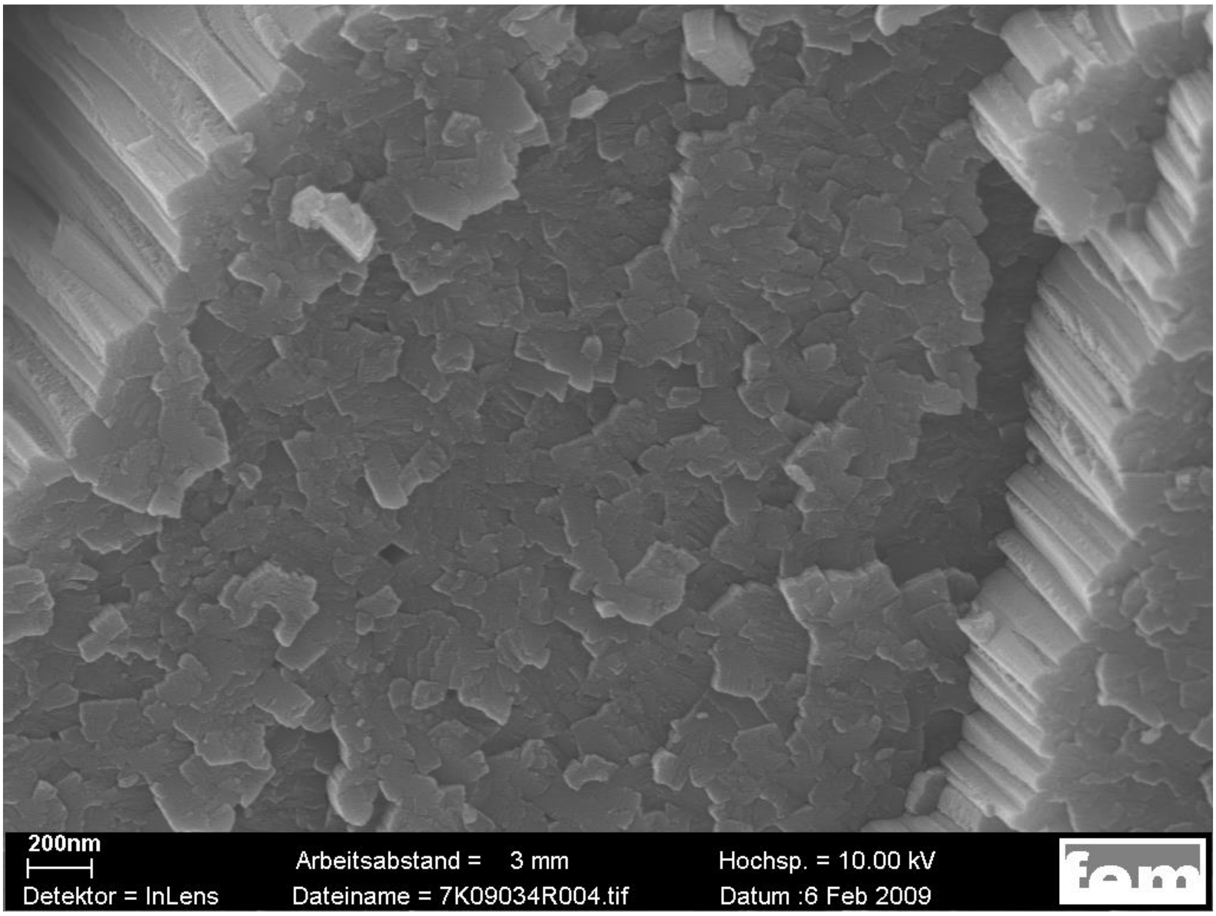

Fig. 6: FE-SEM image of a cross section of a curl illustrating the polygonal shape of individual fibres, photo: R. Bretzler, fem Schwäbisch Gmünd

