e-PRESERVATIONScience

e-PS, 2016, **13**, 23-32
ISSN: 1581-9280 web edition
ISSN: 1854-3928 print edition

e-Preservation Science (e-PS)

is published by Morana RTD d.o.o.
www.Morana-rtd.com

SCIENTIFIC PAPER

CURLY MALACHITE ON ARCHAEOLOGICAL BRONZE: A SYSTEMATIC STUDY OF THE SHAPE AND PHENOMENOLOGICAL APPROACH OF ITS FORMATION MECHANISM

Janneke Nienhuis[1,2]*, Luc Robbiola[3], Roberta Giuliani[4], Ineke Joosten[2], Hans Huisman[2], Bertil van Os[2], Jilt Sietsma[1]

1. Delft University of Technology, Department of Materials Science and Engineering, P.O. Box 5, 2600 AA, Delft, The Netherlands.

2. Cultural Heritage Agency, P.O.Box 1600, 3800 BP, Amersfoort, The Netherlands.

3. Université de Toulouse, CNRS, UMR 5608 TRACES, Maison de la Recherche, 5 allées Antonio-Machado, F-31058 Toulouse Cedex 9, France.

4. Alma Mater Studiorum - University of Bologna, Via Guaccimanni 42, Ravenna 48121, Italy.

*corresponding author:
j.nienhuis@tudelft.nl

Abstract:

Curly malachite (CM) is found as a green cupric carbonate hydroxide corrosion product on archaeological bronze, mostly on artefacts retrieved from graves. In this paper, a morphological characterization approach is proposed, enabling the investigation of the formation process of CM. It is suggested that curly malachite precipitates from an aqueous solution, for which the surrounding soil conditions provide local triggers. Anthropic activities associated with ritual burials do not significantly affect the growth of CM. It is also confirmed that curly malachite is usually not a pseudomorph of formerly organic material. Although the understanding of the formation process is far from complete, this study has shown that CM is expected to be found more often than is currently recognized, due to its relatively simple formation mechanisms and boundary conditions.

received: 13/03/2016
accepted: 02/11/2016

key words:
curly malachite, archaeological bronze, corrosion, nucleation and growth, morphology, pseudomorph

1 Introduction

Curly malachite (CM) is a green, thin, fibrous corrosion product that is encountered on archaeological bronzes (Figure 1), but it is often not recognized. However, this is changing and archaeologists and conservators identify it more and more often. Nevertheless, publications on the matter are nearly absent. The origins of CM are unknown and it is unexplained whether the formation of CM is related to culturally created site formation processes. Also, the implications of the presence of CM on the (future) state of the object remain unclear. Therefore, in this article:

- a formation mechanism of CM is proposed, including boundary conditions for nucleation and growth. Probable correlations between the appearance of CM and the burial environment are established and the possible harmfulness to the bronze object is discussed.
- a morphological approach is proposed, containing parameters that can be used by archaeologists and conservators when encountering CM. This will increase the available data on CM and ultimately test the proposed formation mechanism, so that the implications of CM become more evident.

Figure 1: Example of curly malachite as a mass of curls on archaeological bronze from Zevenbergen site. OM: Optical microscope image.

In the following sections a short overview is given about morphology and possible growth mechanisms of curly malachite.

1.1 Curls in literature

Examples of eriochalcite ($CuCl_2.2H_2O$), nantokite (CuCl) and malachite ($Cu_2(CO_3)(OH)_2$) are amongst the earliest appearances of fibrous corrosion compounds in literature[1]. In 1994, Scott wrote an article where malachite was described in both massive and fibrous form on excavated Roman statues[2]. The shape of malachite fairly often encountered on Chinese bronzes is also called "fibrous"[3]. Peška et al.[4] identified an atypical, curly-like, crystallization type of malachite on Early Bronze Age bronzes found in graves. Eggert[5] is the first author to link a specific curly shape of malachite on bronze artefacts with natural malachite minerals found at copper mines. In other fields, waxy green curly crystals are manifested in entomological collections, at the contact between an insect specimen and its brass display pin[6] or on historical copper alloy objects combined with leather or wood[7].

1.2 Morphological characterization

In this article, (curly) malachite with a copper-based artefact as substrate is called "corrosion product", while the analogous material from mineral deposits is called "mineral"[8]. Azurite ($Cu_3(CO_3)_2(OH)_2$) sometimes co-occurs with curly malachite[5,9,10]. In most mineral examples, CM coexists with massive, bulky, compact malachite[11,12]. Helical shapes are found, while this is not the case for archaeological curly malachite. The diameter of the curls usually varies along its length, being the largest at the base, where it is sometimes still attached to its substrate, and smallest at the free end[10]. The mineral examples are also composed of (bundles of) crystalline fibres[10,12]. Only a few articles specify dimensions, which are given in Table 1.

Massive mineral malachite displays typical macro-scale banding, probably due to periodic precipitation[13]. The transversal laminae, composed of fibrous aggregates[14], are varying in thickness, up to centimetres wide, and with different chroma, ranging from pale to deep green. Kantor[15], however, hypothesized that the lighter areas seen in CM are regions with a higher zinc content, because a bluish and rather pale colouring of crystals usually indicates zinc admixture in malachite.

	Length	Diameter	Fibre diameter	Ref.
Mineral CM	<50 mm	1 mm	/	9
Mineral CM	1 - 50 mm	/	0.5 µm	10
Mineral CM	0.07 - 3 mm	0.01 - 0.2 mm	1 µm	12
Archaeological CM	/	0.1 mm	0.2 µm	5
Archaeological CM	0.05 - 0.15 mm	0.01 - 0.03 mm	/	28

Table 1: Dimensions of malachite curls as found in literature.
/ means "not reported".

1.3 Growth models

A crystal is formed by nucleation and growth, after which solid-state phase transformations may occur as well[16]. Malachite can be formed in two ways: by reaction of cupric ions with carbonate ions from a supersaturated aqueous solution[10,17,18], deposited on a substrate[19], or by the reaction of cupric oxide (tenorite) or cuprous oxide (cuprite) with carbon dioxide and water[17,20,21]. Different additional models have been proposed in literature to explain the growth of fibrous and curly malachite:

- Impurity atoms, such as zinc as measured by Brandstätter[12], initiate screw dislocations (defects in the crystalline structure)[9,18]. Movement of these dislocations will stimulate curvature of initially straight malachite fibres. However, Lieber[10] rejects this theory, since this type of crystal growth occurs at the atomic level will not necessarily result in curl visibility at the macroscopic scale.
- Kantor[15] forms a hypothesis that the curling of a crystal is the morphological expression of a minimization in free energy, acquired by forming a sandwich structure of alternate layers of malachite and rosasite ($(Zn,Cu)_2(CO_3)(OH)_2$) to accommodate the different atomic sizes of copper and zinc in the crystal lattice.
- A lack of space produces mechanical resistance during growth and plastically deforms the material into a curl[10].
- A malachite curl forms by deformation by its own weight[10].
- Unequal growth rate of individual fibres or parts of bundles results into a curly shape[12].

