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Some news about 'Black Spots'

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Abstract

'Black spots', i.e. copper and sulphur containing efflorescences occuring during display or storage, can grow on any material which contains copper when exposed to reduced sulphur gases like hydrogen sulphide, carbonyl sulphide, and elemental sulphur. Besides mineral collections, sulphur may occur in finds from anaerobic sites directly or as a pyrite oxidation product (e.g. in wood or marine crusts), gunpowder, ancient gold hollow objects, cements, and some brands of plasticine.
While some of the black spots could be identified by X-ray diffraction as crystalline copper sulphides various (basic) copper sulphates were also found. Others are apparently X-ray amorphous, their nature needs further research with other analytical methods.

Keywords: (air) pollutants, black spots, copper sulphide, copper sulphate, (elemental) sulphur

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1. Introduction

Helge Brinch Madsen (1977) was the first to note small 'black spots on bronzes' (BSoBs) consisting of copper sulphide in many major European museums and to report on them at conservation conferences in Germany (1978), Scotland (Brinch Madsen and Hjelm-Hansen 1979), and the USA (Brinch Madsen and Hjelm-Hansen 1982). It is now widely accepted that the source of sulphur reacting with copper lies within inappropriate storage and display materials (Oddy and Meeks 1982). Surprisingly, despite the frequent occurence of this phenomenon and the routine testing of display materials, only in two cases has a definite culprit been identified so far: a carpet covering the floor of a case which was woven from a mixture of nylon and wool fibres and backed with rubber (Sease 1994), and rubber bands used for packaging (Moraitou 1995). It is now clear that one has also to look at other artefacts on display as possible sources of pollutants. Besides woolen textiles (Sease 1994), a low fired ceramic vessel from an anaerobic waterlogged site (Green 1992) has been found to emit sulphurous gases. In this case hydrogen sulphide was suspected. Eggert and Sobottka-Braun (1999) showed that the sublimation of elemental sulphur has to be considered as well.

This paper will
1) update information on the corrosiveness of elemental sulphur via the gas phase
2) take a closer look on what materials BSoBs spots can grow, and
3) review the chemical nature of BSoBs.

2. Sulphur, the 'enemy of copper'

According to one theory, the word sulphur 'is derived from Sanskrit *shulbari*, meaning “enemy (*ari*) of copper (*shulba*)“' (Vira 1950). If true this would indicate a deep knowledge of chemistry which is relevant to our modern understanding of efflorescences occurring on copper containing materials in the museum and elsewhere. Sulphur has a low but measurable vapour pressure (1 ppb at 20 °C, 200 ppb at 60 °C). Under the conditions of the standard Oddy test for display materials (60 °C, 100 % relative humidity (rH)) copper coupons are visibly attacked within hours by vapours from flowers of sulphur (Eggert and Sobottka-Braun 1999). In mineral collections specimens are normally grouped according to the mineralogical system; therefore, the naturally occurring elements sulphur and copper are often displayed in the same case. To assess possible dangers of this practice, sulphur crystals from Sicily were stored in small boxes (0.225 dm^3) at room temperature together with copper nuggets from Michigan in the dark (Figure 1). At 100 % rH, the first black needles growing on copper

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Figure 1 Copper nuggets, stored with sulphur crystals (middle), additional water (=100 % rH, left) and blank experiment (no sulphur, right) in polystyrene boxes, after one year.

could be observed microscopically after three days. At ambient rH it took considerably more time, although after one year the test nugget was covered with needles as well. In a display case at the University of Stuttgart collection (see below) one (out of 3) nuggets showed some BSoBs on close inspection. In consequence, sulphur should be exhibited only seperately from metals. The reason why up to now, no case of black spots on native copper displayed together with sulphur could seen in other mineralogical museums and why the two other nuggets were unaffected, is not fully understood.