But they are a beautiful wonder of nature. A recent Dutch publication (Nienhuis et al 2016), while reporting further examples and proposing a scheme for their metric characterisation, could not solve the enigma of their growth either. Interestingly, visually quite similar curls formed by fibre bundles of barium sulfate have been grown in the laboratory. Here nanoparticles diffuse in viscous solution without sedimentation and form aggregates by fusion of high-energetic crystal planes (Wang et al 2006). This might imply a growth form independent of the specific material. Indeed, needle or curly crystals can be grown from solutions in porous terracotta sherds from quite a number of salts. Curled growth seems to be preferred by fast evaporation (Borchardt-Ott and Kleber 1959). For similar experiments with malachite one has to find a solvent which readily dissolves it and leaves no traces on evaporation. And there is one: aqueous ammonia. As we have seen in the section on cupric hydroxide, the $Cu[NH_3]_4^{2+}$ complex decomposes on evaporation and all NH_3 is set free. Therefore, solutions of malachite in ammonia in varying concentrations were filled inside porous terracotta pots which then were covered with an airtight lid. Within days, green efflorescences occurred on the outside of the pot, but, unfortunately, no conditions could hitherto be found to produce curls until now[2]. And as long as there is no way to produce malachite curls in the lab, their occurrence on objects proves long time natural corrosion, i.e. their authenticity. So, at last, this is an information of cultural significance which can be drawn from the occurrence of curls.

Once again, the curls proved the common wisdom: You only recognise what you know. After Stuttgart students were told about the phenomenon 3 out of 8 detected them in block-lifted objects from Alamannic graves. Scott (1994) was definitely right to assume that they are 'probably seen more often by conservators than the literature would suggest'. Therefore, they do not necessarily prove that objects without context belong together.

Rare copper carbonates

There is more to copper(II) carbonates in heritage science than malachite or azurite. SCOTT (117-120) devotes a whole section to chalconatronite, $Na_2[Cu(CO_3)_2]\cdot 3H_2O$, which occurs as a corrosion product on copper alloys in contact with sodium carbonate solutions. It was first identified by Gettens and Frondel (1955) on Egyptian bronzes from soda rich soil. The formation as a secondary product on museum objects is often caused by residues of a sodium sesquicarbonate buffer solution, used for the treatment of bronze disease (Horie and Vint 1982, Pollard et al 1990). Indeed, synthetic chalconatronite can be precipitated by dropping a copper(II) solution into such a carbonate buffer (Gröger 1901).

SCOTT (119) also reports the rare occurrence as a pigment on a 16th cent. manuscript and in Maya wall paintings. His comment: "This finding is intriguing: further research into the etiology of these salts is needed to determine if they are original pigments or alteration products." Indeed, sodium carbonate occurs in migrating salt solutions in wall plasters: possibly the reason, why Bellendorf (2007) detected chalconatronite on 15th to 18th century burial plates cast from quaternary copper alloys (Cu/Zn/Sn/Pb) mounted on the wall of Franconian chapels. - Keeping an open eye for historic recipes for pigment production, SCOTT (118) yielded a mixture containing chalconatronite in his replication experiment of a historic Chinese pigment recipe by adding a sodium salt mixture (including carbonate) to a copper(II) solution prepared from cuprite and alum.

In Stuttgart, we found another sodium and carbonate source for the formation of chalconatronite: corroding soda glass in contact to copper alloys (Fischer et al 2020). The alkaline surface films formed on glass during hydrolysis also contain these ions, as they absorb carbon dioxide from the air. In our research on **g**lass **i**nduced **m**etal-corrosion on **m**useum **e**xhibits (GIMME) in ca 5% of all cases investigated chalconatronite could be detected by Raman microscopy. Objects include baroque reliquaries with set glass gems, enamel on metal (16th century and a modern replica of intentionally

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[2] The competition is still open, give it a try.

unstable composition), Christmas tree glass baubles with wires, glass buttons with metal shanks, a glass figure with a wire support, and miners' lamps (Fig. 7; Fischer et al 2020).