General literature about mineral growth in caves[22] classifies "helictites" as a parallel co-growth of tightly bonded spherulite bunches. A central channel supplies a local capillary film on the helictite"s tip. The curvature of the aggregate is induced by small local variations affecting the wetted spot.

Another analogy can be found in the growth of ephemeral and banded ice crystals, likewise composed of bundled fibres, on dead wood, small rocks and from soil. Periodic freezing and partial melting of the ice between nights will result in growth boundaries that give the crystal its banded appearance.[23] Synthesized $BaSO_4$ fibre bundles have been grown from a supersaturated solution in a laboratory environment on a hydrophilic substrate. Crystallization and oriented attachment growth at high-energy surfaces are established as steps in the formation process.[24]

1.4 Pseudomorphism

Another point to mention when considering CM is that original features in materials, like bone, wood or textile, can be preserved by impregnation with dissolved copper ions[25]. Impregnation occurring simultaneously with fibre degradation can replace the organic composition with a copper corrosion product like malachite. Such a mineralized fibre where only the physical shape is preserved, is called a pseudomorph[26]. This phenomenon is seen in numerous materials, such as wood, insects and even human skin[4]. Examples of preservation by copper ions are given below.

Textile pseudomorphs can be recognized by an interwoven structure and/or the spin direction of hollow threads[27] and animal or human hairs by a straight, cylindrical shape[4]. If the organic material has been degraded, these can also be hollow, usually with the characteristic scales still present[27]. The green corrosion structures are embedded in or closely adhered to the surface of an object. Single mineralized plant or textile fibres can show adhering copper-rich surface encrustations, and an absence of (bundles of) submicron fibres[26].

Eggert[5] argues that curly malachite cannot be a pseudomorph. His samples did not exhibit any of the abovementioned characteristics. Combined with the occurrence of mineral CM and the production of similar structures in the lab, he states this crystal growth phenomenon is unrelated to the presence of organic materials used by men.

Site	Period	Context	Soil characteristics	Object(s)	Microstructure	Proximity of organics	Curl location	Appearance of curls	Ref.
La Fosse Cotheret (FR)	300 BC	Burial chamber, initially atmospheric	Sandy clay	*Ronde-bosse* ornament	Cast	Wood, textile?	In hollow side of *ronde-bosse* ornament; within earthy crust	Isolated curls, mass of curls, co-occurrence with hydroxy-sulfates	Figure 2a, 25, 28
Tintignac (FR)	200-100 BC	Sanctuary	Sandy clay	Carnyx (sheet, rings)	Worked (sheet) cast (rings)	/	On surface patina of carnyx in earthy crust	Isolated curls, mass of curls	Figure 2b, 29
Bocholtz (NL)	300 AD	Burial chamber, initially atmospheric	Silt, clay, löss	Jug, knob	Worked (jug) cast (knob)	/	In soil surrounding jug; inside hollow knob	Mass of curls	Figure 2c
Zevenbergen (NL)	800 BC	Burial mound	Sand, podzol	Studs	Worked	Wood, leather?	In hollow head of small stud; on surface of large stud	Single curl in small stud, mass of curls on large stud	Figure 2d, 31
Uden (NL)	800 BC	Inhumation grave	Sand, podzol	Anklet	Worked	Bone, textile	Inside hollow anklet; also in soil inside anklet	Mass of curls	Figure 2e

Table 2: Detailed informative data on the samples of curly malachite used in this research. / means “not identified”.

Technique Site	OM	XRF	SEM-EDS	XRD	μ-Raman
La Fosse Cotheret	Olympus, Nachet, Nikon	/	Hitachi S2500 with Imix PGT EDS 15/20 kV	Philips PW 1700 Cu Kα, 40 kV 30 mA	/
Tintignac	Olympus, Nachet, Nikon	/	LEO 435 Low Vacuum with Imix PGT EDS 15/20 kV, 50 Pa	/	/
Bocholtz	Zeiss Axioskop 40 on polished thin section	/	/	/	/
Zevenbergen	Hirox KH7700	/	/	/	/
Uden	Hirox KH7700	Bruker ARTAX μ-XRF Mo-source, 50 kV 150/300 μA XFlash 3001 SDD	JEOL JSM 5910 LV with Thermo Fisher Scientific SDD EDS 20 kV, 30 Pa	Bruker D8 Discover Cu Kα, 40 kV 30 mA 0.3/0.8 mm spot size	Thermo Scientific DXR Raman Microscope Laser 532 nm

Table 3: Analytical techniques and settings used for CM samples in this study. / means “not applied”.

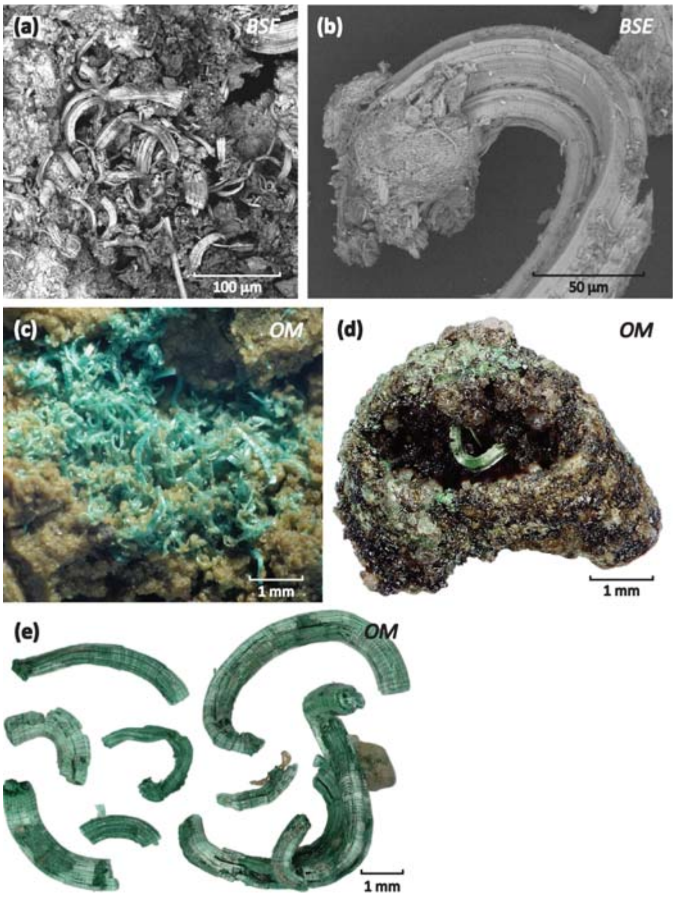

Figure 2: Samples of curly malachite used in this study: (a) mass of curls in hollow ornament from La Fosse Cotheret[28]; (b) curls on carnyx found in Tintignac[29]; (c) mass of curls in soil surrounding jug from Bocholtz[30]; (d) individual curl in stud from Zevenbergen[31]; (e) removed curls from anklet found in Uden. BSE: backscattered electron image, OM: optical microscope image.