While the danger by sulphur crystals is now obvious elemental sulphur might also occur hidden in artefacts. Waterlogged wood from the Mahdia shipwreck was shown to cause black spots on a modern test bronze wire on long term storage (Eggert and Sobottka-Braun 1999). EDX -SEM showed that it contained sulphur (2 $\%_{w/w}$) but no matching metal cations. Apparently it must contain elemental sulphur although XRD and extraction with pyridine could not detect it in the analysed sample. At that time, only one case where elemental sulphur was identified in wood has been reported (MacLeod and Kenna 1991): the Batavia shipwreck where it was formed as an intermediate product of pyrite (FeS_2) oxidation. Now the Vasa has been shown to contain between 0.2 and 6 $\%_{w/w}$ total sulphur in the outermost 2 cm of the wood (Sandström et al. 2002). Tonnes of elemental sulphur still left in the vessel endanger the wood by their oxidation to sulphuric acid. Marine calcium carbonate crusts on metals from similar anaerobic sites were already known to contain elemental sulphur (North and MacLeod 1987: 78, 82). Some of such crusts from the Mahdia bronzes showed black spots. If marine crusts contain reduced forms of sulphur (easily checked by the iodine/azide test, Lee and Thickett 1996: 22f.) this is an argument for removing them from copper alloys.

Some other artefacts may contain sulphur as well:
- Gunpowder may affect objects in contact or in the vicinity (Weichert et al. 2004).
- Ancient gold thin hollow objects were often filled with molten sulphur as cement for embossing and protection against mechanical damage (Eggert, Kutzke, and Wagner 1999). One ring contained BSoBs (copper cations most likely from the debased alloy or a copper wire inside) on a sulphur globule.
- Historical recipes for cements or fillers sometimes contain sulphur as an ingredient. Such a cement caused severe three dimensional silver corrosion inside a baroque game board (Hustedt-Martens 2003). Ivory-coloured inlays in Pennsylvania German furniture can consist of sulphur as well (Mass and Anderson 2003).

Another danger in display, unsuspected by most conservators (Eggert 2004), is posed by the use of ‘plasticine’ for moulding or quick mounting of metal objects. Some brands contain large amounts of elemental sulphur which, by the way, made them useful for repatinating overcleaned bronze objects (Plenderleith and Werner 1971: 261). Black spots have been found on minerals (chalcocite, Ramdohr 1980: 444), metallographic copper alloy samples (Scott 2002: 396), and a mediaeval fibula (Eggert 2004), all mounted for some time with a sulphur-containing modeling clay. Commercial brands can easily be tested for their content of elemental sulphur: gently heat a sample in a reagent tube and test the fumes with a wetted lead acetate paper (Eggert 2004). Those types containing sulphur should principally not be used in conservation departments.

To protect copper-containing objects from their 'enemy', sulphur, they should not be displayed in closed cases together with sulphur emitting substances, be they display materials or artefacts. If this is not possible (e.g. in the case of the game board where brass and cement are part of the same object), ventilation and absorbents have to be used.

3. Where do 'black spots' grow?

'Black spots on bronzes' seem to occur on all materials containing copper. Brinch Madsen found them on archaeological bronzes where they left pits in the metal beneath. Hjelm-Hansen (1984) listed cases of coated (gilding, tinning, lacquer, PVC insulation) modern copper alloys from the technical literature developing black spots. Here the spotty pattern correlates with the pores of the coating. Eggert and Sobottka-Braun (1999) reported black spots in a showcase with waterlogged wood, both on ancient bronzes and uncoated modern display materials (a copper nail and a bronze wire). Obviously, black spots can occur independent of the objects' origin, no matter if coated or not. They can also easily be grown in the laboratory. What matters are only the environmental conditions (concentration and nature of pollutant, rH, T).

Even alloys with low copper content like pewter can be affected (Weichert 2004). Small particles of finely divided copper alloy particles in paper (Daniels and Meeks 1994) react as well. A form of atmospheric copper sulphide corrosion of small inclusions has even been reported from gold coins (Linke et al.1999).

Nevertheless, the formation of black spots is not restricted to metals. Previously, Oddy and Meeks (1982) presented a case of black spots growing on corrosion products (copper carbonate and cuprous chloride). Copper minerals are often chemically identical to copper corrosion products; it is, therefore, no wonder that they also can be affected by sulphurous gases (Howie 1992), e.g. emitted by sulphur or unstable sulphide minerals, and develop black spots as well. Eggert and Sobottka-Braun (1999) described black spots occurring also on copper sulphide specimens (chalcocite, Cu_2S, and covellite, CuS). Because covellite already contains the maximum stoichiometric amount of sulphur, the latter case might even be independent of the presence of pollutant gases. To get an idea of the frequency of 'black spots' on minerals the collection of the University of Stuttgart was surveyed (Weichert 2002). In a display case with crystalline sulphur bornite (Cu_5FeS_4), chalcocite (Cu_2S), algodonite (Cu_6As), domeykite (Cu_3As), and one out of three copper nuggets showed 3-dimensional efflorescences (not only flat tarnish). In another display case without elemental sulphur covellite (CuS) was affected. All alteration products gave a medium to strong reaction with iodine/azide (i.e. contain a form of reduced sulphur). Only the efflorescence on bornite (Figure 2, digenite, Cu_9S_5) could be identified by X-ray diffraction (XRD).