Fig. 7: Corrosion on a nickel silver reflector (p-RFA: ca 60% Cu, 24% Zn, 13% Ni) of a miner's lamp in contact with glass: chalconatronite and a basic zinc copper formate (see below), photo: A. Schorpp, ABK

Despite being a resourceful collector of compounds, SCOTT missed (and from hindsight, rightfully) an arcane basic sodium copper(II) carbonate: $Na_3[Cu_2(CO_3)_3(OH)]\cdot 4H_2O$ (ICDD 00-28-1084) was listed – without any further information – as a corrosion product identified by powder diffraction (Barger and White 1991: 167) on a cover glass of a daguerréotype (photosensitised silver layer on copper). By synthesis experiments and evaluation of XRPD peak lists and FTIR spectra, we could prove (Eggert et al 2016) that the postulated compound (Sengupta and Nandi 1974) is nothing other than also chalconatronite; consequently, ICDD now deleted this chart. Therefore, the listing by Barger and White can now be taken as another proof for chalconatronite on another group of combined glass/metal objects.

One reason for the misidentification is the limited quality of the XRPD reference for chalconatronite (ICDD 00-22-1458) taken from a Guinier film in 1969 and still in use for modern studies of heritage corrosion products (e.g., SCOTT: 424, 446). In opposite to modern diffractograms, angle measurements are not precise and stopped at $2\Theta = 51°$, intensities are only estimated visually. To analyse complex mixtures, it should nowadays better be replaced by high quality data derived from the crystal structure, e.g., ICDD 01-71-1490 (Eggert et al 2016: Table 1) covering a larger range with truly quantitative values for intensities. Such a re-evaluation could possibly solve the riddle of chalconatronite reported as a minor component together with quartz, atacamite, and cuprite in the outer concretion of the Riace Warrior A recovered from the sea off Calabria (SCOTT 120 & 328; Formigli 1985: 169). Because of its high solubility chalconatronite cannot form in seawater. This might, therefore, indicate some kind of treatment of the bronze after salvage before it entered the conservation labs in Florence in 1975 as SCOTT (328) suggests. But given the limited resolution in angle and intensities of earlier powder diffraction instruments and the quality of the JCPDS reference card at the time of measurement one would recommend re-analysis of the old sample with modern instrumentation to confirm its pre- or absence in a complex mixture.

Another copper carbonate alteration product, sodium copper(II) acetate carbonate, $NaCu(CH_3COO)CO_3$ was detected by SCOTT (302) in samples from the Burrell collection. Thickett and Odlyha (2000) first described and detected it on 184 Egyptian artefacts in the British museum stored in oak cupboards emitting significant amounts of acetic acid. Paterakis (2010) showed by desiccator experiments that it can form from chalconatronite exposed to acetic acid vapours. Storage of chalconatronite (as corrosion product on combined glass/metal objects) in oak cupboards might, therefore, be the explanation for our few encounters of this compound in the GIMME survey (Fischer 2016: 111-113).

There is another compound which has a nearly identical Raman spectrum (so contains both acetate and carbonate). Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX) showed that potassium and copper are the only heavier elements present (no sodium). It was detected by us on the silver mounting of a gold ruby glass (known to be produced from potash glass) of the Dresden Green Vault (Fig. 8; Eggert and Fischer 2012).

Fig. 8: Unknown Potassium-copper compound at the gilded silver mounting of a gold ruby glass cup (Green Vault IV 227), photo: R. Richter, Green Vault Dresden

Original diffraction data published by SCOTT (447) proved its identity with his sample from a brass chandelier (Kelvingrove A 1960.28 bf, not A6082 BF as published) containing K, Cu, C, and O (Environmental SEM). SCOTT (301) even was able to isolate single crystals, but unfortunately their measurement got lost during the accidental flooding of crystallographer Kenneth Hardcastle's lab (email to the author by Hardcastle). Therefore, the crystal structure stays hitherto unknown. With our additional information from the Raman spectrum ($KCu(CH_3COO)CO_3$?) synthesis of this compound and the determination of the crystal structure might be possible. Single crystals are no longer a mandatory prerequisite for this (see below).

