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**DOI**

[10.1186/s40494-022-00710-9](https://doi.org/10.1186/s40494-022-00710-9)

**Publication date**

2022

**Document Version**

Final published version

**Published in**

Heritage Science

**License**

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**Citation for published version (APA):**

van der Stok-Nienhuis, J., Beentjes, T., Ngan-Tillard, D., van Eijck, L., Joosten, I., & van Bommel, M. R. (2022). Unravelling the construction of silver filigree spheres from a seventeenth century shipwreck using non-invasive imaging. *Heritage Science*, 10, [98]. <https://doi.org/10.1186/s40494-022-00710-9>

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RESEARCH

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# Unravelling the construction of silver filigree spheres from a seventeenth century shipwreck using non-invasive imaging

Janneke van der Stok-Nienhuis<sup>1\*</sup>, Tonny Beentjes<sup>1</sup>, Dominique Ngan-Tillard<sup>2</sup>, Lambert van Eijck<sup>3</sup>, Ineke Joosten<sup>4</sup> and Maarten R. van Bommel<sup>1,5</sup>

## Abstract

The structure of five rare filigree spheres from a seventeenth century shipwreck was examined in order to unravel their condition, manufacturing process and function. This study focuses on the application of non-invasive imaging techniques: optical microscopy, X-radiography, X-ray micro-computed tomography and neutron computed tomography. A valuation of different aspects of the applied techniques was made, aiding stakeholders in decision-making on research and conservation. The combination of theory and scientific information was used to obtain an improved understanding of the manufacturing process and function of the filigree spheres.

**Keywords:** Silver-gilt filigree, Seventeenth century, Maritime archaeology, Corrosion, Non-invasive imaging, Optical microscopy, X-ray micro-computed tomography, Neutron computed tomography

## Introduction

In 2014, a group of maritime archaeological finds was discovered in a seventeenth century shipwreck (labelled BZN17) near the coast of Texel, a Dutch island [1]. The ship is most likely Dutch but still of unknown origin and destination. Over a thousand objects, including textiles, book bands, ceramics and precious metal finds were salvaged. The entire find complex is still under investigation, but the finds are believed to originate from different geographical areas, predominantly from current-day Germany, the Netherlands and several countries around the Mediterranean Sea. Among the group of precious metals, five almost identical hollow silver filigree spheres were found (Fig. 1). Their diameter is about 30 mm and even though corrosion hinders visual identification,

they appear to be gilded. Their function is unclear<sup>1</sup>—the current hypothesis is that these were either so-called pomanders<sup>2</sup> [2], used to spread perfumes, or decorative buttons [3–5], applied to clothing or purses (see Fig. 2). Hardly any spherical jewellery filigree examples from a secure context from 1500 to 1700 AD have survived, making this shipwreck find a rare opportunity.

To date, one silver-gilt filigree pomander [6]<sup>3</sup> and one button [7]<sup>4</sup> of this design and size have been tracked down. Filigree objects are often not hallmarked and are difficult to assign to a time period and geographical area (see “Theory on manufacturing of silver filigree spheres” section). The presence of an internal opening mechanism could provide

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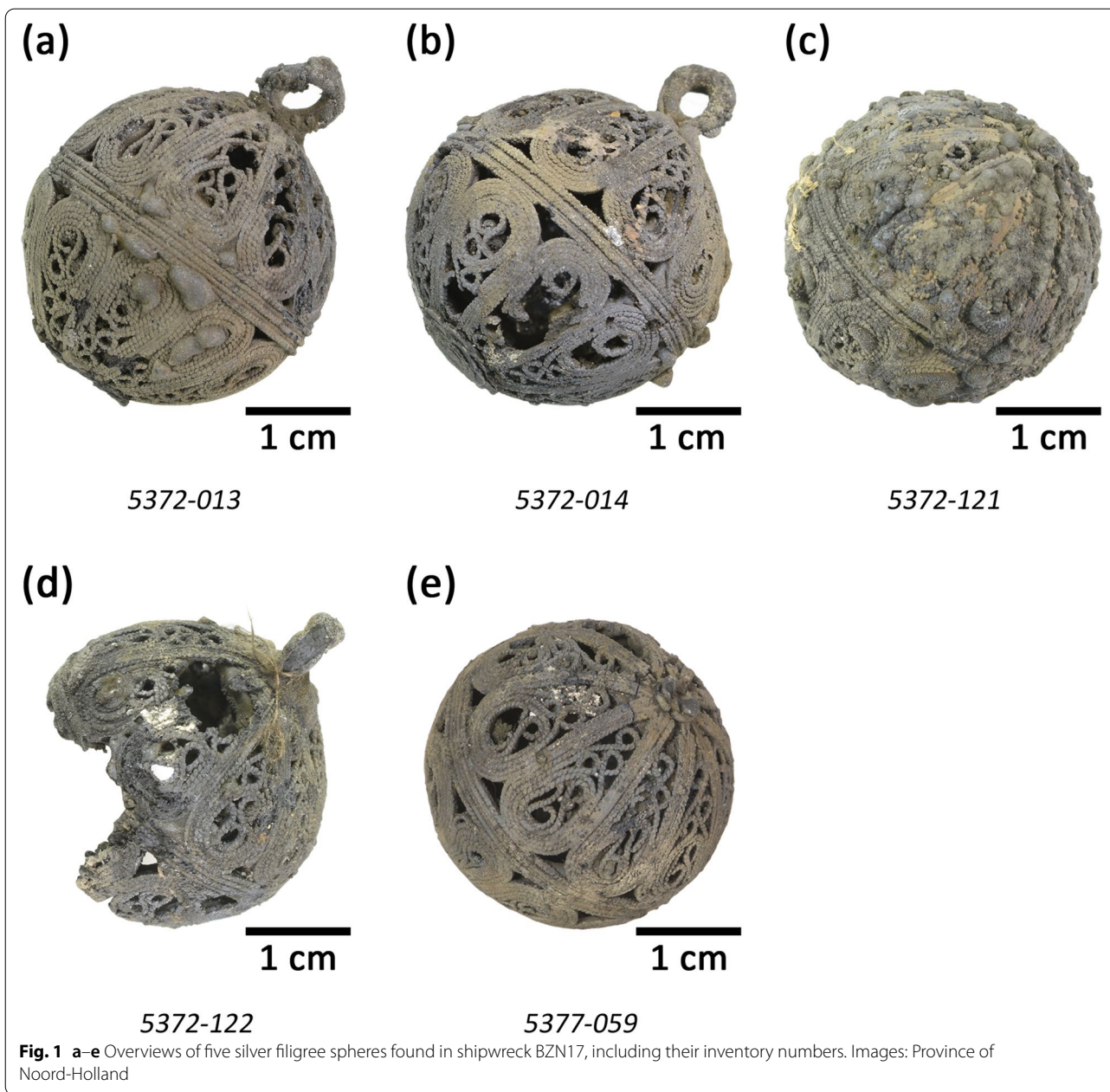
Full list of author information is available at the end of the article

<sup>1</sup> It is currently assumed that the majority of objects in BZN17 was not intended for trade. The number of spheres found to date in the wreck, would in first instance indicate personal use, even though a merchant stock is a possibility as well. On the other side, usual dimensions for buttons are around 20 mm.

<sup>2</sup> From the fourteenth century onwards, the term pomander was used for mainly spherical containers of precious materials containing aromatic substances.

<sup>3</sup> This seventeenth century pomander has an opening mechanism with an internal rod.

<sup>4</sup> A nineteenth century silver filigree button with a diameter of 30 mm.



**Fig. 1** a–e Overviews of five silver filigree spheres found in shipwreck BZN17, including their inventory numbers. Images: Province of Noord-Holland