2 Materials and methods

2.1 Samples

Available curly malachite samples from different regions in France and the Netherlands were studied (Figure 2, Table 2).

As summarized in Table 2, the CM samples were found on or near thin-walled (millimetre-scale thickness) archaeological bronzes, mostly from burial sites. The curls co-occur with the more common massive shaped malachite as corrosion product. For all of these sites, the curls are found under wet conditions, with intermediate drier periods, yet the soils are not waterlogged. The soils contain particles varying from coarse sand (~210-2000 μm) to fine silt (~2-50 μm). The objects date from 300 BC to 300 AD. More differences lie in their specific local burial conditions: inhumation and cremation ritual grave deposits are exemplified. Some of the graves were initially exposed to atmospheric conditions before being covered by soil or sediment. Here, “ritual” refers to deliberate action by people with characteristics repeatedly seen. Examples are the choice for inhumation or cremation, the addition of specific metallic grave goods or the use of a textile shroud. Sites with and without clear evidence of (former, degrading) organic material like textile and bone can be compared in the sample set from this study. Finally, objects covered with masses of curls and only isolated curls are present as well.

2.2 Analytical techniques

The CM samples have been investigated applying analytical techniques and instruments as shown in Table 3.

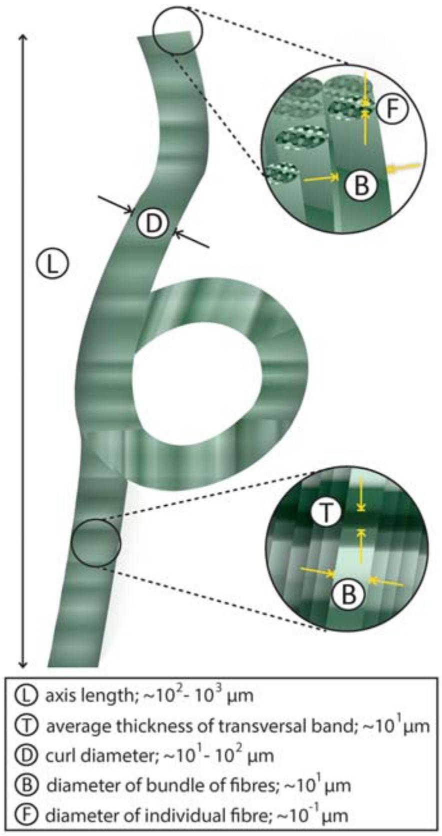

Figure 3: Proposed approach for morphological characterization. N.B. Schematic model with all parameters combined into one overview. © Illustration by J. van Donkersgoed.

Parameter Site	L (µm)	D (µm)	B (µm)	F (µm)	T (µm)	# curls analyzed
La Fosse Cotheret	100 ± 50	20 ± 10	15 ± 5	0.6 ± 0.4	26 ± 25	12
Tintignac	800 ± 300	80 ± 30	17 ± 5	0.4 ± 0.2	n.d.	8
Bocholtz	475 ± 225	60 ± 10	n.d.	0.4 ± 0.2	36 ± 35	3
Zevenbergen	1000 ± 800	115 ± 85	90 ± 10	n.d.	16 ± 15	5
Uden	3500 ± 1500	375 ± 125	20 ± 15	0.3 ± 0.2	56 ± 55	9

Table 4: Dimensional characterization of morphology of curls used in this study. N.d. indicates “not determined”.

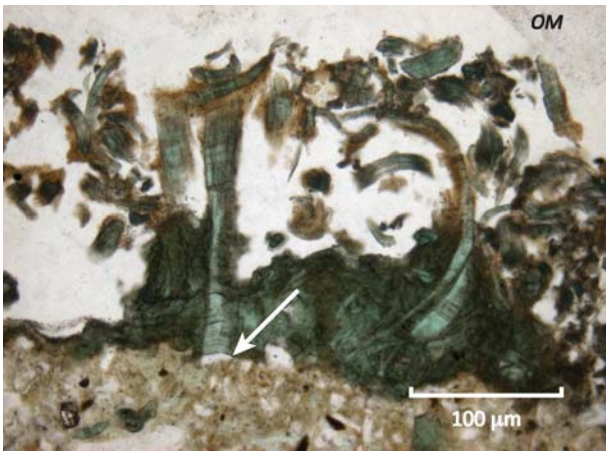

Figure 4: Malachite curls seen in cross-section, thin section of corrosion crust from Bocholtz site. One curl is located on a quartz grain, indicated with the arrow. OM: optical microscope image (in plane polarized light).

In addition, the composition and microstructure of the objects featuring CM were studied and are shortly summarized in Table 2. The reader is referred to the cited literature in Table 2 for more archaeological context and information.

To give a clear morphological characterization of the malachite curls, an approach of parameters is developed in this research and schematically shown in Figure 3. The illustration does not intend to be a representation of a realistic malachite curl, but it is merely a combination of possible curvature options combined into one figure.

Five parameters can be quantified: axis length (*L*), the average thickness of a transversal band (*T*) and diameter of the curl (*D*), of a fibre bundle (*B*) and of an individual crystalline fibre (*F*). Curvature is also an important parameter. However, specific radii are difficult to assess on curls from archaeological remains and the radius often varies along the curl. Therefore, curvature is not incorporated into the qualitative approach in Figure 3. Qualitatively, a curl can be characterized like a clock-spring with decreasing radius, a corkscrew with constant radius, or a mixed or deviating variant.