By the way, SCOTT (302) did mention another pale blue compound detected by Thickett and Odlyha (2000) whose diffraction pattern matched with ICDD 31-453 given as "copper chloride acetate" with $C_2H_2ClCuO_2$ as sum formula. SCOTT (302, 316 note 28) noticed that copper(II) acetate chloride should have one more hydrogen: $Cu(CH_3COO)Cl$. Consulting the ICDD reference literature (Hardt and Weber 1978) now showed that the error is not with the formula, but with the name: correct is copper(I) chloroacetate, the covalently bound chlorine replaces a hydrogen atom in the acetate anion. ICDD now corrected its error (email to the author, Nov. 2nd, 2016). Although the match of the diffraction data looks quite good (Thickett and Odlyha 2000: Table I) and no alternative match could be found in ICDD in Nov. 2016 there is no reasonable explanation how such a compound could form on a bronze.

There is absolutely no evidence and no rationale for the use of chloroacetic acid, a laboratory chemical not occurring in nature, by metal conservators. But if it's not $Cu(I)(CH_2ClCOO)$, there must be another hitherto unknown compound with a very similar diffraction pattern. The search for rare copper corrosion products in heritage science is not finished yet.

The Formation of Copper(II) Formates

Routine business: A green corrosion product (spot test for Cu positive) was detected during conservation on a 17th century limewood box of board games between turquoise enamel and silver (ca 5.5% Cu), but its diffraction data (Debye-Scherrer camera; Eggert et al 2008: Table I) could not be matched with anything in the Powder Diffraction File (PDF). A search in SCOTT's Appendix D could not find a match as judged by the three strongest peaks in the tables either. A year later, another object, the same corrosion product: a wire spiral on a Chinese theatre hat showed corrosion where it was in contact with an apparently unstable glass bead showing iridescence and crizzling. Another search in SCOTT's tables: When neglecting Scott's third strongest peak at d= 6.76 Å there was a very good match with an unidentified sample from the Fitzwilliam Museum discussed in the organic salts chapter (SCOTT: 301, 446). This led us to Trentelman et al (one of the co-authors being Scott) paper on "a new pale blue corrosion product" (2002) detected mainly on archaeological bronze finds. According to their XPS and Raman data it is a mixed **so**dium **co**pper (1:1) **form**ate **ac**etate, therefore, I coined the abbreviation 'socoformacite' (Eggert et al 2008). As the formate:acetate ratio was estimated by the authors between 1:2 and 2:1, the general formula might be given as $NaCu(HCOO)_{1+X}(CH_3COO)_{2-X}$, with $0 \le X \le 1$. With sodium from the glass and copper from the alloy, this was the first time that we understood that there are joint glass/metal corrosion products and our research on glass-induced metal corrosion started. Other than expected, carbonates are rare as corrosion products and formates dominate (Fischer et al 2018). This corresponds with analyses of the salts present in films on glass (Verhaar et al 2016) as the ubiquitous formaldehyde can react directly in alkaline medium to formate via the Cannizzarro reaction, which is trapped in the liquid.

Fig. 9: Glass figure with internal copper wire, sodium copper formate efflorescence out of a fracture in the arm (KHM Vienna KK4144), photo: W. Bernhard, ABK

In 50 % of the more than 250 GIMME cases 'socoformacite' was detected (Fischer et al 2018), but we were unable to synthesise the compound from solutions with varying Cu^{2+}:Na^{+} and acetate:formate ratios (Eggert et al 2008). In our Raman spectra, the peak at ca 940 cm^{-1} for the highly Raman active symmetric C-C stretch in the acetate anion was surprisingly small, variable, and even sometimes missing. Therefore, we started to doubt the necessary presence of acetate at all. As the formation of chalconatronite is proven for bronze finds and GIMME (see above), a synthetic sample was stored in a desiccator with formaldehyde/formic acid-rich atmosphere (ca 200 ppm each, no acetic acid or acetaldehyde, 75% relative humidity) for a period of ~six months. The idea derived from SCOTT (446): his unmatched peak at ca 6.76 could very well be explained as a residue of some unchanged chalconatronite (strongest peak at 6.9). Indeed, we obtained 'socoformacite' together with sodium formate. There were two lessons to be learned: firstly, the product can be produced acetate free, and, secondly, don't coin a compound name before you are absolutely sure of its composition.