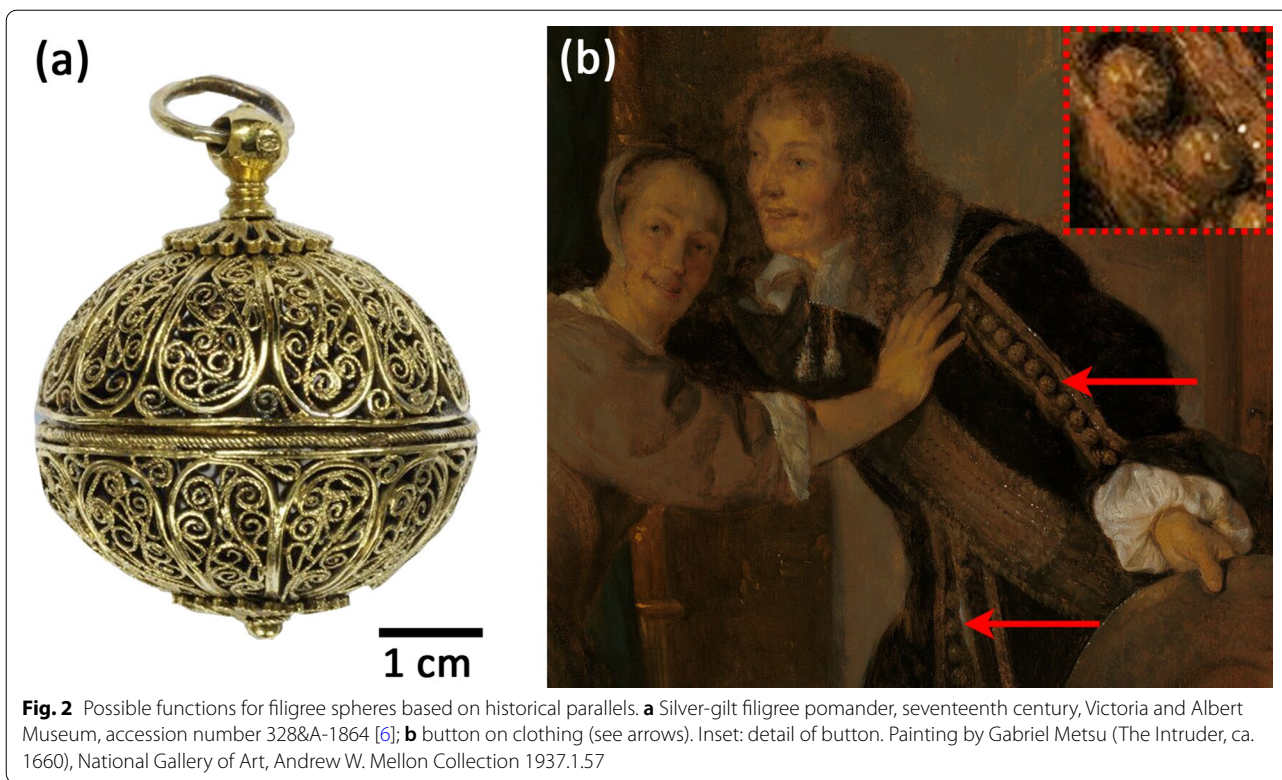
evidence to whether these spheres were either pomanders or buttons. To find indications for such a mechanism, the inner structure of the spheres had to be studied. Since the spheres, in their current corroded state, can't be opened, non-invasive imaging techniques were applied in order to aid in examining the construction of the objects.

The aim of the research<sup>5</sup> presented in this article is therefore to use the unique opportunity to study the

structure of the spheres, informing us on the manufacturing process and, in addition, their function. The structure of the filigree spheres is investigated with a focus on using non-invasive imaging techniques: X-radiography, X-ray micro-computed tomography and neutron computed tomography. In addition, application of optical and electron microscopy, X-ray fluorescence and X-ray diffraction assist in gaining a better understanding of the chemical composition of the corroded objects [8]. The combination of theory and scientific information is used to obtain an improved understanding of the manufacturing process

<sup>5</sup> The current study is part of a larger research program, entitled AMOR: Archaeological Metal Surface (Dutch: Oppervlak) Research. One of the program aims is to work out a clear overview of the data yielded per analytical method in order to aid future research of archaeological metal objects.





and function of the filigree spheres, adding knowledge to the corpus of known and studied artefacts. Also, the application of the different analytical techniques used is assessed, aiming to aid different stakeholders with making well-informed decisions on research and conservation.

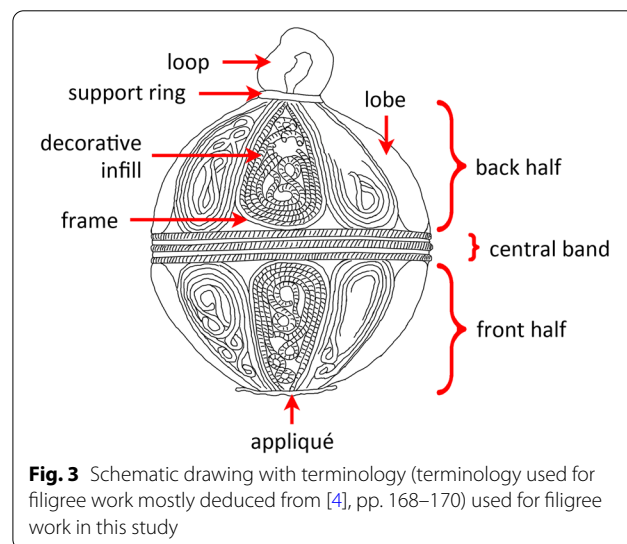
### Filigree spheres

#### Theory on manufacturing of silver filigree spheres

The techniques discussed in this section are those typical of silver filigree manufacture in European workshops in the sixteenth and seventeenth century. The hollow spheres are made in the filigree technique, a type of metalwork made from wire, a craft that is thousands of years old and still in use today [9, 10]. With this technique finely drawn wires are soldered together in decorative patterns to form objects. One speaks of open filigree work when the wires are not supported by metal backing. The wires are usually made of silver, alloyed with copper. Finished objects were sometimes fully or partially gilded. Specific terminology related to filigree in this study can be found in Fig. 3.

Pomanders were used to create a scented atmosphere, that protected individuals against the ‘poisonous smell’ of the plague, until the end of the seventeenth century [11]. Examples made from metal sheet were produced in this period in the Near East, often with floral designs [12]. Filigree examples are also known, especially for the higher social classes [13], and are often attributed to Western Europe (e.g. [14]).

Filigree spheres were used throughout the Mediterranean and Europe as buttons as part of regional costume, also called peasant jewellery [15]. Their decorative aspect was at least as important as the functional and their use was not limited to the lower classes: the elite in many countries would wear similar dress on occasion, but executed in finer materials [16]. Peasant buttons are often difficult to identify. This [11] is mainly because there is a



limited number of ways in which twisted silver wires can be arranged, so the same design can be found in multiple regions. Also, especially open filigree work provides less places to put a hallmark. Peasant jewellery was rarely marked anyway. Spherical filigree buttons, made of two hemispheres, are known to be produced in Germany, Hungary and Russia [17, 18].

The manufacturing of a filigree sphere requires multiple steps, which are summarised below.

[A]

The first step would be to make the rosette-shaped **frame** consisting of ten teardrop-shaped lobes. These are formed out of wires of a rectangular cross-section, usually made by wire drawn using draw plates with rectangular holes. The frame can be either made out of one strip or ten separately bent lobes (Fig. 4). These lobes are bent into the teardrop shape using a mandrel and pliers [19] and are subsequently placed next to each other to form a circle, after which they are soldered together.

[B] Two types of **soldering**<sup>6</sup> were likely practiced around 1650 to solder filigree work:

- (1) Colloidal (or eutectic) soldering [9] using a colloidal mixture<sup>7</sup> of copper salts and tragacanth gum as organic binder that burns away completely. It works on the principle of introducing copper in the contact areas and thus locally lower the melting point, enabling local fusion [20]. This results in a very smooth joint.
- (2) Soldering using snippets or paillons<sup>8</sup> [21] or filings<sup>9</sup> of a silver alloy solder [22], that was often composed of silver and brass. The joints, where the wires touch each other, are filled with the solder that has a lower melting point than the wires to be joined. Depending on the amount of solder used, a smooth joint is obtained, but remains of molten solder might be visible.

[C] The next step would be to (partially) **fill the structure** of the wired frame with decorative scrolls of multi-twisted wires (i.e. two or more round wires twisted together<sup>10</sup>). These are usually flattened, using a rolling mill or light hammering, to make them easy to bend and easier held within the outer wire frame. The

multi-twisted wire is subsequently shaped using pliers and then soldered inside the outer frame (Fig. 4).

[D] The filled frame is then **shaped** in a doming block: a metal block with concave depressions, which forms a die. When the frame is placed in a deep concave depression and hit from above with a convex form, such as a punch or hammer, a perfect hemisphere will form (Fig. 4). This is possible because all the parts are connected to each other with solder and the silver is relatively soft due to annealing during the soldering process.

[E] Before the two hemispheres are joined, the **loop is added** to the back half and **appliqué is added** to the front half. The loop, made of bent wire, is inserted through the centre of the lobbed frame and soldered on the inside where it protrudes.

[F] The rims of the two **hemispheres are joined** together against a central band (Fig. 4). This band can be used to connect both halves permanently, or can contain an opening mechanism. In order to make a perfect fitting joint, the rims of the hemispheres, should be perfectly flat. This can be achieved by filing or sanding.

[G] A complete sphere is now created, and this is the moment when **gilding** could be applied. During the sixteenth and seventeenth century, three methods were in use for gilding this type of object:

- (1) Amalgam gilding, also called fire-gilding, where a paste of gold and mercury is brushed onto a freshly cleaned surface. The object is subsequently heated to about 300 °C to evaporate the mercury and to enable diffusion of gold into the silver, thereby establishing a well-adhered, but porous gilding layer, with an average thickness of 2–10 µm, depending on the number of applications [23], up to 100 µm [8]. Polishing, by burnishing, will result in a compact, lustrous appearance. This is the method that was generally used for filigree work.
- (2) Electro-chemical replacement gilding, also called cold or dry gilding. This a gilding method whereby a gold-chloride compound is applied at room temperature [24]. This results in a relatively thin layer of gold on the surface (< 5 µm) [25].
- (3) The use of pre-gilded silver wire. This wire, whereby the gold layer on the surface has been applied by diffusion bonding (joining with heat only, so without the use of solder) [26], was used for example for textile threads. Not much is known about the use of pre-gilded wire for filigree work.

<sup>6</sup> Gold and silversmiths have used the term soldering traditionally for high temperature joining of precious metals with a filler metal, in preference to the more appropriate term brazing.