3 Results

3.1 Morphology

All parameters of the proposed system of the curls studied in this research are given in Table 4. Several factors lead to an approximation of dimensions. Only a limited number of curls was analyzed. Even though the curls are three-dimensional objects, their size is so small that they can only be specified through two-dimensional OM/SEM-pictures. The given dimensions of CM are thus defining an order of magnitude. Also, a lot of curls are fragmented, clustered and/or cemented in corrosion crusts or soil material. That is also the reason why the curl base in this sample set is not clearly recognized and described. The thin cross-section from Bocholtz is an exception, because curls appear to be located on a quartz grain (arrow in Figure 4). Curly malachite is observed on the corroded surface of metals or soil rather than on the interface of the corrosion layer with the bare metallic substrate.

The curls are systematically built up of fibres, only visible at the micrometric level (see Figure 5). It is not possible to determine whether they are hollow at this resolution.

These fibres can combine into bundles of fibres, which are all more or less polygonal: pseudo-circular as well as pentagonal shapes can be discerned (Figure 2d, Figure 5). Their diameter seems to remain constant along their length.

Usually, the fibre length does not correspond to the full curl length. The individual fibres are composed of smaller, straight segments (Figure 5a, 6). A slightly wedge-shaped band of segments can be seen, with its narrow end at the inner curve and its broad end at the outer curve. The average thickness *T* of these transversal bands varies in one curl from a few microns to about 100 µm. The bands are defined by boundaries, appearing across the entire curl diameter, in a plane perpendicular to the growth axis of the curl. They can

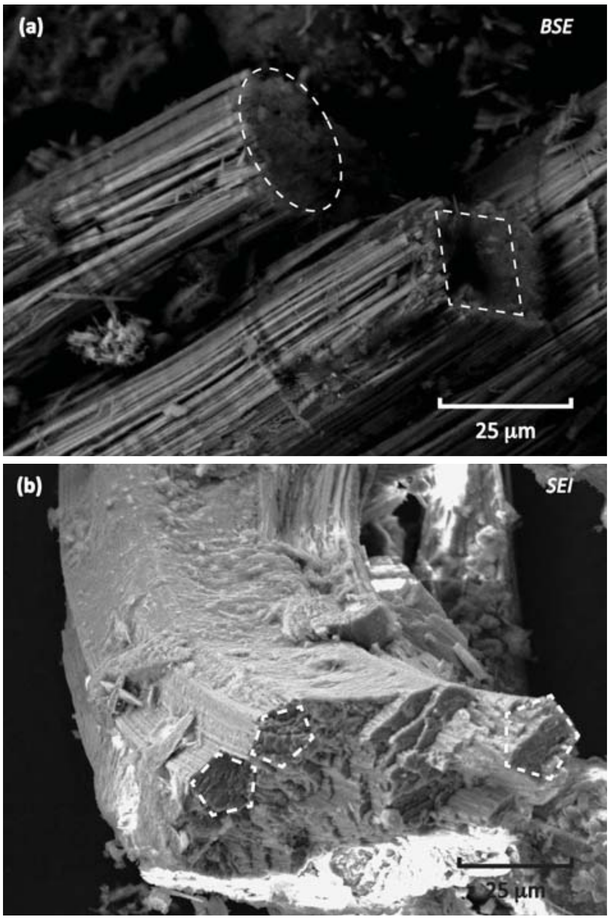

Figure 5: Curly malachite is actually built up of (bundles) of fibres. Bundle cross-sections are all more or less polygonal to circular. (a) Uden site; (b) Tintignac site. BSE: backscattered electron image, SEI: secondary electron image.

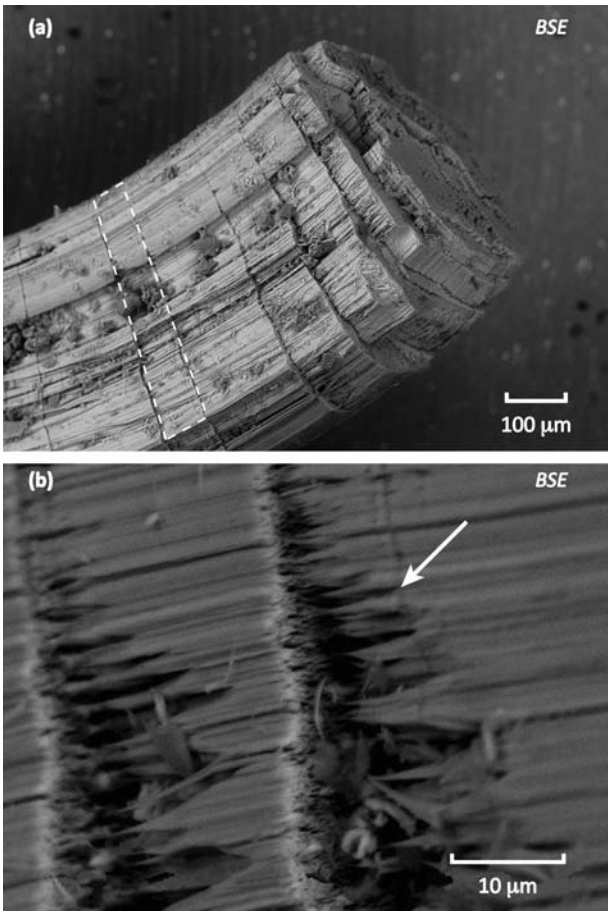

Figure 6: Banding in a curl from Uden site. The wedge-shape of the bands is accentuated in (a). The arrow in (b) indicates one of numerous sawtooth-shaped features at a boundary between two bands. BSE: backscattered electron image.

be seen with the naked eye as variations in green (see Figure 1) and under the electron microscope as black striations (Figure 5a, 6a). On some boundaries, sawtooth-shaped features can be discerned (arrow in Figure 6b).

3.2 Composition

XRD and µ-Raman measurements reveal that all curls as well as the coexisting unbanded massive green corrosion layers from this study are solely malachite ($Cu_2(CO_3)(OH)_2$). No other crystalline compounds are identified. The samples from Uden, Roissy and Tintignac were the only curls analyzed for impurity elements. As far as SEM-EDS possibilities allowed, fibres without visible soil contamination only showed copper, carbon and oxygen as components with an approximate detection limit of ~0.1 wt%. Aluminium, silicon, iron and calcium are measured as minor elements in all cases. Lead and silver are only found in trace quantities in the curls from Uden. No significant differences in composition between bands have been found within a single curl.

