# Pseudomorph or corrosion? The enigma of the curly malachite

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Abstract

*Rare bundles of curved green fibres ('curls') and spirals growing on or near copper alloy finds were identified as malachite with a little zinc; occurrences on mineral specimen are also known. The individual sub-µm fibres are loosely packed and adhere by secondary forces. They are formed by a not well understood crystal growth phenomenon and are not related to the former presence of any organic material. Until now, they may be taken as proof for the authenticity of objects from unknown sources.*

Keywords: archaeology, bronze corrosion, (curly) malachite, pseudomorph(osis), wire silver

**Introduction**

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 noticed during a students' project in the study programme 'objects conservation' at the State Academy of Art and Design Stuttgart. So far this phenomenon has only been mentioned on Roman bronzes by Scott (1994) as a form of malachite, not to be mistaken as textile. But what do they tell us? Is it really malachite? Does it occur only on artefacts and under human influence? On which types of objects? Under what conditions? Is it a pseudomorph replacing former organic material or not? How rare does it occur? Over the years, a report in BROMEC 2 (2002) and many talks with specialized conservators yielded enough samples for scientific investigations and observations to tackle these questions.

*Figure 1: Stereomicroscopic view (width 6 mm; A. Stäbler) of an assemblage of malachite curls on a Frankish copper alloy bowl (RLMB WW 2004/61 499-7)*

**Malachite?**

Scott (1994) reported the material of his curls as malachite, but the identification method (Polarization microscopy? Debye-Scherrer?) was not stated explicitly. Other copper corrosion products reported earlier as fibres in addition to malachite curls on a Roman seal-box (Fabrizi and Scott 1987) were eriochalcite ($CuCl_2 \cdot 2H_2O$; literally: wool copper!) and nantokite (CuCl). Already in 1986 this author identified curls from a fibula from Bonn-Lannesdorf (142/86, no.29; RLMB lab no. 8520) by qualitative spot tests as copper carbonate. To exclude any phases other than malachite (e.g. the basic zinc copper carbonate rosasite), enough curls could be sampled under the microscope from a Frankish copper alloy bowl (see figure 1) for X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) analysis; only malachite could be detected. Energy dispersive X-ray analysis (EDX, Röntec XFlash Detector 3001) in a scanning electron microscope (SEM, Zeiss EVO 60) on samples from different sites found also a little Zn in the range of 0.6-2.1% together with traces from typical soil elements like K, Mg, Fe, Al, and Si. Curls from the same object seem to agree quite closely in their Zn content.

**On artefacts only?**

A number of samples from early Mediaeval copper alloy objects could now be found in addition to Scott's Roman leaded bronzes (Zn ≤ 0.05 %, AAS). A. Bartel (letter to the author from Nov. 20th, 2001) had seen also 3 Pre-Roman examples. Time of manufacture or soil logging is apparently not crucial.

One curl lay close to an Alamannic strap-end made of brass (Lauchheim burial 1200; ca 15% Zn and 2% Sn, EDX-SEM), another to a debased silver fibula (Lauchheim burial 1022). Therefore, the type of alloy also seems not to be decisive for its occurrence. Correlation of the occurrence of curls with special

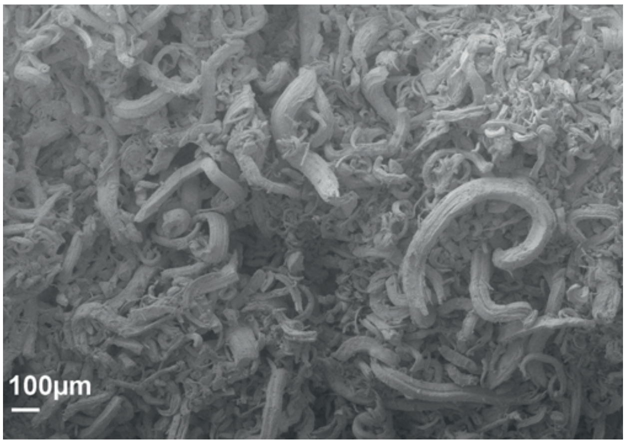


*Figure 2: SEM micrograph (U. Haller) from the same find as figure 1*

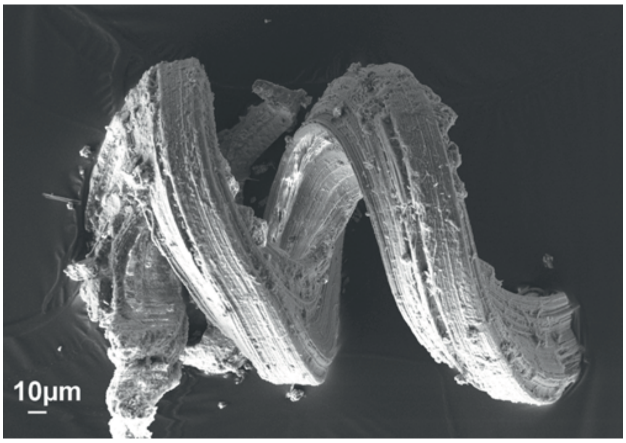


*Figure 4: SEM micrograph (U. Haller) of a 'cork screw' spiral from a belt, Kirchheim ID 7297*