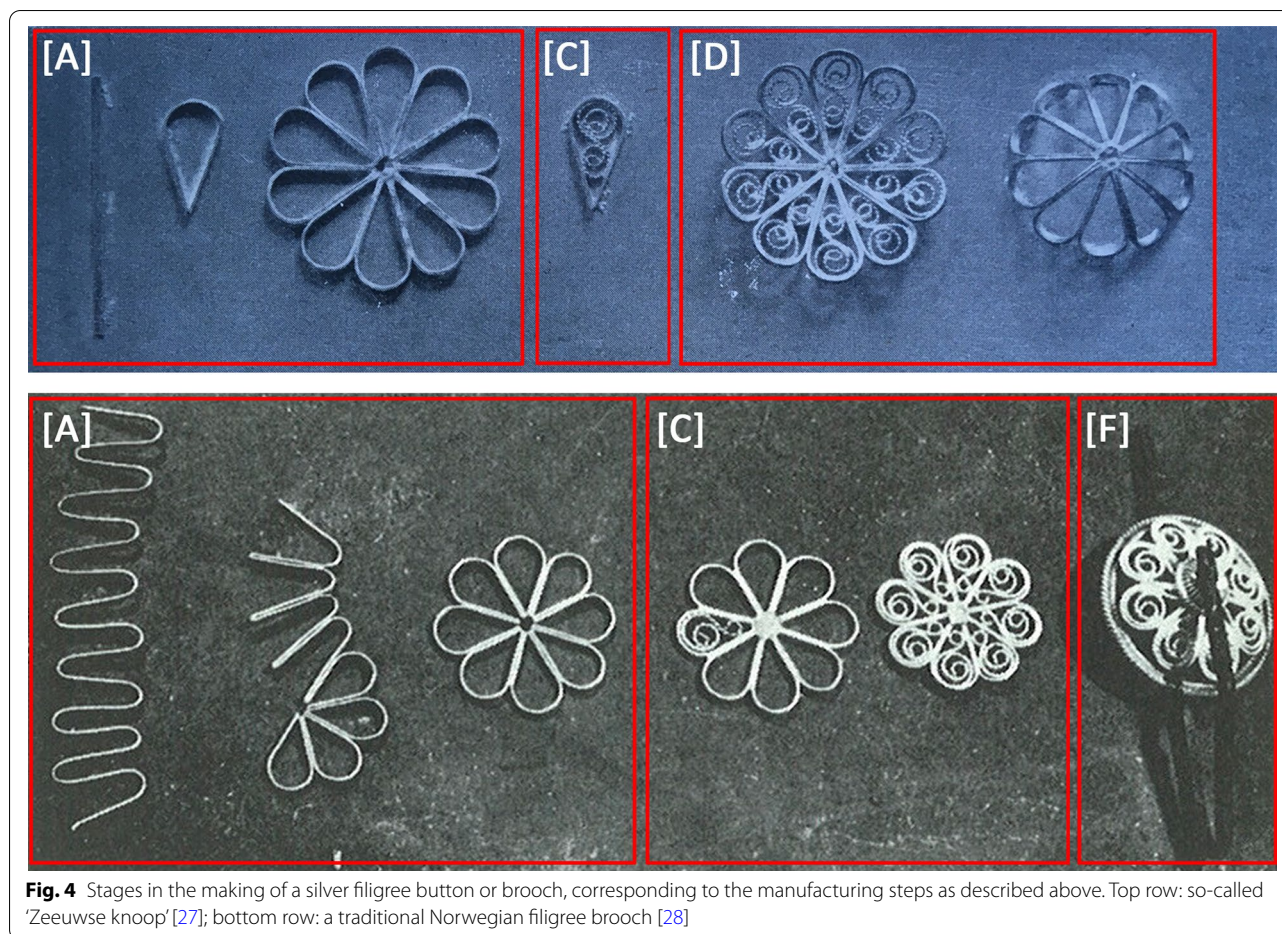
<sup>7</sup> Cellini describes the use of Verdigris, salts of ammonia and powdered borax.

<sup>8</sup> Paillons are small snippets of solder and are usually of the same composition as filings of solder.

<sup>9</sup> Cellini describes that silver solder was filed and together with powdered flux sprinkled over the joints.

<sup>10</sup> Multi-twisted wire is superficially similar to single twisted wire (i.e. an oval wire twisted on its own axis), but the turns are much tighter and closer together (e.g. [4, 15–17, 34, 35], p. 169).





**Fig. 4** Stages in the making of a silver filigree button or brooch, corresponding to the manufacturing steps as described above. Top row: so-called 'Zeeuwse knoop' [27]; bottom row: a traditional Norwegian filigree brooch [28]

### Spheres from shipwreck BZN17

In total, five hollow spheres made in the open filigree technique are present in the excavated collection from BZN17 (Fig. 1).<sup>11</sup> Two are (nearly) intact (inventory numbers 5372-013 and 5372-014), two whose loop is broken off (5372-121 and 5377-059) and one is missing its front half (5372-122).<sup>12</sup> No hallmarks or any other markings were detected that might have helped dating or geographically locating these objects.

The spheres consist of two decorated hemispheres, connected along their rims with a band, that consists of alternating multi-twisted wire and rectangular cross-section wire. Each hemisphere is built up of a rosette with ten teardrop-shaped lobes, which are each made of a frame consisting of a single wire with rectangular cross-section ( $\sim 0.4 \times 0.8 \text{ mm}^2$ ) and a decorative infill of multi-twisted wire with a rounded rectangular cross-section

( $\sim 0.4 \times 0.6 \text{ mm}^2$ ). The centre of the rosette that forms the front half of the sphere is decorated with a flower-like appliqué (see Fig. 12a).

The diameter of all spheres in this research varies around 30 mm. One has to keep in mind that the current dimensions are influenced by the presence of corrosion products. The visible part of the loop is about 5 mm in height and outer diameter.

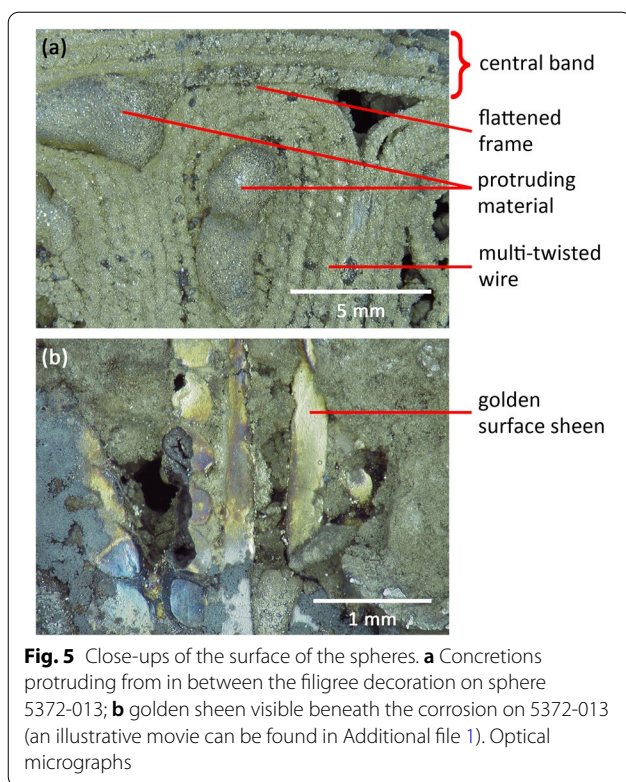
All spheres are heavily corroded and fragile. Multiple different corrosion colours can be distinguished, ranging from grey to brown to black. Also, millimetre-thick concretions can be seen within the open filigree work (Fig. 5a). A golden sheen can be seen occasionally (Fig. 5b), suggesting that the spheres are partially or entirely gilt.

### Analytical methods

All spheres have been studied with **optical microscopy** (a Leica MZ7.5 and a Hirox KH-7700 Digital Microscope). One sphere (5372-013) was selected, based on its completeness, to be analysed by multiple imaging techniques.

<sup>11</sup> Three of the spheres are already cleaned and consolidated with ethyl-methacrylate copolymer Paraloid B-72 (5372-121, 5372-122, 5377-059).

<sup>12</sup> Although sphere 5372-122 was damaged in such a way that the interior could be studied, it was not clear whether parts of a possible closing mechanism were missing as well.



**X-radiography** was used to assess the mechanical integrity of the sphere and to gain insight in its construction by providing two-dimensional images. The instrument used is a General Electric Eresco 280 MF, 2 mm thick copper filter and BIX- and FP-detectors. The pixel size provided is 125  $\mu\text{m}$ .

To enable non-invasive inspection, computed tomography using both X-rays and neutrons, was performed, which resulted in 3D-computed models of the sphere. **X-ray micro-computed tomography** ( $\mu\text{CT}$ ) was done with a GE Phoenix Nano Focus X-ray System, and **neutron computed tomography** (NT) at the FISH beam line [29] of Delft University of Technology, the Netherlands. The tomography voxel size provided is  $40 \times 40 \times 40 \mu\text{m}^3$  by  $\mu\text{CT}$  and  $150 \times 150 \times 150 \mu\text{m}^3$  by NT. The two techniques have a complementary sensitivity to various chemical elements. **Neutron powder diffraction** (NPD) was done at the PEARL instrument [30] of Delft University of Technology, the Netherlands.