3.3 Colour change and feature obscuration

Studying the malachite curls with an optical microscope, a deceptive local colour change was experienced on the curls from Uden (Figure 7a), which were

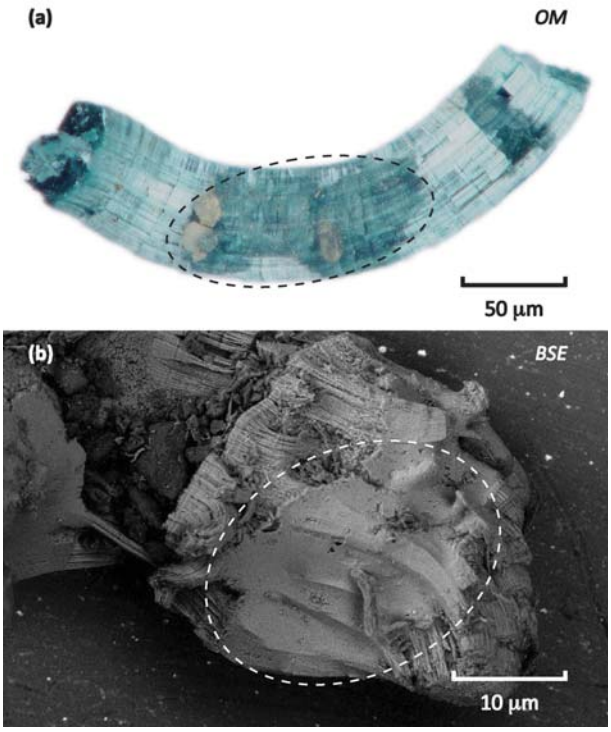

Figure 7: Changes in the appearance (encircled areas) of curly malachite from Uden site. (a) Colour change; (b) unclear details. OM: optical microscope image, BSE: backscattered electron image.

impregnated by accident with polymeric conservation material. Details are invisible when viewed with an electron microscope, because the polymer forms a non-conductive surface. The presence of a fibrous CM structure and other structural features of CM are obscured (Figure 7b).

4 Discussion

4.1 Morphological characterization

The proposed approach of morphological characterization for curly malachite (section 2.2) enables the comparison between samples from this study and material described in literature. The presented methodological approach on CM could be employed by archaeologists and conservators and expanded in future research on CM to improve completeness of qualitative data and comparability.

Cross-sections of the base-structure may provide additional information on the nature of the substrate: (interface of corrosion and) bare metal, corrosion layer or soil particle. It may also show whether the curl grows on top of the substrate, or forms inside it.

The colour, dimensions and banding of mineral (curly) malachite (section 1.2) and the fibrous and curvy properties of helictites (section 1.3) are comparable to CM from this study (Table 4). Therefore, the growth mechanisms for these materials are used to propose a formation process appropriate to curly malachite.

4.2 Formation mechanism

In an attempt to gain a better understanding of the formation of CM, a distinction is made in this study in describing the first two stages of crystal formation: nucleation (of fibres) and growth (of curls).

4.2.1 Nucleation of fibres

Because a malachite curl consists of an aggregate of clearly defined fibres and bands, it is suggested here that CM nucleates according to a precipitation process. Once the bronze object is buried in soil, a water film lines irregularities of the object surface or pores in the immediately surrounding wet soil ("cavities"). Cupric ions are then released and dissolve in the (carbonate-containing) water. (Figure 8a)

Changing conditions like water evaporation, pH-fluctuations or temperature changes, trigger the formation of a supersaturated aqueous solution of cupric and carbonate ions. Malachite consequently nucleates as a single crystal in a polyhedral shape[19], with its monoclinic prismatic crystal system enabling the preferential formation of needle-like structures or fibres. The substrate can either be the object, or neighbouring soil particles. Nucleation on specific features of the substrate may lead to heterogeneous precipitation, which is possible on hydrophilic substrates[24], like malachite or quartz. Adjacent deposition of polyhedrons leads to a bundle of single-crystal fibres. The ordered arrangement of fibres in bundles would therefore be a result of favourable nucleation, in combination with consequent growth. (Figure 8b)

The ubiquitous, coexistent corrosion layers of malachite on the object have a different appearance from curly malachite (Figure 2d)[3]. The layers are usually neither fibrous nor banded and develop slightly on top or below the original object surface, as opposed to CM, which forms an outgrowth. This suggests that different formation mechanisms are involved: layers of malachite may form with cuprite as precursor by penetration of corrosive agents like oxygen, while CM precipitates directly from an aqueous solution (section 1.3).

4.2.2 Growth of curls

The next step is growth and particularly curvature in the case of CM. When adopting the precipitation theory, it is assumed that a fibre elongates by the addition of new material to the tip of the crystal[22]. In the case of curly malachite, it is hypothesized that the capillary capacity of a bundle of fibres enables the wicking of (supersaturated) water to the fibre tips (Figure 8c). During a drier period the growth of the malachite fibres nearly ceases and a boundary is induced, resulting in the formation of a band (Figure 8d). These bands are slightly wedge-shaped (Figure 6a), which implies that curvature takes place during the growth stage and not the nucleation phase (Figure 8e). The observation from this study that the fibre segments in the studied samples are straight and not curved strengthens this hypothesis. Continuous periodic deposition forms a banded malachite curl (Figure 8f).

An unequal growth rate between individual (segments or bundles of) fibres and/or a different rate of volume accumulation are seen as the most plausible causes for curling. A larger distance between the fibres may result in less material transport, thereby forming the shorter side of the wedged band. This also correlates to the formation of helictites with variations in growth direction[22].

Other options, as described in section 1.3, are considered to be less plausible. The minor elements measured in samples from Uden are most likely environmental contamination (section 3.2). Banding and/or curling as a result of impurities and the inherent movement of screw dislocations is thus improbable, thereby following Lieber"s theory[10]. This also renders curvature due to mixed crystal structures unlikely. Mechanical resistance during growth as well as deformation by its own weight would result in bent fibres and/or cracks, which are not seen here.

The hypothesis of formation of fibres by the process of solid-state transformation from cuprite or tenorite is assumed less likely, because this would not result in a shape restraint, as is the case for a solution being drawn to the surface due to capillary action. Since azurite is sometimes associated with malachite (section 1.2), it may be hypothesized that it can act as a precursor, after which transformation to malachite occurs[17]. However, the coexistence of massive malachite corrosion layers and curly malachite implicates that in these contexts, malachite is the abundant and stable form. Also, no traces of azurite have been found in any of the curls. But, the millennia-long burial time may allow complete transformation of azurite into malachite, so it cannot be ruled out as a possibility.