Figure2 Bornite, Cu_5FeS_4, with fuzzy tarnish of digenite, Cu_9S_5.

To further study the sensitivity of copper minerals (Howie 1992) samples of cuprite (Cu_2O), chalcocite (Cu_2S), covellite (CuS), and malachite (polished, gemstone quality) were exposed to 4 ppm hydrogen sulphide (prepared by exposing aluminum sulphide, Al_2S_3, to 100 % rH, Hjelm-Hansen 1984) over three months (Weichert 2002). All developed 'black spots'. Those of cuprite and chalcocite were analysed by XRD, covellite was found in both cases.

Copper minerals are no exception to the formation of 'black spots'; observations and descriptions in the mineralogical literature might help to further elucidate the phenomenon.

4. What are 'black spots' really?

Common conservation wisdom has it that BSoBs consist of copper sulphides. They are normally analysed by X-ray diffraction, a method which is sensitive to crystalline phases only. The first reported black spots were thus found to consist of covellite (CuS, Brinch Madsen 1977/8). Lee and Thickett (1996) reported also brown digenite (Cu_9S_5) and black chalcocite (Cu_2S). Other copper sulphide phases (see Scott 2002: 227 for a full list) could also be identified (Lee 1996) but may be difficult to distinguish in small, poorly crystalline samples.

The Pourbaix predominance area diagram for the system Cu-S (Figure 3) created with Poigdomenech's (2004) MEDUSA software shows that sulphates (depending on the pH which is decreased in the environment to slightly acid values (below the neutral pH 7, dashed line) by the presence of CO_2, SO_2, and NO_x in the air: chalcanthite $CuSO_4 \cdot 5H_2O$, antlerite $Cu_3SO_4(OH)_4$, brochantite $Cu_4SO_4(OH)_6$) are the only thermodynamically stable sulphur form in presence of air (upper region). The oxidation of sulphides to sulphates is therefore favoured.

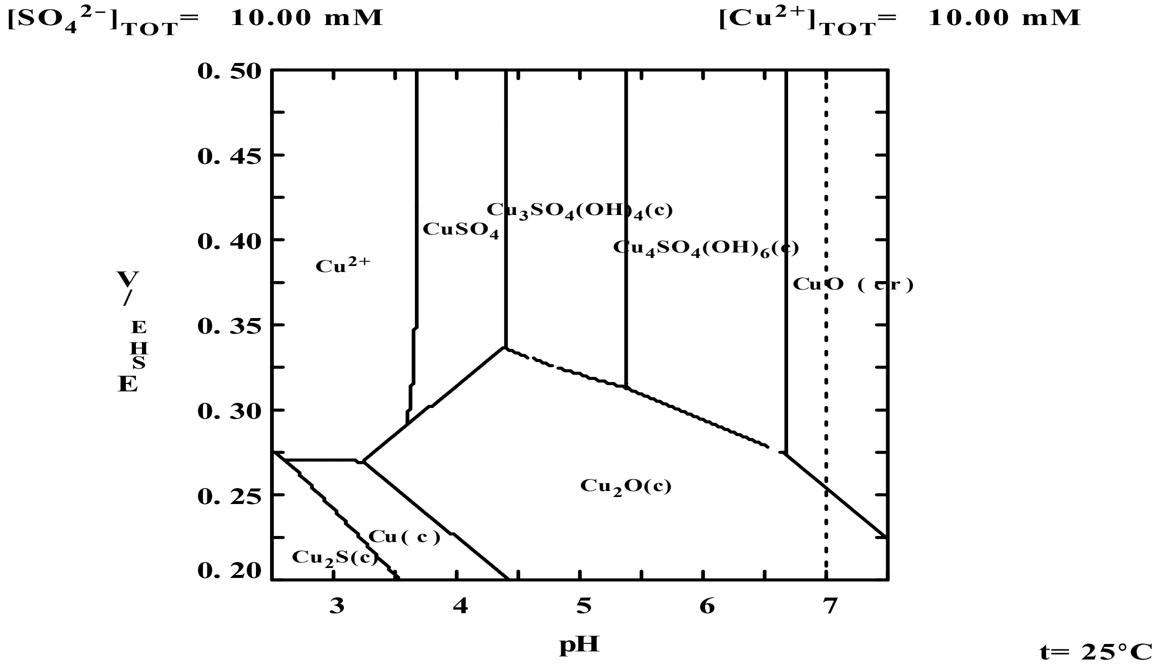

Figure 3 Pourbaix diagram showing predominant phases in the Cu-S-system (MEDUSA software, Poigdomenech 2004)