Additionally, **X-ray fluorescence** (XRF) was used to qualitatively identify the chemical elements present on the surface of the sphere. The instruments used are a portable Olympus Delta Professional X-Ray Analyzer (Mo-tube, spot size 10 mm) and a Bruker Artax portable micro-XRF spectrometer (Rh-tube, spot size 90  $\mu\text{m}$ ). ARTAX Spectra resp. PyMCA software was used to process the data. **X-ray diffraction** (XRD) was used

to qualitatively identify crystalline components. The instrument used is a Bruker D8 Discover with a  $\text{Cu-K}_\alpha$  source and spot size of 0.3 mm equipped with GADDS and EVA software containing the JCPDS-database. A detached sphere fragment was embedded in epoxy resin and prepared by grinding and polishing. **Scanning electron microscopy–energy-dispersive X-ray spectrometry** (SEM–EDS) was applied on this cross-section to obtain information on the alloy, the surface finishes and manufacturing techniques. The instrument used is a JSM IT7000HR from JEOL, coupled to a JED-2300-Fully integrated JEOL EDS system (100  $\text{mm}^2$  Silicon Drift Detector).

### Results and discussion on filigree spheres from BZN17

This section discusses the construction elements and manufacturing steps of the filigree spheres from BZN17, based on the results obtained by various analytical methods (“Analytical methods” section).

#### Frame construction

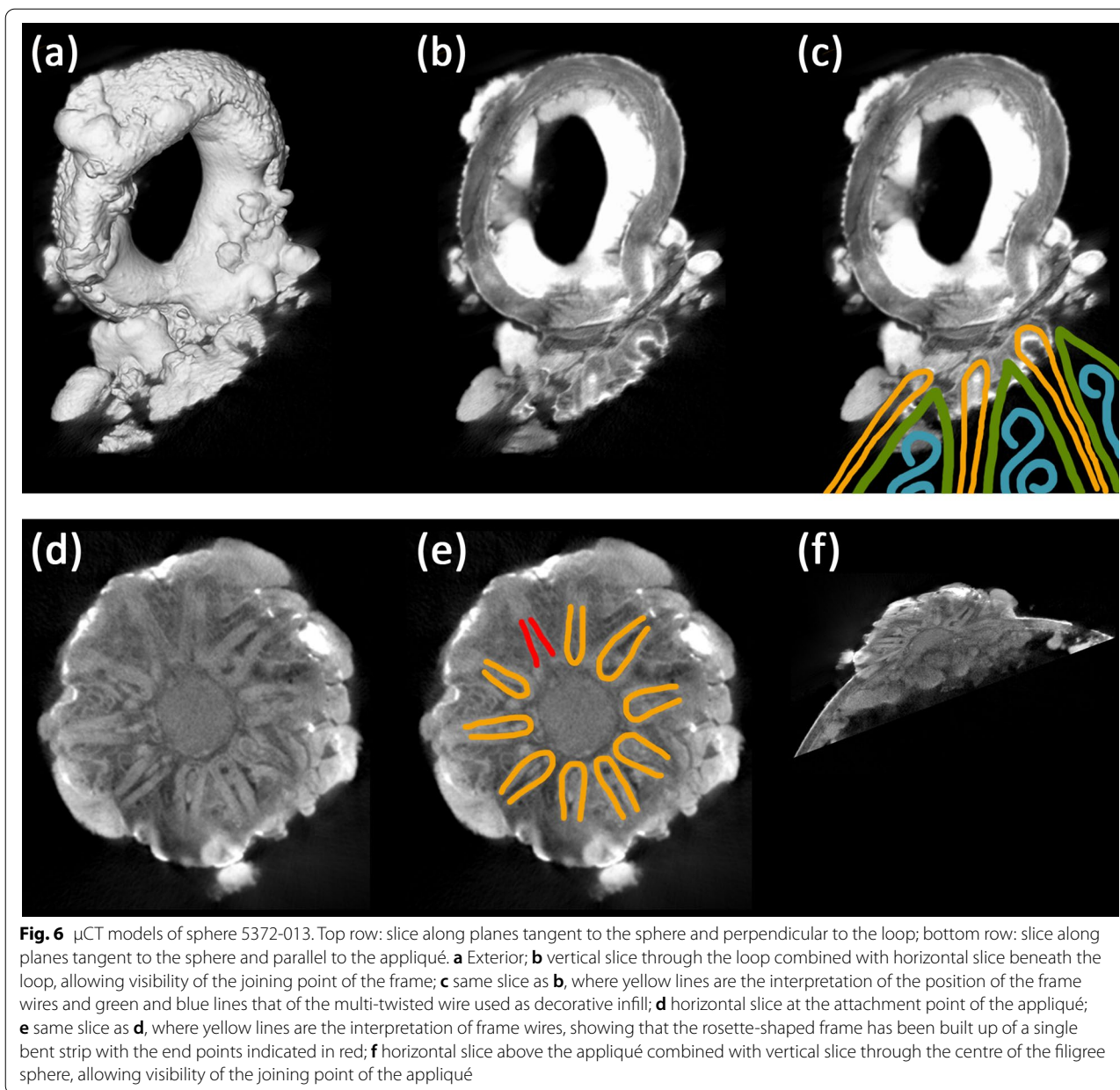
As mentioned in “Theory on manufacturing of silver filigree spheres” section, the frame can be either made out of ten separately bent lobes or one strip. The structure of the frame cannot be determined by visual examination as the locations where the lobes converge are hidden by the corrosion around the loop and the appliqué. Computed tomography provides the possibility to visualise the interior of the sphere. By digitally slicing the three-dimensional reconstructed model (see also Additional file 2), the manufacturing method of the frame can be deduced with more certainty than visual inspection alone. Figure 6 shows that the outer ends of the frame appear to be bent, suggesting that the frame of both hemispheres was made out of a single strip that was bent into teardrop-shape lobes.

#### Pomander or button?

The presence or absence of an opening mechanism is an important factor in characterising whether the spheres are pomanders or buttons. In the case of a pomander, there are primarily two types of opening mechanisms one can find: a vertical internal rod (from loop to flower-like appliqué) that screws the upper and lower halves together and a screw (or bayonet) mechanism around the central band.

If an internal rod is present, it usually protrudes on the exterior of both hemispheres. Visual inspection does not reveal any externally protruding part through the appliqué. The interior of the spheres can be visualised with X-ray imaging.





**Fig. 6**  $\mu$ CT models of sphere 5372-013. Top row: slice along planes tangent to the sphere and perpendicular to the loop; bottom row: slice along planes tangent to the sphere and parallel to the appliqué. **a** Exterior; **b** vertical slice through the loop combined with horizontal slice beneath the loop, allowing visibility of the joining point of the frame; **c** same slice as **b**, where yellow lines are the interpretation of the position of the frame wires and green and blue lines that of the multi-twisted wire used as decorative infill; **d** horizontal slice at the attachment point of the appliqué; **e** same slice as **d**, where yellow lines are the interpretation of frame wires, showing that the rosette-shaped frame has been built up of a single bent strip with the end points indicated in red; **f** horizontal slice above the appliqué combined with vertical slice through the centre of the filigree sphere, allowing visibility of the joining point of the appliqué

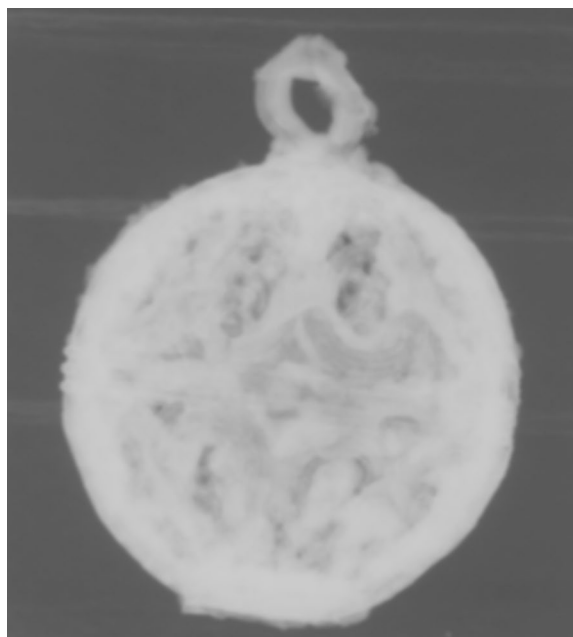
With X-ray imaging (Fig. 7), no remnants of an internal (threaded) rod and/or a tube attached to the loop and appliqué was detected on any of the spheres. Contemporary western European guild regulations usually stated that non-precious material was not allowed to be used in precious metal objects. It is therefore unlikely that an internal rod had been present during use, but corroded away during its time on the seabed. In addition, there are no corrosion colours, morphologies or cavities present that point in the direction of an entirely corroded rod.

In the case of a screw closure, an extra bright area is expected in the central band in the X-radiographs, due to

the double amount of material in that location. This was not seen in any of the filigree spheres from BZN17.

However, details like the frame and filigree wire are also obscured, and one cannot conclude on the absence of an opening mechanism solely based on X-radiographic results. This is due to the limitations of the technique and the used equipment: a two-dimensional image is yielded from a three-dimensional object and the equipment has a relatively low resolving power. It was therefore decided to explore the possibilities of three-dimensional reconstructions made by  $\mu$ CT and NT and the results concerning the central band are seen in Fig. 8.