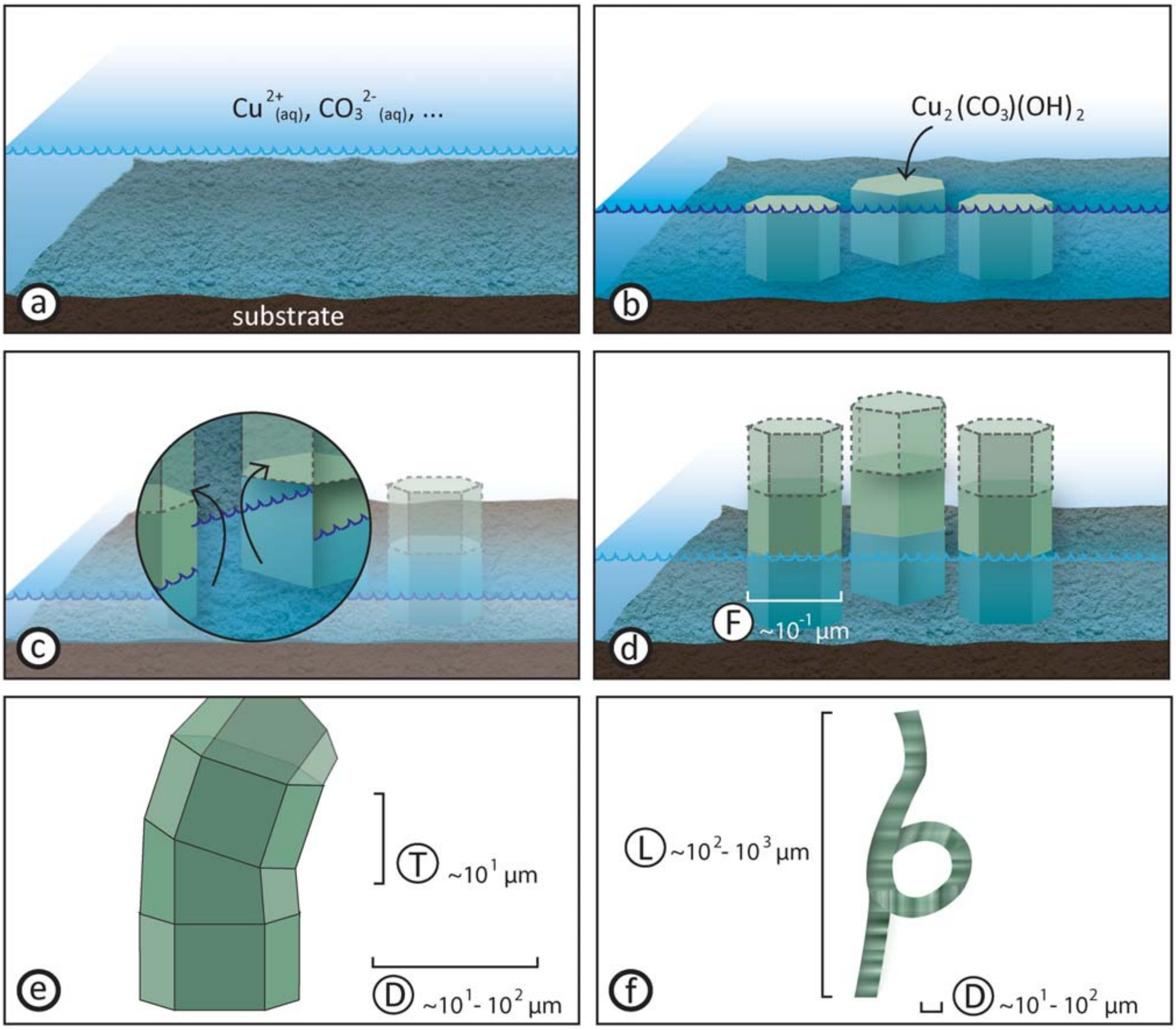

Figure 8: Proposed nucleation and growth mechanism for curly malachite. Parameters *F, T, D* and *L* as defined in Figure 3.
(a) substrate with water film, (b) nuclei deposition from supersaturated solution, (c) fibre formation due to capillary action, (d) band formation, (e) curvature, (f) continuous periodic deposition forms a banded malachite curl. © Illustration by J. van Donkersgoed.

The observed sawtooth-shaped features show remarkable resemblance to the dissolution characteristics of silicate minerals and are therefore thought to be originating from post-formation dissolution processes[32].

Summarizing, the proposed formation mechanism for malachite curls is schematically illustrated in Figure 8. Malachite grows in a monoclinic (prismatic) crystal system[8,16], but for sake of clarity and readability of the figure, a hexagonal basic crystallographic shape is chosen to represent the nuclei.

4.2.3 Rate of formation

In literature, the rate of formation of (malachite) curls is not described. However, the formation of micrometre-sized synthetic malachite crystals, also from solution, is reported to take place within a week[33]. Furthermore, the amount of released cuprous and cupric ions is highest in the first stages of corrosion[21,34]. Combining this information with data on curly malachite may lead to an approximation of curl age and eventually even the establishment of a relation with the copper alloy object age.

However, at the moment there is not enough data on the specific influences of the environment on the rate of formation of CM and no correlation is found with object age. Laboratory experiments growing CM under various environmental conditions on different substrates, in combination with a suitable technique to measure impurities (section 3.2) may validate the formation method and yield data on the rate of formation, allowing to give a realistic estimation of curl age.

4.3 Factors influencing growth modality

In general, the formation of corrosion products during the long-term burial of bronzes is quite complex, depending on numerous factors[3,35] that temporally change. Examples are geochemical conditions like pH, soil composition, redox processes and the presence of bacteria and other ions or metals. The study presented here has only taken a limited number of parameters into account. As pointed out previously, this paper is exploring possible relationships between the typical features of curly malachite and the environmental conditions of burials. The contextual parameters as summed up in Table 2, combined with known variables in burials, enable a comparison to find common factors for the growth modality.

4.3.1 Soil and organic remains

Table 2 shows that curly malachite with equivalent morphological features (section 3.1) can be formed in different soil environments. No systematic link between aspects of the burial ritual listed here (such as the proximity of organic material) is found. When adopting the theory of CM formation by precipitation, it is assumed that the fibres form from polyhedrons, which are formed when local growth conditions are only slightly different from the immediate equilibrated environment[19].

Burial sites contain either decomposing bodies or cremation remains. They accommodate a high concentration of amongst others fatty acids and CO_2[27], localized in soil pores. Fatty acids and their breakdown products may interact with copper alloys to form a copper soap that can grow in the shape of curls[6,7]. A notable common characteristic of mineral CM is that is predominantly forms in the presence of percolating acidic water[11,12].