All our samples (> 100) were finely grained, never was a single crystal at sight under the stereomicroscope. No chance to determine the crystal structure and with it the overall formula of the compound? Robert E. Dinnebier from the Max Planck Institute of Solid State Research Stuttgart took up the challenge, and succeeded to determine the structure from high precision X-ray powder diffraction (XRPD) measurements alone by applying sophisticated methods of structure evaluation yielding a sodium copper(II) formate with $Cu_4Na_4O(HCOO)_8(OH)_2 \cdot 4H_2O$ as formula (Dinnebier et al 2015). Indeed, no acetate appears in the structure. The powder diffraction data derived from the structure fit extremely well with Trentelman et al's measurement (2002: Table I) proving the identity of the compounds. By the way, the formula does not exclude that real samples might be contaminated with acetate (e.g., absorbed on the surface of crystallites) as we could detect acetate by ion exclusion chromatography as well (Fischer et al 2018).

And this was not the only unknown copper formate identified because of SCOTT's diffraction tables. At the border between enamel and copper on a small copper fitting (Ø 6.3 cm) in quatrefoil form with *émail champlevé* depicting a kneeling angel (MAK Frankfurt inv. no. 6341, early 14th century, Limoges) occurred light blue and green corrosion products (Eggert et al 2011), the blue one being the sodium copper formate (Fig. 10). The diffraction data of the green one perfectly matched with SCOTT's film 770 (433), a synthetic basic copper(II) formate without PDF reference card. Just by chance, we obtained single crystals of this compound when treating copper coupons in patination experiments with ammonia and formic acid. This allowed to solve the structure and determine the formula as copper(II) formate trihydroxide, $Cu(OH)_3HCOO$ (Euler et al 2009), correcting the formula by Scott et al (2001: Table I) taken from the synthetic literature. The compound contains no sodium, but as it can form only at a pH > 8 the influence of glass hydrolysis providing the alkaline environment is clear. Normal condensed humidity on surfaces is slightly acidic (pH 5.6) because of the equilibrium with the carbon dioxide in the air.

Fig. 10: Copper fitting (Ø 6.3 cm) with *émail champlevé*, light blue and green corrosion in the contact zone, photo: A. Schwarz, MAK Frankfurt

The compound was also detected on a glass flute (1807) with silver mountings, a silver box with gold ruby glass inlay, a glass framed daguerreotype, and a Limousin *émail peint* copper plaque, c. 1500 (Eggert et al 2011). In the GIMME project (Fischer 2016), $Cu(OH)_3HCOO$ was detected in one third of all cases, often together with the sodium copper(II) formate. This indicates that the (unknown exact) conditions of formation for both might be similar. And it, again, emphasises the dominance of formates in glass-induced metal corrosion while they occur quite rare without glass contact.

Latest example of a hitherto unknown copper formate corrosion product on heritage objects structurally characterised by XRPD: a mixed basic copper(II) zinc formate, occurring on brass in contact to glass and in simulation experiments: $Zn_{(10-6x)}Cu_{(3+6x)}(HCOO)_8(OH)_{18}\cdot 6(H_2O)$ (Bette et al 2019; Fischer et al 2019). On the reflector of a miner's lamp (Fig. 7), this compound occurred together with chalconatronite.