**Fig. 7** X-radiograph of sphere 5372-013. Hardly any details can be discerned

With tomography, no construction for either opening mechanism type can be observed as well: no internal rod (see also Fig. 11b) and no overlapping parts in the central band. This leads to the conclusion that the central band is formed by soldering alternatively multi-twisted wire and rectangular cross-section wire, into a sandwich of three twisted wires with two flat rectangular cross-section wires in between. These wires have dimensions comparable to the wires used for the frame and the decorative infill of the lobes. The band is subsequently connecting both hemispheres, also by soldering. Evidence for making a perfectly fitted joint (see [F] in “[Theory on manufacturing of silver filigree spheres](#)” section) in the BZN17-spheres is the fact that some of the lobes are flattened (Fig. 5a). The absence of an opening mechanism indicates that the spheres have not been used as pomanders.

#### Wire characteristics and corrosion

The individual multi-twisted wires can be visualised by optical microscopy and tomography. Their cross-section is rounded rectangular (Figs. 8 and 9), which indicates that this decorative wire is flattened (see [C] in “[Theory on manufacturing of silver filigree spheres](#)” section).

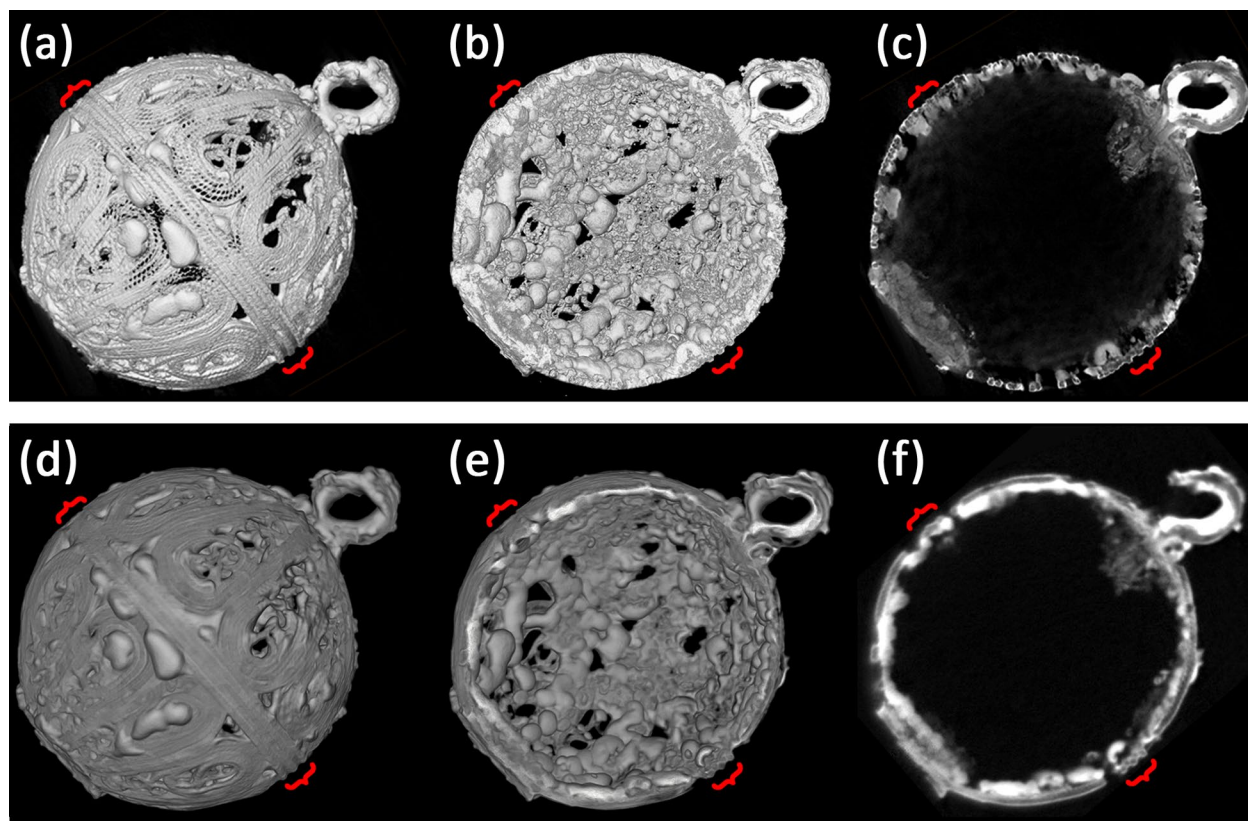
Optical micrographs (Fig. 9) show that the core of damaged wires consists of a relatively loose infill with crumbled material. This stratigraphy of the wires is confirmed by tomographic images: the core of the wire appears to be dark-grey to black and therefore either partly hollow

(see Fig. 8) or filled with porous or low-attenuating material. The exterior of the multi-twisted wire has a higher density for about 90 mm on average, which can be identified as the gilding layer (see “[Gilding](#)” section), according to both XRF (see Additional files 3 and 4) and SEM–EDS (Fig. 10). The material that is still left in the interior of the wires (see Fig. 10) is mainly composed of silver (Ag), sulphur (S) and copper (Cu). Mercury (Hg) is seen throughout the entire wire structure and at the exterior of the sphere. It is possible that its presence is the result of the use of silver that has been extracted with the so-called patio process, that makes use of mercury [31]. Extensive heating during the fire gilding process could have led to a relatively large compositional gradient from exterior to interior, but this does not explain the presence of mercury concentrations in the possible solder area. The presence of mercury at the exterior of the sphere suggests that corrosion processes cannot be ruled out as explanation.

A compositional gradient of gold (Au) can be seen, which is indicative for diffusion during fire-gilding. The spheres currently consist mainly of corrosion products: acanthite ( $\text{Ag}_2\text{S}$ ), covellite ( $\text{CuS}$ ) and possibly chalcocopyrite ( $\text{CuFeS}_2$ ), as confirmed by XRD (see Additional file 5). The NPD data can be fitted with  $\sim 95\%$   $\text{Ag}_2\text{S}$  and  $\sim 5\%$  pure Ag. Iron (Fe) is present mainly in heavily degraded areas, indicating that this material is likely deposited during the degradation of the spheres on the seabed. There is no clear correlation between iron and chlorine, which would point in the direction of harmful active corrosion that should be actively treated.

Considering the possible manufacturing process, it would be unlikely that one uses a wire with a hollow core or a lower-density core, like silk or wool, with a metallic cladding. Such a filigree structure could not be shaped into a hemisphere due to the fragility of the wire. In addition, the soldering and gilding of these wires at elevated temperatures would not allow the use of cores of organic material. Also, there are no known examples of the use of non-solid wires for filigree work.

The protruding corrosion seems to display an irregular pattern on the exterior surface (Figs. 1 and 5a). The  $\mu\text{CT}$  and NT models show that these relative highly absorbing concretions are omnipresent in the interior (Fig. 8b). This implies that the concretions on the exterior have grown mostly from the interior of the sphere, and/or along the outside of the wires. The high-quality of the finish of the spheres suggests that these concretions were not present as a result of manufacture and are therefore the effect of corrosion during their time on the seabed. The interior of the sphere has not been protected by a gilding layer and is therefore expected to be the first area where dissolving of silver into seawater will take place and where the silver alloy wire



**Fig. 8** Reconstructed tomography models of sphere 5372-013, where bright areas indicate highly absorbing material. The central band that joins the hemispheres is indicated by the red accolades. Top row:  $\mu$ CT; bottom row: NT. **a, d** The exterior; **b, e** the interior, centrally sliced through the loop; **c, f** a single (30  $\mu$ m thick) slice, corresponding to the frontal view shown in **b** and **e**

will eventually be converted into  $\text{Ag}_2\text{S}$  and  $\text{CuS}$ . Corrosion of silver and eventually copper is expected when a porous gilding layer is present [32]. Continuous silver dissolution and diffusion results in the formation of relatively large volumes of corroded material, that ultimately protrude from the interior to the exterior through the open filigree work. A wire core with relatively lower density material is the result. The higher-density outside of the wires therefore represents chiefly the intact, non-corroded gilding, which has probably prevented the sphere from dissolving entirely. Unravelling the complex corrosion mechanisms, including biological influences, is outside the scope of the current study and to test the above hypotheses, more research should be carried out.

Different colours can be identified on the spheres, ranging from brown to black (see Fig. 1). The spot size of the Olympus instrument used for XRF is too large to be able to measure separate areas, and appropriate standards for quantification are not available for the Bruker XRF instrument. A reliable quantification of the heterogeneous surface is therefore not possible.