Many bronze objects have been found in ritual graves in contact with water, without showing the presence of CM. As is argued before, CM seems to form in periodically wet environments, enabling the formation of a (supersaturated) water film, as opposed to waterlogged surroundings. Also, it is suggested here that a certain combination of soil environmental conditions, like pH, moisture content and porosity, triggers nucleation and growth of curly malachite. Possibly, a localization of decomposition products of organic matter provides an extra incentive. It is therefore argued that it cannot be evidenced that anthropic activities are the cause for the curved morphology to develop, as the existence of curly malachite as a mineral emphasizes.

4.3.2 Microstructure of the object

In literature, the possible influence of the microstructure of bronze on the growth modality of curly malachite has never been given attention. However, it is observed in this study that different cross-sections of fibre bundles can be present. They may represent a pseudomorph of for example a vegetal fibre, or a pseudo-circular shape may correspond to a dendritic grain nucleus, whilst a polygonal shape has a polygonal grain at its base. But a curl is an aggregate of fibre bundles, with dimensions (B, F) that do not match those of organic fibres or metallic grains. Also, banding is not observed in organic fibres. Pseudo-circular bundles appear on worked objects from Zevenbergen and Tintignac and both types of fibre cross-sections can be observed on the same artefact. Therefore the abovementioned theories linking microstructure and bundle cross-section are rejected. Assuming that CM grows by deposition of compounds on a substrate rather than by pushing out material of the object, it is thus argued that the artefact microstructure is not an important parameter to take into account.

4.4 Pseudomorph of organic material or not?

In the field, the perception exists amongst archaeologists and conservators that curly malachite is a mineralized remains of textile or other organic material. The results of this study show that CM is composed of individual fibres and bands, as opposed to the structures seen as pseudomorphs of formerly organic material (section 1.4). Supporting Eggert"s arguments[5], it is argued that these pseudomorphs are clearly distinguishable from the curly malachite that is the subject of this study.

4.5 Recommendations for the approach of archaeological curly malachite

Keeping malachite curls and documenting the five quantitative parameters as well as curvature type (as defined in section 2.2) will aid in understanding the boundary conditions for curly malachite growth. It is advisable to measure or deduce environmental parameters, preferably soil geochemical characteristics. One should also be alert for the waxy green curly crystals displayed on the interface of copper and organic material, in order to study whether the same growth mechanism may be applied. It is preferable to leave the curls in their original place if they are attached to the object, since it enables study of the direct environment. Also, at the moment, there is no reason to assume that CM is detrimental to the object. The curls have probably formed on top of the surface of the object (see also section 4.3.2), and therefore any local features have likely not been disturbed. Also, malachite growth will likely not proceed under dry conditions.

As shown in section 3.3, changes in appearance due to impregnation with a polymer can be observed. These can lead to misleading conclusions, like linking colour change to the presence of impurities. It is likely that these changes are the result of conservation material impregnating the curls. It is not uncommon to use consolidating organic polymers during the conservation process of archaeological artefacts. But, when green curls are identified in the vicinity of the object, one should prevent curl impregnation by conservation material to preserve their original nature for further investigation.

5 Conclusions

In this research, the special curly shape of malachite as corrosion product on archaeological bronze in ritual burials was investigated.

- An initial characterization system is developed, based on several morphological parameters, which should aid in understanding possible formation mechanisms of curly malachite (CM) in the future. The malachite curls are built-up of (bundles of) individual fibres, forming bands. Current observations do not allow a complete model explaining all CM characteristics yet. It is suggested that the following series of nucleation and growth events take place in the formation of a malachite curl on archaeological bronze:
- Cavities in or around the buried object are lined by a water film in a wet environment.
- Cupric ions are released and dissolve in the water.
- A supersaturated aqueous solution of cupric and carbonate ions forms.

- Malachite nucleates on the object or on soil particles and grows into a bundle of single-crystal fibres.
- Elongation is induced by the capillary capacity of these bundles.
- Precipitation under periodic wet and dry soil conditions results in transversal bands, visually observed as different shades of green.
- Curvature is probably caused by an unequal growth rate between individual (segments or bundles of) fibres and/or a different rate of volume accumulation at the bundle surface.

The foregoing sequence shows that anthropic activities do not have a major influence on the formation of curly malachite. However, a localization of decomposition products of organics may be beneficial. Most likely, a certain combination of soil conditions, such as porosity, pH and changes in soil moisture content lead to small local deviations in equilibrium conditions that facilitate the formation of curly malachite. It is thus argued that malachite curls are not restricted to ritual burial sites and it is expected that they appear more often on copper alloy objects than currently conveyed. Recording of soil geochemical parameters and environmental conditions in the future may provide additional insight in the proposed formation mechanism, so that the implications of the occurrence of CM will become more evident.

It is also discussed that pseudomorphs of formerly organic material are clearly distinguishable from the curly malachite that is the subject of this study, based on the abovementioned formation process.

6 Acknowledgements

The authors warmly thank Florence Bertin, Joris Dik, Joëlla van Donkersgoed, Monique Drieux-Daguerre, Pascale Gardin, Richard Jansen, Thierry Lejars, Ronald Louer, Arjan Mol, Inocencia Queixalos, Hanco Zwaan and the reviewers.

This research is part of a PhD project about the conservation of archaeological bronze, funded by Delft University of Technology, Leiden University and the Cultural Heritage Agency of the Netherlands. It was partly carried out in the context of a scholarship founded by Fondazione Flaminia.

7 References

1. M. Fabrizi, D.A. Scott, *Unusual copper corrosion products and problems of identity*, in: J. Black, Ed., *Recent Advances in the Conservation and Analysis of Artifacts*, Summer Schools Press, London, 1987, 131-133.

2. D.A. Scott, *An examination of the patina and corrosion morphology of some Roman bronzes*, JAIC, 1994, **33** (1), 1-23.

3. W.T. Chase, *Chinese Bronzes: Casting, Finishing, Patination, and Corrosion*, in: D.A. Scott, J. Podany, B.B. Considine, Eds., *Ancient & Historic Metals: Conservation and Science Research*, The Getty Conservation Institute, Los Angeles, 1994, 85-118.

4. J. Peška, M. Králík, A. Selucká, *Organic Matter Residuals and Imprints in Products of Copper and Copper Alloy Corrosion: A Preliminary Study - Early Bronze Age industry*, PAMATKY ARCHEOL, 2006, **97**, 5-46.

5. G. Eggert, *Pseudomorph or Corrosion? The Enigma of the Curly Malachite*, in: C. Degrigny, R. van Langh, I. Joosten, B. Ankersmit, Eds., *Metal 07*, Vol. 1, Rijksmuseum, Amsterdam, 2007, 57-60.