Some News on an Old Pigment: Verdigris

Verdigris (from *vert-de-Grèce,* green of Greece) is a collective term for green pigments occurring as transformation products on copper containing materials. It is here only used in its narrower meaning for different copper acetates formed by the action of vinegar, e.g. on sheet copper. As artificial corrosion product this pigment fits into this review of research – and again illustrates the brilliant concept of SCOTT "combining information on pigments and corrosion products, which are usually treated separately but are often chemically identical" (SCOTT, backcover citing G.E.).

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Verdigris is one of the oldest synthetic pigments used by mankind until the First World War. It was already mentioned by ancient Greek (Dioscorides, Theophrastus) and Roman (Pliny, Vitruvius) authors. “Verdigris is prepared in numerous ways” (*nat. hist.* 34.26) states Pliny and reports various recipes. Chemically a number of basic copper(II) acetate hydrates of the general formula $x[Cu(Ac)_2] \cdot y[Cu(OH)_2] \cdot zH_2O$ have been found in addition to neutral verdigris (pure copper(II) acetate monohydrate, x-y-z = 1-0-1). Gauthier (1958) described the compounds x-y-z = 2-1-5, 1-1-5, 1-2-0, and 1-3-2. These syntheses were replicated by Schweizer and Mühlethaler (1968). They deposited samples in reference collections like the National Gallery London and the Doerner Institute Munich. Rahn-Koltermann et al (1991) prepared also 1-4-3, but doubted 1-1-5 which later was confirmed again by SCOTT (273). Technical products are normally mixtures of various compounds depending on their preparation. SCOTT (406-415) replicated a number of syntheses from the chemical literature and historical recipes and provided diffraction peak lists (SCOTT 434-442). He concluded: “The previously published X-ray diffraction data for the basic copper (II) acetates are sometimes contradictory and difficult to understand.” (SCOTT: 273). Bette et al (2017 Table I) tabulated the, indeed, sometimes contradictory literature on the properties of these phases, including also 1-3-0 which is easily formed from 1-3-2 by reversible thermal dehydration (Masciocchi et al 1997).

One reason is the poor replicability of syntheses. For example, SCOTT (408-409, 437) yielded two totally different materials for 1-2-0 (compound C and C2) which are not the same as the Schweizer and Mühlethaler sample C^c from the National Gallery measured by SCOTT (437).

Another reason: Only the crystal structures of the 1-0-1 and the 1-3-2 compounds were known and, therefore, reliable data for powder diffraction were only available for these phases. All other compounds need further investigation. In the framework of our DFG funded research project “In search of structure”, Bette et al (2017) were now able to develop a reproducible synthesis for 1-2-0. Powder diffraction measurements at the Diamond Synchrotron allowed solving the crystal structure. Sheets in the structure are only bound by small van der Waals forces, the compound has a tendency for stacking disorder. In general, disorder might change the shape of peaks and even move their position, again changing diffractograms. And intensities are often dependent on the measurement geometry: Measurements with the sample in a spinning capillary in Debye-Scherrer geometry are to be preferred in opposite to measurements on flattened powder samples in Bragg-Brentano geometry which might show stronger texture effects (e.g., horizontal alignment of plates). Unfortunately, experimental details are not always reported in the literature (including SCOTT).

Identifying another crystal structure is a step forward for a better understanding of verdigris diffractograms as illustrated here with a sample of 1-2-0 synthesised by Schweizer and Mühlethaler (1968) from the Doerner Institute Munich. Our high precision lab measurement (spinning capillary) is compared to that reported by SCOTT (437) from the sample stored in the National Gallery in Table I.