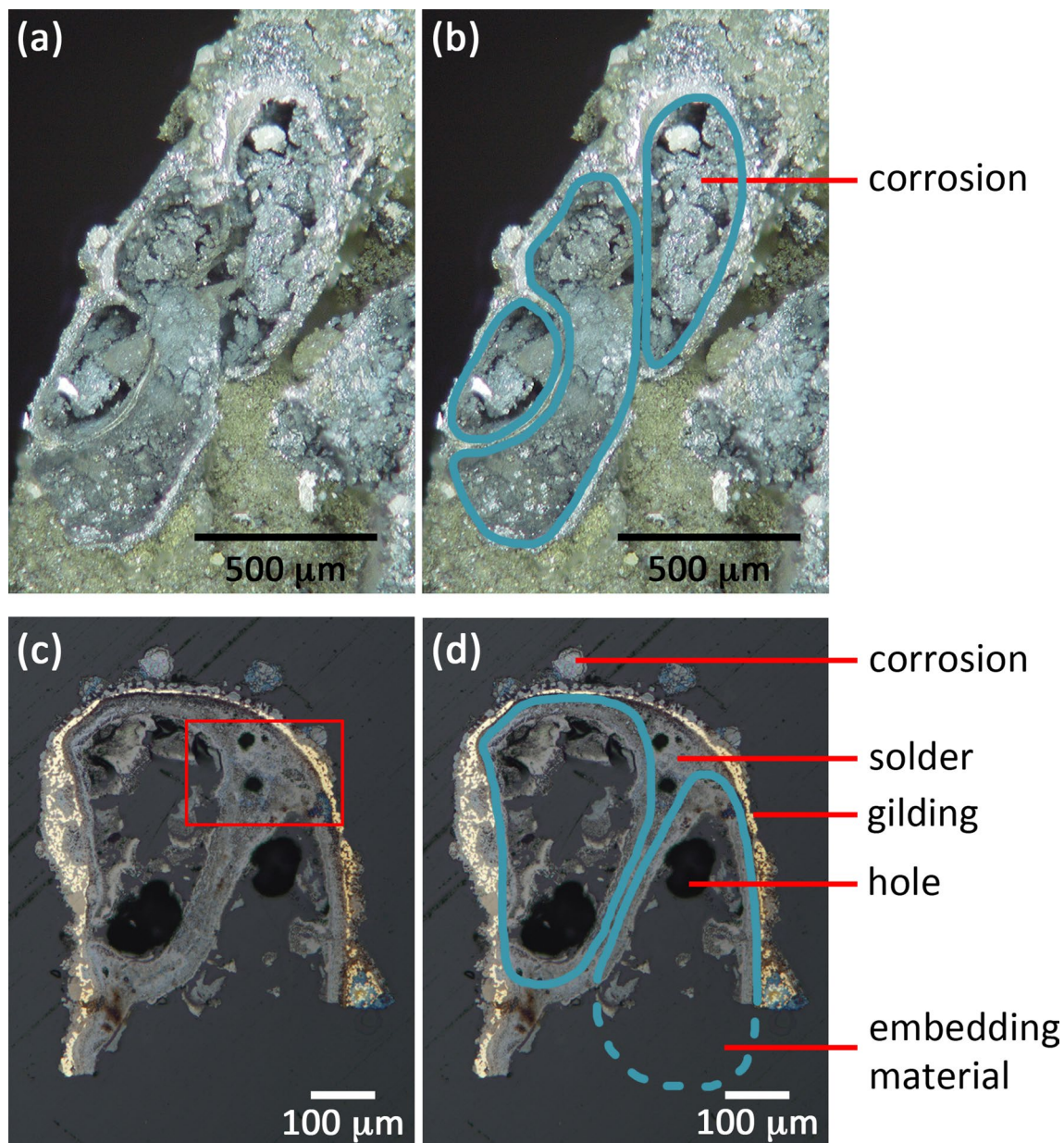
General assumptions can be made, based on SEM–EDS of the cross-section, XRD and NPD. Acanthite ( $\text{Ag}_2\text{S}$ ) is a black compound, as is covellite ( $\text{CuS}$ ), especially when present as a thick layer. Chalcopyrite ( $\text{CuFeS}_2$ ) is usually brownish. Mixtures of compounds can result in varying colours, and adhering concretions from the seabed have influence as well.

#### Loop and appliqué

The wire used for the loops on the spheres from BZN17 has a D-shaped cross-section. On the outside of the hemisphere, where the lobes join, an extra ring was added as a reinforcement where the loop enters the hemisphere (see Fig. 11a) and probably as a cover for the area where the lobes converge and is the loop is soldered into.

The composition of the loop and ring could not reliably be quantified with XRF due to the presence of corrosion. The elements that are identified in both structural components are copper, silver, gold, mercury and lead (see Additional file 4). In addition, the relative absorbance of the materials of the loop and the ring in tomographical images is comparable to that of





**Fig. 9** Damaged wire, showing that its core is completely filled with corroded material. Blue lines are the interpretation of wires. **a** In situ on sphere 5372-013; **b** same image as **a**; **c** cross-section of a decorative fragment from sphere 5372-122. The red area indicates the location measured by SEM-EDS (see Fig. 10); **d** same image as **c**. Optical micrographs

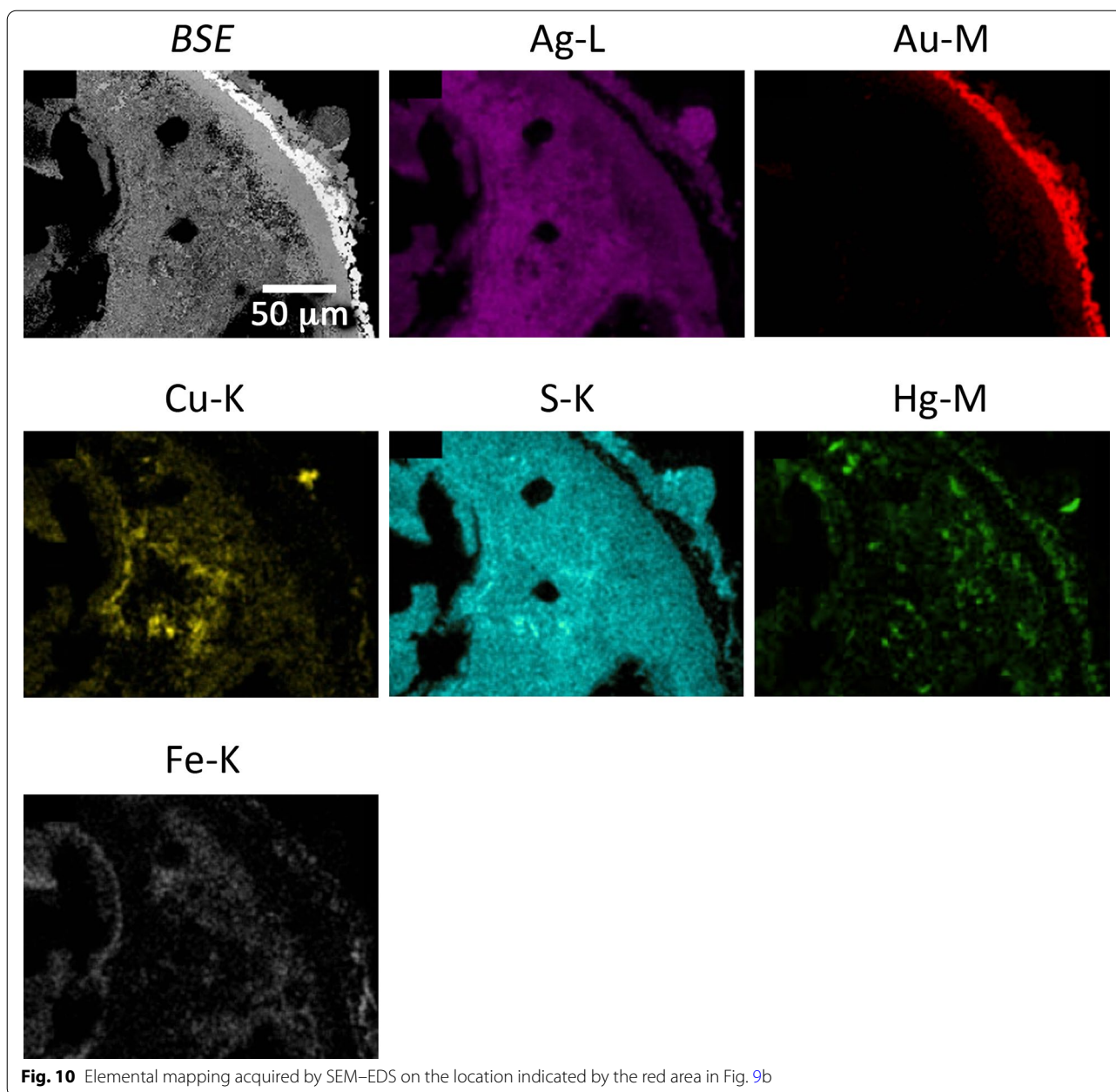
the corroded filigree wires. It is therefore highly plausible that the loop and the ring are also made of silver alloyed with copper, possibly alloyed with a small amount of lead.

With tomography, a layered appearance of the core of the loop can be seen (Fig. 11b). To create the D-shaped wire for the loop, wire is drawn through draw plates. This mechanical action leads to plastic deformation of the metal, which results in a heavily deformed

microstructure in the longitudinal direction of the wire. The subsequent defects in the microstructure might lead to decreased resistance to corrosion, which could eventually lead to enhanced visibility of a directional ‘layering’ when the material is completely corroded.