This is in accordance with the following observations:

- Freshly precipitated CuS shows oxidation to sulphate after 30 days (Babkin 1947).
- Hjelm-Hansen (1984) found covellite and brochantite in artificially grown black spots.
- Duncan and Ganiaris (1987) exposed bronze finds with golden or black sulphide patina to 80 % rH. After one week first changes were observed, after five weeks all patinas have changed. Green oxidation products were found to be the sulphates antlerite and guildite ($CuFe(SO_4)_2(OH) \cdot 4H_2O$). The amount of water might be crucial for the formation of sulphates. Steger and Desjardins (1980) exposed mineral chalcocite Cu_2S to 52 °C and 68 % rH for five weeks and found CuO and CuS, but no sulphates.
- Eggert, Kutzke, and Wagner (1999) analysed covellite and chalcanthite on BSoBs on sulphur inside a hollow gold ring.
- Twilley found primarily chalcanthite in the whiskerlike growth on metallographic sections stored on plasticine-mounted glass slides (Scott 2002: 396).
- Scott (2002: 233f.) reports namuwite, a zinc substituted brochantite in 'black spots' on brass objects.
- Weichert (2002) could replicate Hjelm-Hansen's finding of covellite and brochantite in laboratory tests on tin bronze and leaded tin bronze, but not on copper. On brass, schulenbergite $(Cu,Zn)_7 (SO_4)_2(OH)_{10} \cdot 3H_2O$ was identified. All these sulphates grown in the lab formed a compact layer, no loose 'black spot' morphology. Antlerite was found in 'black spots' on a brass nail from a wooden shield (MR 82 A 2954) of the *Mary Rose*.

Clearly, some BSoBs contain copper sulphate phases. Besides attack by sulphur dioxide air pollution, the oxidation of sulphides as primary corrion products caused by reduced sulphurous gases is another reaction route to copper sulphates (schematically: $CuS + 2O_2 \rightarrow CuSO_4$). Therefore, the presence of copper sulphates alone can no longer be taken as sufficient proof for corrosion by acidic air pollution as has been done formerly, e.g. in the namuwite case. On the other hand, a negative iodine/azide test (i.e., no sulphide present) cannot totally rule out the occurrence of a BSoBs type process because initial sulphide might have totally reacted to oxidation products.

Many samples of BSoBs analysed by X-ray diffraction (XRD) showed no or nearly no signals (Figure 4) despite optimisation of the signal to noise ratio by long time measurements and computer processing of the data. Apparently, some of the black spot material is not crystalline. That BSoBs can be amorphous has been observed before (Daniels and Meeks 1994, Lee 1996) and, from our experience, seems not to be a rare phenomenon. Now knowing that oxidation can occur one cannot automatically assume that these compounds are amorphous sulphides. They might contain (non-stoichiometrically?) more or less oxygen atoms; Howie (1992: 58) postulated (meta)-stable sulphide-oxygen-(hydroxyl)-complexes for the tarnish developing on sulphide minerals in air. Other methods (e.g. XANES or EXAFS) which can give information on the chemical surrounding of the sulphur atom are needed to get a full picture of what compounds can all hide behind the phenomenological term 'black spots'; first results are promising (Hahn 2004).

When dealing with XRD (only crystalline phases) and EDX-SEM (low sensitivity for light elements like O) analyses of BSoBs in the literature it must be kept in mind that they might show only part of the picture.