SCOTT		Bette		Assignment
I_{rel}	d [Å]	d [Å]	I_{rel}	
20	15.42	15.60	5	U
100	10.52	10.43	100	1-2-0

		9.30	10	1-3-2
15	6.54	6.53	20	1-2-0
		6.16	5	U
10	5.39	5.39	13	1-2-0
		5.23	8	1-2-0
		5.09	6	1-3-2?
		4.67	9	1-3-2
		4.15	7	U
		4.09	22	1-2-0
2	4.03	4.03	12	1-2-0
		3.97	12	1-2-0
		3.89	11	U
5	3.59	3.59	23	1-2-0
		3.55	18	1-2-0
		3.51	16	1-2-0
		3.49	19	1-2-0
10	3.44	3.40	35	1-2-0
5	3.12	3.12	39	1-3-2

Table I: Peak lists (d>3.00) for the 1-2-0 sample of Schweizer and Mühlethaler (1968) as measured by SCOTT (437, Compound C^c) and us (Bette; only peaks $I_{rel}\geq5$ are listed). Right column: tentative assignment to the phases 1-2-0 and 1-3-2 and U (=unknown).

It is evident that modern measurements show much more peaks and allow a better quantification of intensities. The peaks can be compared with those of 1-2-0 and 1-3-2. Indeed, unexpectedly, both phases are present – and one or more unknown as illustrated in Fig. 11.

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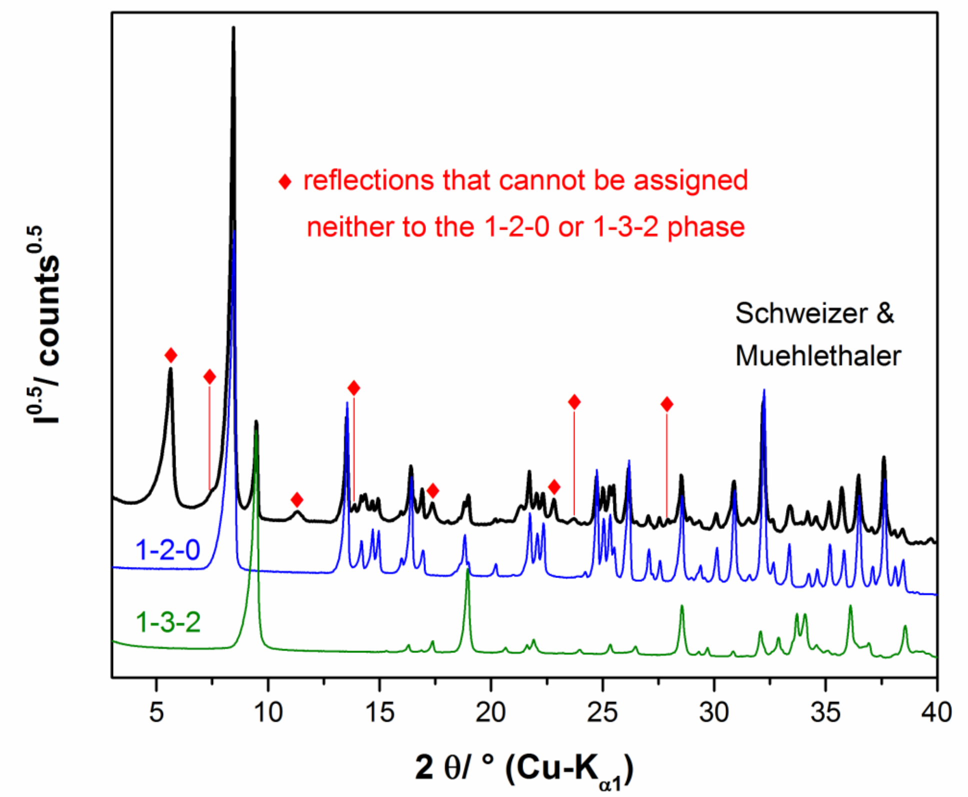

Fig. 11: Comparison of the diffraction patterns of the sample denoted as 1-2-0 phase synthesised by Schweizer and Mühlethaler (1968) and of a pure 1-2-0 and 1-3-2 phase, synthesised by Bette et al (2017). ◊ = other unknown phase(s)

In a replication experiment for verdigris production according to recipe V in the mediaeval *Mappae clavicula* by San Andrés et al (2012) copper sheets were exposed to vinegar fumes in a closed container for 6 month at 40 °C. Compounds 1-0-1 and 1-3-2 were identified on the copper by XRPD by their existing PDF cards, the unknown one (sample V-v-2) is clearly 1-2-0 as a comparison with our new data now proves.