*Figure 3: Malachite curl from a bronze fitting (B.-Krozingen, Unterer Stollen, burial 143, no. 24676) in transmitted light (25X; A. Fels)*

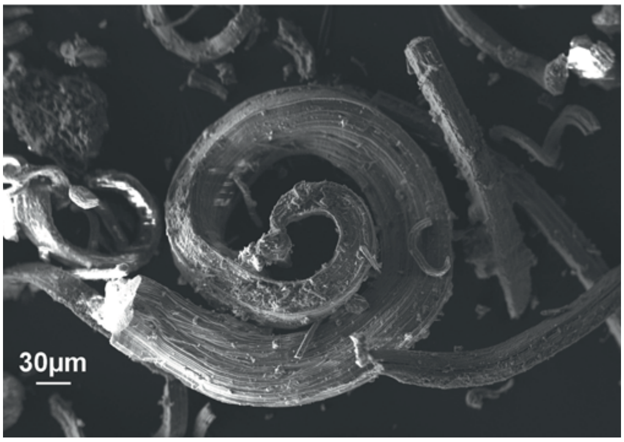


*Figure 5: SEM micrograph (U. Haller) of a 'clock spring' spiral from a belt, Kirchheim ID 7297*

types of sediments have not been observed so far. Apparently they need some hollow space to grow freely, so objects may not be totally sedimented.

In nature, malachite may be 'internal radial or divergent fibrous on a coarse to fine scale, and banded in colour. Also in delicate fibrous aggregates, sheaf like or compact' (Palache et al. 1951). According to Chase (1994) such fibrous malachite is also 'seen fairly often on Chinese bronzes'.

Curls from mines were first reported from Schwaz-Brixlegg (Austria) in the 1970s (Meixner and Paar 1975) and a relationship with rosasite discussed. Brandstätter and Seemann (1983) could identify them by XRD as malachite. The Zn content (2.7-5.7%) was twice as high as in matrix malachite from the same sites. Despite these (rather arcane) publications malachite curls were virtually unknown to mineralogists until 1997 when sensational finds from Schwaz-Brixlegg were presented at the Munich mineral fair and widely published in collectors' journals (e.g. Jahn 1997; Wight 1998 and Lieber 2004) with spectacular pictures. Curls have also been described from other localities, e.g. the Flambeau Mine in Wisconsin (Rosemeyer 1997). They are often associated with azurite particles which in few cases also have been observed for curls on artefacts.

**The structure of the curls**

Curls occur either in manifolds directly on copper alloy finds (see figures 1 and 2) or individually in the surrounding sediment. Their typical diameter is in the range of a tenth of a mm, so they are normally only detected under magnification. In the optical microscope in transmitted light, they can show a dark banded structure typical for malachite (see figure 3). They can form spirals like a cork screw (helices, see figure 4) or a clock spring (see figure 5). The Natural History Museum of Vienna even owns a specimen from St. Gertraudi which combines both forms: a conical helix with 16 (!) coils (Brandstätter and Seemann 1983).

Curls have a tendency to split off at their end. The individual fibres have a diameter of some 0.2 µm (see figure 6). The fibres seem to be loosely packed without cementing material between them and adhere possibly by secondary forces only acting on their large surface. In cross section (see figure 7), free spaces between fibre aggregates are visible. Sometimes, fibres are grouped to bundles of sub-curls which can be resolved also by optical microscopy at the end of the curls.

**Pseudomorph?**
Even when totally gone, structures of former organic material may be conserved in copper corrosion products ('pseudomorphs'). Fur had been the first spontaneous idea to explain the malachite curls. Studies with optical and electron microscopy showed no interwoven fibres (as e.g. for leather), cell walls (as e.g. for wood), mammal hair cuticle, or any other known organic structure. In one case curls were observed inside a Roman bronze inkpot (HA 127, 44-61 from Elsdorf, letter of F. Willer to the author of Feb. 19th, 2002) were no solid organic material can be expected.
Together with the occurrence of curls on mineral specimen and the production of similar structures (of chemically different compounds, see below) in the lab, all these facts speak for a special crystal growth phenomenon unrelated to the presence of organic materials used by men. No pseudomorph!