Highly absorbing areas are identified with tomography at the inside of the loop and surrounding the support ring (see also Fig. 8). Neutron bright regions mean the presence of strongly neutron absorbing material,





**Fig. 10** Elemental mapping acquired by SEM-EDS on the location indicated by the red area in Fig. 9b

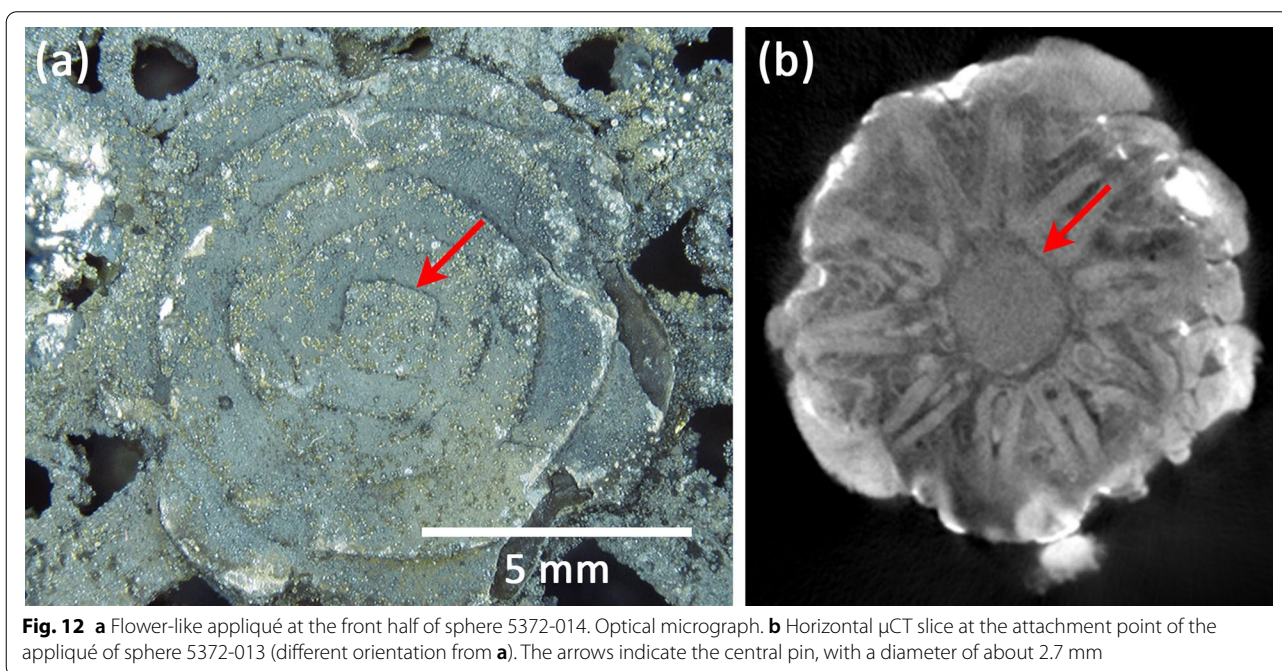
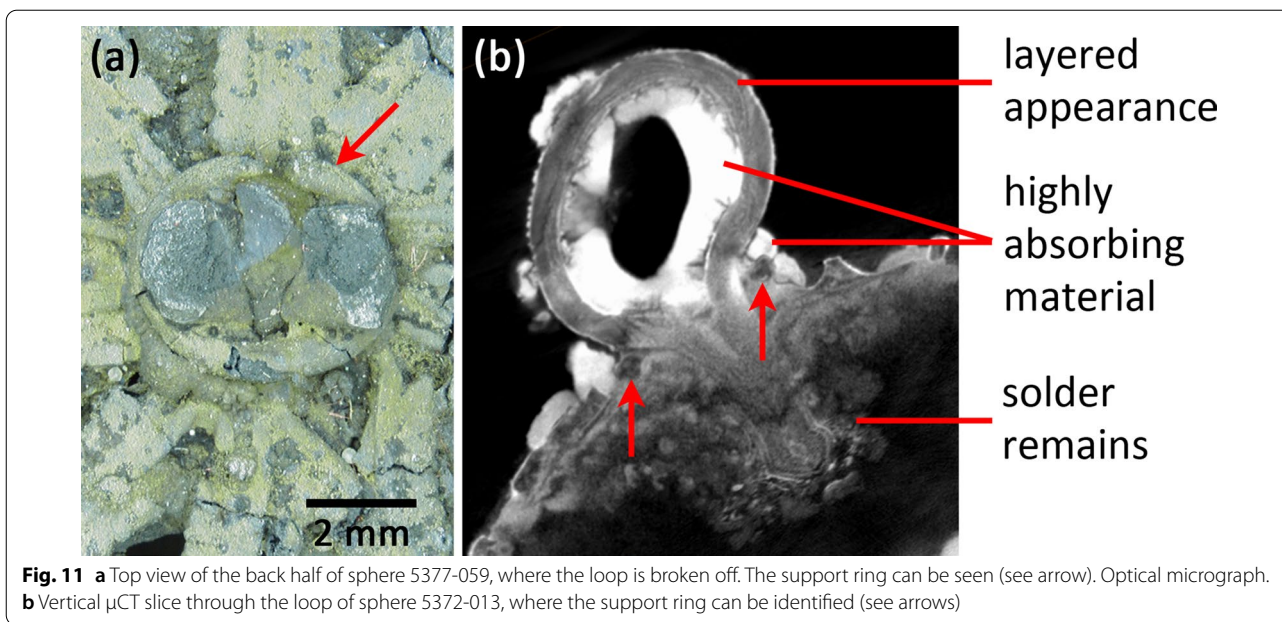
which can be e.g. silver, gold, lithium (Li), hydrogen (H), boron (B) and chlorine (Cl); X-ray bright regions mean high-density material. As these highly absorbing areas are bright in both tomographies, it means that they are not low-density materials like Li, H, B and Cl and that they are most likely highly absorbing metals like silver, gold and/or copper.

XRF measurements exclude the presence of large amounts of silver, gold and lead at the surface, which could have accounted for a high atomic number leading to a highly absorbing area. It is therefore hypothesised that this is the result of a high density of silver corrosion

products, probably also containing copper, in a densely-packed structure. It is currently unknown to the authors what mechanisms could cause different corrosion phenomena to occur on a single object.

The flower-like appliqué was probably made by cutting petal-shaped discs or segments, placed on top of each other and held together by a short central pin with a square base that was soldered in place (see Figs. 6f and 12).

Material surrounds the loop and the flower-like appliqué in the interior of the spheres (see Figs. 8c and 12b). Its location and relative X-ray and neutron absorbance suggest that this is (corroded) solder material, indicating



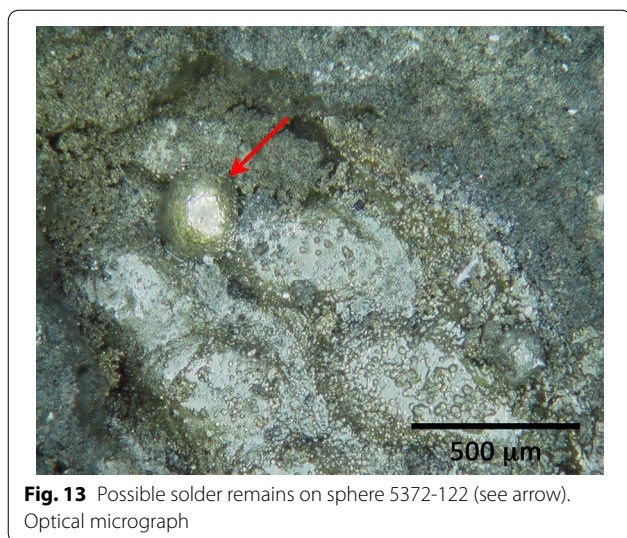
that both parts are fixed to their relative hemisphere by soldering with silver alloy solder in the construction process, before adding the central band.

**Solder**

It can be convincingly argued that the filigree spheres are soldered using silver alloy solder (method [B](2) in

“Theory on manufacturing of silver filigree spheres” section). A spherical feature (diameter  $\sim 250 \mu\text{m}$ ) with a metallic appearance can be observed on the exterior (Fig. 13). This suggests that the solder material has been in a liquid phase before solidifying into a spherical shape. This is indicative for the use of additional material in the form of snippets, paillons or filings of silver solder, and not of a mixture of copper salts with tragacanth





**Fig. 13** Possible solder remains on sphere 5372-122 (see arrow). Optical micrograph

gum (colloidal soldering: method [B](1) in “[Theory on manufacturing of silver filigree spheres](#)” section). The golden colour is most probably the result of gilding after soldering.

A plausible solder area is identified in the cross-section of the multi-twisted wire (see Fig. 9b). Its location, between the outside of the individual wires and the inside of the gilding layer, suggests that it corresponds to soldering the decorative infill inside the outer frame (step [C] in “[Theory on manufacturing of silver filigree spheres](#)” section). The area is mainly composed of silver, with a relatively increased copper concentration compared to the wire and gilding layer, and sulphur (Fig. 10). One would expect a higher copper concentration and hardly any silver if colloidal soldering had been applied, but the effect of corrosion might have resulted in the current chemical composition. The size of the area implies the addition of a relatively large amount of material, which also corresponds to soldering with silver alloy solder.

### Gilding

Of the three possible types of gilding, the filigree spheres from BZN17 display all characteristics of amalgam gilding of the finished object: the presence of (localised) gold and mercury (as measured with XRF and SEM–EDS) and a corresponding layer thickness of several to 80 μm (deduced by OM, tomography and SEM–EDS). The gilding layer shows gold-rich areas that are hardly deformed. This morphology corresponds to, at the most, slightly burnishing after gilding [33]. This layer is too thick to be an electro-chemical replacement gilding. Pre-gilded wire is also not an option because there is no gilding layer between the individual wires (as visible from tomography). To fabricate an object out of pre-gilded wire

requires the use of gold solder to avoid a colour difference. High amounts of gold, without mercury but with silver and possibly copper, at the exterior of a sphere were not detected (compare with Fig. 10), thereby rendering the use of gold solder highly unlikely.