The phase 2-1-5 (Compound A, SCOTT 271) has now also been synthesised in Stuttgart and the structure solved. It could be detected in old samples from pharmacies (Bette et al 2018). Comparing the diffraction data for this compound with SCOTT's (437 & 442) shows that these samples certainly did not consist of pure 2-1-5 phase. – The crystal structure of neutral anhydrous copper (II) acetate (1-0-0 phase = Compound E, SCOTT 272) could now also be determined by us from XRPD measurements (Bette et al 2019).

The final goal is to solve all structures of basic copper(II) acetates in order to allow full quantification of mixtures via Rietveld analysis. As illustrated by SCOTT's verdigris tables, composition varies greatly. Therefore clues to production methods are to be expected from such studies contributing to technical art history. Given the significance of colour to man historic pigments have been investigated since the beginning of analytical chemistry. It's really time now to better understand verdigris, and modern XRPD provides us with a tool to overcome former limitations.

Concluding Remarks

To deal with decay in conservation, you need to know its causes. Identifying corrosion products is a prerequisite for this. While the common corrosion compounds got more and more understood, research interest in the 1980ies and early 1990ies moved to rare products, Fabrizi and Scott's (1987) contribution on "Unusual copper corrosion products and problems of identity" being a paradigmatic example. But since then people moved to other themes: What could you do with only low resolution Debye-Scherrer films and a comparably small PDF reference database at the time? You were stuck with unidentifiable patterns and would miss any non-crystalline matter. Without easy access to SEM-EDX you would not be able to visualise your samples with high magnification and get an idea about their homogeneity and elemental composition. Raman microscopes indicating characteristic molecular vibrations (e.g., of multiatomic anions) were unknown in conservation labs.

When David commented my research results on corrosion products (e-mail of Sept 10th, 2015): "…you are the only one left standing who is doing this work!", I first felt heroic, but later idiotic (the others had good reasons to flee…). Some thoughts later, I see myself not as the last one standing, but as the first one reviving the field in a situation which has totally changed. SEM-EDX and Raman microscopy are now widespread in conservation science labs. High precision XRPD measurements and the now larger number of known structures allow much better quantification of mixtures, even the amount of hitherto overlooked amorphous material can be calculated. And you do not need necessarily single crystals anymore for the determination of the crystal structure, even complicated structures can be solved from powder diffraction data as demonstrated by us. This is not restricted to metal corrosion products and pigments as has been also shown for a number of acetate efflorescence compounds on calcareous objects (Eggert et al 2021). As these methods of data evaluation will become much more widespread in crystallography, this will revolutionise conservation science.

Sulfates in brown fuzzies, the rarity of cupric hydroxide, the wonder of curly malachite, unexpected occurrences of chalconatronite, diffraction data for hitherto unknown copper formates, and the 'verisimilitude of verdigris': we owe all this knowledge to SCOTT's 'Copper and Bronze in Art' providing a sound starting point for our research. And this was just copper, not to tell of all the steely ideas I developed from working with David on the sequel 'Iron and Steel in Art' (discussed in Eggert 2009).

Certainly, David's curiosity as documented in his many publications will continue to inspire new generations of researchers. The notion that we can see only so far because we are standing on the shoulder of giants was first expressed in the 12th cent. by Bernard of Chartres (Wikipedia 2021). It has now become a literary *topos* of our culture. In the bible, David is not the giant, but in conservation science! Thank you, giant David, for carrying us dwarves around and enlarging our horizon so much.

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Scribal Abbreviation

SCOTT
Scott, D. A. 2002.
Copper and Bronze in Art: Corrosion, Colorants, Conservation. Los Angeles: Getty Conservation Institute.

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