6. B. Garner, A. Giusti, M. Kerley, *Conservation of Insect Specimens Affected by Verdigris*, NatSCA News, 2011, **21,** 50-59.

7. B. Brühl, *Copper soaps on ethnographic and decorative art objects*, in: E. Hyslop, V. Gonzalez, L. Troalen, L. Wilson, Eds., *Metal 2013 Interim Meeting of the ICOM-CC Metal Working Group Conference Proceedings*, Historic Scotland, Edinburgh, 2013, 265-269.

8. http://www.webmineral.com/data/Malachite.shtml (visited on 4 March 2016)

9. Q. Wight, *The Curly Malachite of Schwaz-Brixlegg, Tyrol, Austria: New Find from 5,000-year-Old Locality*, Rocks & Minerals, 1998, **73** (5), 314-318.

10. W. Lieber, *Locken, Ringe und Spiralen - kuriose Wachstumsformen von Kristallen*, Der Aufschluss, 2004, **55**, 3-16.

11. T. Rosemeyer, *In memoriam: The Flambeau Mine*, Rocks & Minerals, 1997, **72**, 344-347.

12. F. Brandstätter, R. Seemann, *"Malachit-Excentriques" auf Kupfervererzungen in paläozoischen Gesteinsserien Kärntens und Tirols,* Annalen des Naturhistorischen Museums in Wien, 1983, **85**/A, 85-92.

13. R.J. Hartman, E.W. Kanning, F. Gretchen Klee, *The Liesegang phenomenon applied to banded malachite*, J CHEM EDUC, 1934, **11** (6), 346-349.

14. T. De Putter, F. Mees, S. Decrée, S. Dewaele, *Malachite, an indicator of major Pliocene Cu remobilization in a karstic environment (Katanga, Democratic Republic of Congo)*, Ore Geology Reviews, 2010, **38**, 90–100.

15. B.Z. Kantor, *On the Malachite Spiral Crystals*, New Data on Minerals, 2004, **39**, 160-163.

16. C. Klein, C.S. Hurlbut, *Manual of Mineralogy*, John Wiley & Sons, Inc., New York, 1993.

17. B.W. Vink, *Stability relations of malachite and azurite*, MINERAL MAG, 1986, **50**, 41-47.

18. K. Sangwal, *Growth kinetics and surface morphology of crystals grown from solutions: recent observations and their interpretations*, PROG CRYST GROWTH CH, 1998, **36** (3), 163-248.

19. Y. Oaki, H. Imai, *Experimental Demonstration for the Morphological Evolution of Crystals Grown in Gel Media*, Crystal Growth & Design, 2003, **3** (5), 711-716.

20. F. Schweizer, *Bronze Objects in Lake Sites: from Patina to "Biography"*, in: D.A. Scott, J. Podany, B.B. Considine, Eds., *Ancient & Historic Metals: Conservation and Science Research*, The Getty Conservation Institute, Los Angeles, 1994, 33-50.

21. T.H. Merkel, H. Groß, W. Werner, T. Dahlke, S. Reicherter, G. Beuchle, S.H. Eberle, *Copper corrosion by-product release in long-term stagnation experiments*, WATER RES, 2002, **36**, 1547–1555.

22. C.A. Self, C.A. Hill, *How speleothems grow: An introduction to the ontogeny of cave minerals*, Journal of Cave and Karst Studies, 2003, **65** (2), 130-151.

23. J.R. Carter, *Flowers and Ribbons of Ice*, AM SCI, 2013, **101** (5), 360-369.

24. T.Wang, A. Reinecke, H. Cölfen, *In Situ Investigation of Complex $BaSO_4$ Fiber Generation in the Presence of Sodium Polyacrylate. 2. Crystallization Mechanisms*, LANGMUIR, 2006, **22**, 8986-8994.

25. L. Robbiola, P. Moret, T. Lejars, *A case study of arthropods preserved on archaeological bronzes: micro-archaeological investigation helps reconstructing past environments*, ARCHAEOMETRY, 2011, **53** (6), 1249-1256.

26. H.L. Chen, K.A. Jakes, D.W. Foreman, *Preservation of Archaeological Textiles Through Fibre Mineralization*, J ARCHAEOL SCI, 1998, **25** (10), 1015-1021.

27. R.C. Janaway, *The preservation of organic materials in association with metal artefacts deposited in inhumation graves*, in: A. Boddington, A.N. Garland, R.C. Janaway, Eds., *Death, decay and reconstruction: Approaches to archaeology and forensic science*, Manchester University Press, Manchester, 1987, 127-148.

28. L. Robbiola, D. Vilbert, T. Lejars, D. Bourgarit, B. Mille, *Characterisation of a buried archaeological bronze from the Celtic tomb n°1002 of La Fosse Cotheret (Roissy-en-France)*, in: I. MacLeod, J.M. Theile, C. Degrigny, Eds., *Metal 2001 international symposium*, Western Australian Museum, Perth, 2004, 237-242.

29. C. Maniquet, T. Lejars, B. Armbruster, M. Pernot, M. Drieux-Daguerre, P. Mora, P. Piccardo, *Le carnyx et le casque-oiseau celtiques de Tintignac (Naves-Corrèze) - Description et étude technologique*, Aquitania, 2011, **27**, 63-150.

30. T. de Groot, *Resultaten van de opgraving van een Romeins tumulusgraf in Bocholtz (gem. Simpelveld)*, Rijksdienst voor het Oudheidkundig Bodemonderzoek, Amersfoort, 2006.

31. J. Nienhuis, J. Sietsma, D. Fontijn, I. Joosten, J. Dik, *Bronze studs: colouring, reconstruction, and conservation*, in: D.R. Fontijn, S.A. van der Vaart, R. Jansen, Eds., *Transformation through Destruction. A monumental and extraordinary Early Iron Age Hallstatt C barrow from the prehistoric ritual landscape of Oss-Zevenbergen*, Sidestone Press, Leiden, 2013, 213-238.

32. M.A. Mange, D.T. Wright, *Heavy Minerals in Use*, Elsevier, Amsterdam, 2007.

33. T.L. Woods, R.M. Garrels, *Use of oxidized copper minerals as environmental indicators*, APPL GEOCHEM, 1986, **1**, 181-187.

34. L. Robbiola, R. Portier, *A global approach to the authentication of ancient bronzes based on the characterization of the alloy–patina–environment system*, J CULT HERIT, 2006, **7**, 1-12.

35. R.F. Tylecote, *The Effect of Soil Conditions on the Long-term Corrosion of Buried Tin-bronzes and Copper*, J ARCHAEOL SCI, 1979, **6**, 345-368.