### Concluding remarks on the function and origin of spheres from BZN17

The previous sections have shown that the filigree spheres from BZN17 can be regarded as buttons. Concerning the attribution to a geographical origin, it is only possible to compare with known parallels. Since only a few relevant publications and comprehensive museum collections exist (see also “[Theory on manufacturing of silver filigree spheres](#)” section), one should keep in mind that a distorted image might be created.

The presence of a central band joining both hemispheres is found only in the eastern Mediterranean and the eastern part of Central Europe. A relatively broad band and a dense infill is a characteristic of Hungarian buttons. A flower-like appliqué at the front half is also found exclusively on nineteenth century buttons from Austria and Hungary and/or Slovakia. These buttons would have been worn by both men and women [34]. The conservative nature of traditional jewellery makes it well possible that these buttons are variations on a type that was produced in the seventeenth century. Buttons were often kept detached from their associated dress [35]. Since the recovery of the buttons was not properly documented during salvage, there is no way of knowing whether these specific filigree spheres belonged to a garment<sup>13</sup> or were part of the cargo.

### Considerations about results

#### Considerations about non-invasive imaging techniques

















In this section, several comparative observations concerning the applied imaging techniques are discussed, based on results and experiences from this study.

For all non-invasive imaging techniques, it is desirable that the object is being viewed prior to a conservation treatment. Not only does this give the conservator a better idea of the morphology and condition of the object, but materials added as part of a treatment such as consolidants or glues, could interfere with the imaging. Neutron computed tomography specifically, is very sensitive to hydrogen-containing compounds, such as polymers. Also, sampling original material for further analysis should ideally be carried out prior to treatment, especially when (remains of) organic material is expected.

<sup>13</sup> The School of Historical Dress, London, is involved in the research of the textile salvaged from BZN17. They could not link the filigree buttons to any of the textile currently investigated.



**Table 1** Comparative overview of several aspects of the non-invasive imaging techniques applied in this study, based on results and experiences concerning the filigree spheres from BZN17

	Resolving power	Composition characterisation		Accessibility/costs
		Qualitative	Quantitative	
OM				
X-ray imaging				
μCT				
NT				

There is a preferable order for applying imaging techniques to corroded precious metal objects. Optical microscopy is the first technique to examine the object and its condition, to find clues about its manufacturing process and possible active degradation mechanisms. When a complex construction of the object is expected, one can then apply the long-established and relatively easily accessible and cost-efficient technique of X-radiography to gain more information. When the object interior needs to be visualised in a three-dimensional way and/or a higher resolution is needed, μCT can be employed. When, in addition, organic materials are expected in a metallic object, NT can be applied, as this technique is sensitive to chemical elements with low atomic number.

X-radiography usually produces images with lower resolution than that of tomography and in this study, the μCT models produced the most detailed images. NT is able to provide gamma spectroscopy in addition to diffraction and imaging, which may contribute to information about chemical composition of the object in its entirety, especially complementary to the results gained with XRF and SEM–EDS. In this article, the gamma spectroscopy results are not shown because the XRF and SEM–EDS data proved to be the most representative for the discussion.

Table 1 is a visual summary of several aspects of the non-invasive imaging techniques applied in this study and where a relative rating is given. Even though the rating is over-simplified, the table nevertheless shows possibilities and limitations and can therefore aid future research. It must also be kept in mind that results are dependent on the actual instruments used and that the ones used in the current study might not necessarily be representative for the entire field. Resolving power might vary from commercial set-ups to tailored equipment. Information about material composition yielded

with imaging techniques is based on colour information (OM), grey values (X-ray imaging, tomography) and possibly gamma spectroscopy (NT). Accessibility and costs are dependent on the availability of instruments, ranging from omnipresent optical microscopes to several neutron facilities across the globe.

**Implications for decision-making on research and conservation**

The archaeological process involves different stakeholders, with varying degrees of responsibility for finds. Here, we focus on those stakeholders that generally make decisions on research and conservation of objects: (local) authorities, archaeologists, conservators, storage facilitators and archaeological researchers. It is argued here that studies like this one aid informed decision-making, including aspects like costs and accessibility of multiple options.

This study has shown that the application of analytical techniques contributes to deducing the manufacturing process of artefacts, which may be subsequently linked to a geographical origin. All this additional information may aid in the decision on whether to put the artefacts on display in a museum. Research like in this study may confirm the cause of a golden sheen on maritime silver: gilding or corrosion. The insights gained about metal composition may facilitate decision-making (e.g. on methods and location) when sample taking for material provenancing [36] is considered.

Additionally, the condition of the silver can be assessed in more depth<sup>14</sup> by making use of XRF, X-ray imaging, tomography and possibly SEM–EDS. Not only the surface [37], but also the inner structure of the objects

<sup>14</sup> For recent practice concerning shipwreck finds, see: Middleton A, Roche K. The Rooswijk finds. *ICON News*. June 2019; 82. And: <https://historicengland.org.uk/whats-new/research/rooswijk-shipwreck-excavation-the-post-excavation-phase/#materials>. Accessed 4 April 2022.

can be non-invasively studied. For example, no chlorine compounds were identified in the filigree spheres. The stakeholders may then decide to opt for preventive conservation only, by controlling the storage or display climate, instead of active conservation by means of chemical action. Another example is the confirmation of the fragility of the filigree wire. The analytical results may aid in deciding whether to mechanically clean and how to stabilise or consolidate the artefacts. Additional guidelines for handling the spheres can also be considered.

### Conclusions and future perspectives

The group of filigree spheres from the shipwreck BZN17 has been studied with multiple analytical techniques, with a focus on non-invasive techniques, to gain a better understanding of their function, condition and manufacturing techniques. All spheres are thought to be made using the same techniques and materials, possibly in the same workshop.

The frame of a sphere has been made out of a single strip with rectangular cross-section of silver alloy, bent into lobes. Multi-twisted circular cross-section wire has been flattened and used as decorative infill of the lobes. The loop and flower-like appliqué were soldered to their relative hemispheres before joining both halves to a central band by soldering. The gilding was applied by amalgam gilding after completion of the object.

Because of the thick corrosion layers on the surface, it is impossible to establish by naked eye or optical microscopy whether these spheres originally could be opened. X-radiography was not sufficient to discern enough details, therefore more advanced tomographical techniques (X-ray micro-computed tomography and neutron computed tomography) were used. No opening mechanisms were found, dismissing the theory that these spheres might have functioned as pomanders and making it more likely they may have been buttons, on men's or women's dress. Their geographical origin is currently thought to be Austria, Slovakia or Hungary.

Finally, a comparison between the applied non-invasive imaging techniques was made, where different aspects are valued. This may aid stakeholders in the archaeological process in making decisions about the possibility of applying such techniques. The implications of this study for the conservation of maritime silver is also discussed.

The results related to the manufacturing process as described in this article give reason to make an experimental replica of a filigree sphere. This will yield complementary insights from a practical point of view. Currently, the making of such a replica is in progress and the results are intended to be published separately.

### Abbreviations

$\mu$ CT: X-ray micro-computed tomography; NT: Neutron computed tomography; NPD: Neutron powder diffraction; OM: Optical microscopy; SEM-EDS: Scanning electron microscopy—energy-dispersive X-ray spectrometry; XRF: X-ray fluorescence; XRD: X-ray diffraction.

### Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40494-022-00710-9>.

**Additional file 1.** Illustrative movie where a golden sheen is visible beneath the corrosion on filigree sphere 5372-014.

**Additional file 2.** X-ray micro-computed tomography animation of filigree sphere 5372-013, including a separate file with scan acquisition data and a description of the animation.

**Additional file 3.** X-ray fluorescence data (Olympus delta professional X-ray analyzer).

**Additional file 4.** X-ray fluorescence data (Bruker Artax portable micro-XRF spectrometer).

**Additional file 5.** X-ray diffraction data.

### Acknowledgements

Sigrig van Roode (Bedouin Silver), Jane Perry (independent researcher) and The School of Historical Dress are acknowledged for their help on providing background information on the history of filigree jewellery, Jilt Sietsma for his help on information on corrosion processes, Zhou Zhou (Delft University of Technology) for his help on processing the neutron computed tomography data and Arie Pappot (Rijksmuseum Amsterdam) for his help on data processing of XRF data gained by the Olympus instrument.

### Author contributions

JSN and TB are both responsible for the main body of the study carried out and the preparation of the manuscript and are therefore both acting as first author. JSN performed XRD and processed the data. JSN and TB performed OM, X-radiography and XRF and processed the data. DNT performed  $\mu$ CT and processed the data. LE performed NT and NPD and processed the data. IJ performed SEM-EDS and processed the data. JSN and TB interpreted all data in this study. MB contributed to the conception of the work and supervised the AMOR-project. All authors reviewed the final manuscript. All authors read and approved the final manuscript.

### Funding

The study presented in this article is part of a larger research program, entitled AMOR: Archaeological Metal Surface (Dutch: Oppervlak) Research. AMOR is funded by the Dutch Research Council (NWO-342-60-003) and the Province of Noord-Holland. The NT experiments and interpretation were carried out in the framework of the Beeldvorming NICAS project (NWO-628-007-032).

### Availability of data and materials

The datasets supporting the conclusions of this article are included within the article and its additional files.

### Declarations

#### Competing interests

The authors declare that they have no competing interests.

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Received: 2 February 2022 Accepted: 29 April 2022

Published online: 27 June 2022

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