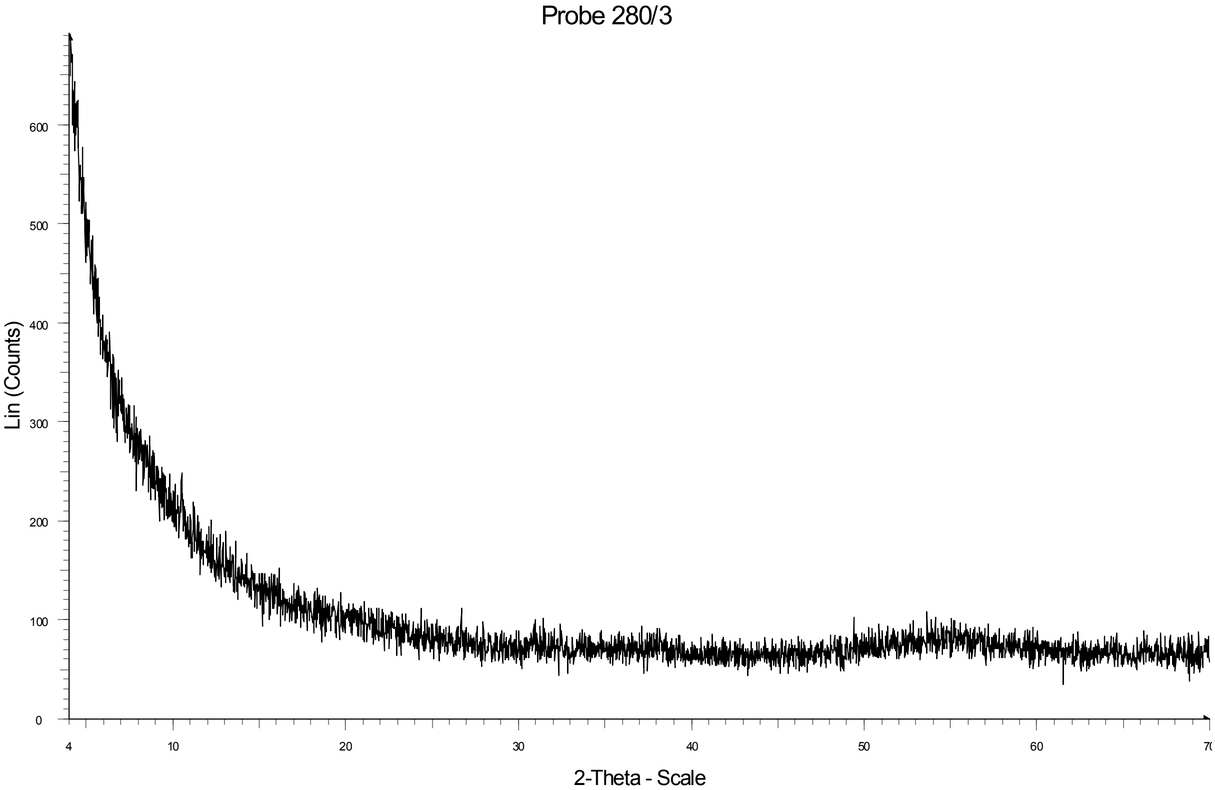

Figure 4 Powder diffractogram of X-ray amorphous ‘black spots’ from a bronze neckring, Landshut A280/3, (4° ≤ 2θ ≤ 70°; step width 0.02°, step time 15 s, Cu radiation, Siemens D5000)

5. Summary and Conclusion

'Black spots' can occur on every material which contains copper independent of its age or previous history: metal alloys, corrosion products, minerals, and semi-precious stones all develop them when exposed to reduced sulphur gases like hydrogen sulphide, carbonyl sulphide, and elemental sulphur. Apart from mineral collections, sulphur may occur in finds from anaerobic sites directly or as a pyrite oxidation product (e.g. in wood or marine crusts). Gunpowder, ancient gold hollow objects, cements, and plasticine may contain sulphur as well. While some of the black spots could be identified as crystalline copper sulphides and others as copper sulphates, their oxidation product, others are amorphous. Their stoichiometry, including the question of if and how many oxygen atoms they contain besides copper and sulphur, needs further research., but clearly there is no general chemical formula for BSoBs.

In hindsight, the term 'Black spots on Bronzes' now used universally is not an optimal one, as it might be misleading. BSoBs are not always black: brown and other colours have been described. The term 'spot' might lead to the notion of a flat 2-dimensional phenomenon, while instead BSoBs grow 3-dimensionally like 'trees', 'bunches', or 'cauliflower' (Weichert 2004). Their occurrence is not restricted to bronzes (i.e. copper alloys), but to anything which contains copper. Therefore, the term 'Black Spots on Bronzes' should be used only in quotation marks or abbreviated form (BSoBs) or be replaced. ‘Copper-Sulphur-Efflorescence (Cu-S-F)’ might be an alternative which better represents today's knowledge.

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