**Why curls?**
Curved mineral forms like curls, spirals, and even rings are not unknown in the mineral kingdom (Lieber 2004). The reason why and under which conditions malachite grows this way –and in the case of some spirals with such an amazing regularity- seems to be not clear. Brandstätter and Seemann (1983) suspected different growth speed of individual adhering fibres (e.g. because on one side there is a better supply of copper ions). Jahn (1997) and Wight (1998) discussed the Zn content and argued with a screw dislocation model for whisker growth. Curvature under its own weight, as proposed by Lieber (2004), cannot explain spirals with many coils.
Interestingly, quite similar curls formed by fibre bundles of barium sulphate have been grown in the laboratory (Pietschmann 2006). Here nanoparticles diffuse in solution without sedimentation and form aggregates by fusion of high-energetic crystal planes (Wang et al. 2006). Can the chemically totally different basic copper carbonate grow similar? Further (experimental) research is clearly needed!
By the way, silver can also form 'hairy' structures (German term: Haarsilber) when re-deposited from solution. Despite widely occurring in nature this seems only to be reported once on artefacts (Scharff et al. 2000). Interestingly, the silver spiral in figure 8 occurred together with a malachite curl, easily distinguished by its colour.

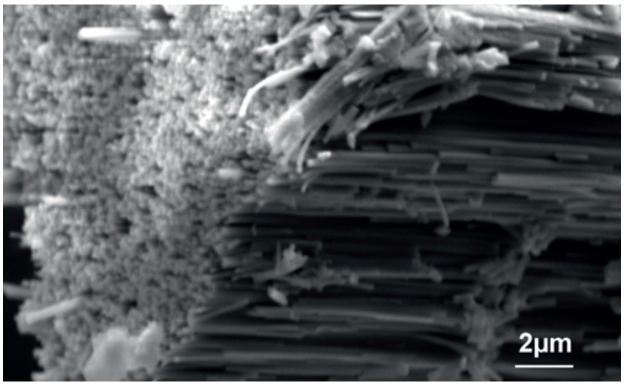


*Figure 6: SEM micrograph (U. Haller) of a fresh fracture surface of a curl from Lauchheim burial 271).*

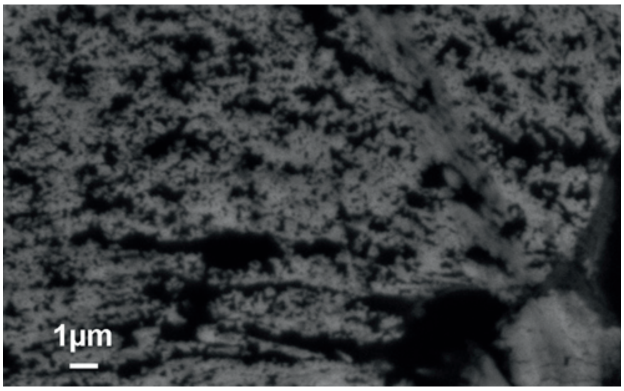


*Figure 7: SEM micrograph (U. Haller) of a curl in cross section (A. Stäbler), find as figure 1*

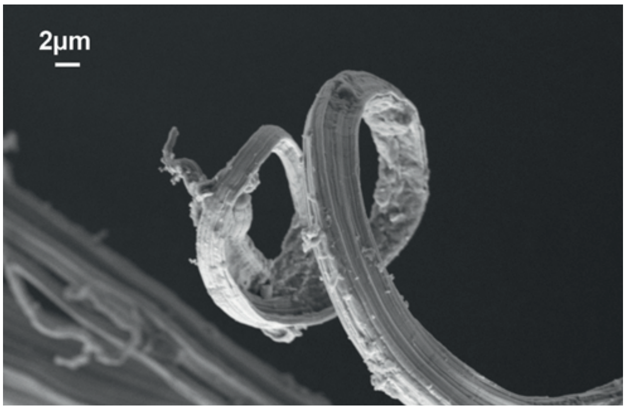


*Figure 8: SEM micrograph (U. Haller) of a silver spiral from Lauchheim burial 1022*

**How rare?**
H. Farke (Schleswig), A. Bartel (Bamberg), and F. Willer (Bonn) observed only a few examples in decades of search for organic remains on metals (private communications in 2001); Farke estimated 4-5 in 20 years. The fact that conservators once made aware of their existence then found examples themselves during few years (T. Kreß (Tübingen), B. Nowak-Böck (Munich)) recalls the common wisdom that you only see what you know. In a students' project in 2006/7 at the Stuttgart Academy with 8 metal finds lifted as earth block from the Alamannic graveyard of Lauchheim 3(!) of them contained individual curls. Finds carrying many curls are of course rarer, but Scott (1994) was definitely right to assume that they are 'probably seen more often by conservators than the literature would suggest'.

## Conclusion

This study confirms Scott's identification of the rare fibrous curls as malachite not growing as a pseudomorph of organic material. They are bundles of sub-µm fibres with a tendency to split off at the end. Occurrences on non-artefacts have also been reported. As long as the conditions for their growth (which may or may not be related to their minor Zn content) is not clearly understood one may not derive any conclusion from them. Despite their relative rarity one should better not 'suggest the close association' (Scott and Podany 1991), i.e. the same site, for objects with curls from the art market. On the other hand, at least as long as no method is known to produce curls artificially, curls which are growing out of an object are a sign of natural growth of patina, and, therefore, speak for the authenticity of an object.

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