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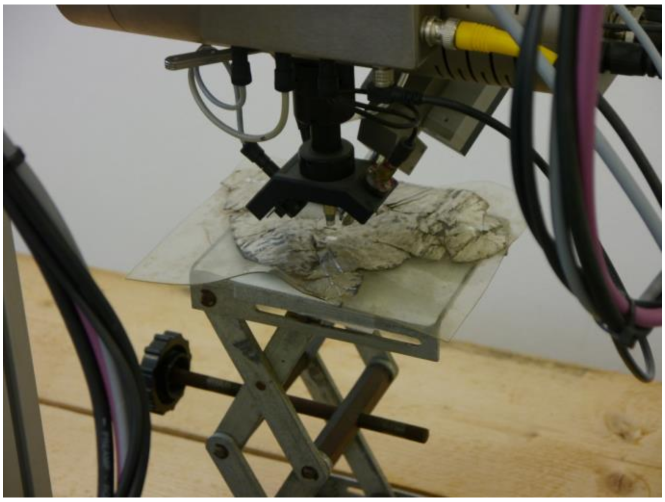
DIPLOMA THESIS:

XRF-ANALYSIS OF SILVER OBJECTS FROM OLYMPIA



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Abstract

For this study, XRF analyses were performed on silver objects and silver decorations of helmets from the archaeological site of Olympia (Greece) to find possible correlations between their metal composition and the period of their manufacture. The analysed finds date from the archaic to the Byzantine period, with a focus on the archaic period. Quantitative results were gathered for 24 finds, including silver decoration of 6 helmets dating to the archaic period.

The obtained results show a correlation between the silver content and the period of manufacture, as well as an increasing percentage of minor chemical elements with time. Differences between the elemental compositions of decorations of three helmets and the archaic objects, respectively, were observed.

A measurable amount of zinc in some helmet decorations raises the question if it derives from the incomplete smelting of the ore or from the alloying material. The objects from Roman and Byzantine times contain zinc that certainly derives from brass added to the silver. The bismuth/lead ratio and gold content allow an insight to a discrimination of ore sources between the analysed finds, leading to an estimation of 6-8 different sources for the objects found in Olympia. The observed lead and bismuth values are helpful for the understanding of the process and ore type used to produce the silver. Although a positive identification of provenance was not possible but would require complementary analysis, some ore sources could be excluded.

Acknowledgements

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Finally, I sincerely thank my family, partner and friends who always supported and believed in me. Thank you for always being there for me, I could not have done this without you.

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1 Introduction

The archaeological site of Olympia, the Panhellenic sanctuary for Zeus and birth place of the famous Olympic Games, was an important place in ancient Greece. People there worshiped Zeus, but also the athletes that were competing in the games. Many objects found in Olympia were brought to the sanctuary from all over the Greek world to show devotion. So far, few archaeometric studies have been carried out on the metal objects from Olympia (for example on the helmets by Manti (2011), and on the bronze tripods by Kiderlen et al. (2016)). For this thesis, the silver finds from Olympia were analysed with X-ray fluorescence (XRF) spectroscopy to identify their composition and a possible connection to the period of manufacture. Another attempt was to identify or eliminate possible ore sources for the silver.

1.1 The archaeological site of Olympia

Olympia, situated at the confluence of the rivers Kladeos and Alfeios in the modern prefecture of Elis in the western Peloponnese (Greece), looks at a long lively past.

It was described in detail by Pausanias in the 2nd century CE but was covered by large amounts of sediments from the 6th century. The still on-going excavations started in 1875, with few interruptions between 1881-1906, 1929-1936 and 1966-1977, and are carried out by the German Archaeological Institute (responsible since 1936) in accordance with the Greek ephorate of antiquities (Kyrieleis 2011).

1.1.1 Chronological overview

The first signs of a small settlement date back to the 3rd millennium BCE, but there is no evidence for continuous use until the late 11th century BCE. At this time, the first appearance of the Zeus-cult, probably in the form of rural festivals, is evident in the archaeological material. It was a rather local event, where chieftains from Messinia and Arcadia gathered. The big amounts of offerings during the 8th century indicate that it became a broadly known and recognised sanctuary. It is in this time (776 BCE) that the foundation of the Olympic games is traditionally dated (Hall 2014). The increasing importance during the 7th and 6th century BCE shows through the monumental buildings and the number and quality of offerings dating to this timespan. The 5th century BCE can be seen as the golden age of the sanctuary, when the most impressive and important buildings were erected. However, this does not show in the number of finds, which is rather low compared to the archaic time (Frielinghaus 2013). The beginning of Hellenism in the 4th century BCE led to changes in the political situation, and a decreasing importance of Olympia is reflected in the decline of archaeological material of this time. The shift of focus towards the east during the 3rd and 2nd century led to a decreasing importance of the site as a sanctuary. The buildings that were erected are mainly donations from kings to show their power. No continuation of the cult is observed in the archaeological material after Greece was defeated by the Romans in 146 BCE, but new wealth raised to Olympia during the 1st and 2nd century CE under Roman reign, when the games were used as a representation for Roman emperors. The importance of Olympia decreased drastically when barbaric peoples looted the site in the 3rd century CE and Theodosius banned the feasts in 393 CE. Nevertheless, a Christian settlement in Olympia starting in the 5th century CE indicates a continuity of inhabitation until the end of the 6th century CE, when natural disasters like earthquakes and flooding led to a coverage of the site by large amounts of sediments. The Christian settlement in the periphery probably lasted until the 7th century (Gehrke 2012; Kyrieleis 2011; Völling 2001).

1.1.2 Metalwork in Olympia

As the most important Panhellenic Zeus sanctuary, offerings from all over the Greek world were brought to Olympia. In many cases, these were brought as already manufactured objects, but it is known that bronze casting workshops existed in Olympia for local production (Hall 2014). One of these workshops was the one of Phideas (built in classical times around 430 BCE), where moulds for statues were found (Schneider 1989). So far, no evidence for silver production on-site was found, but for the early classical period, the presence of jewellery workshops is most likely (Philipp 1981).

One piece of unworked silver in the form of a melted lump with clear filing marks (inventory number *V13,* Fig. 1) was analysed. It was found "at the workshop place"[1] in spring 1937 and might be considered raw material for a local production of silver objects in Olympia. Although there is a cross-link from the inventory book to the excavation diary, no further information about the circumstances or dating of this find could be found in the latter. The furnaces excavated in the same place date to the archaic period.

Fig. 1: Inventory number V13, unworked piece of silver with filing marks

Helmets were probably not produced in Olympia but brought to the sanctuary from all over the Greek world (Frielinghaus 2011). There is only a small number of helmets or helmet fragments with silver decoration (13 in total) of which most (9) could be analysed for this study.

1.2 Silver

Silver is a white noble metal that is malleable and castable. It is a common material used for jewellery or other precious objects. Silver objects first appear in the mid-4th millennium BCE in the Near East. Lead and silver ores in the Aegean were exploited since the early 3rd millennium BCE (Pernicka 1987).

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[1] Cited from the inventory book of Olympia "Varia".

1.2.1 Ores

Native silver does exist in nature but is too scarce to represent a common source for silver objects. Therefore, silver is usually retrieved from different ores.

The so-called “dry ores” chlorargyrite (cerargyrite/horn silver/silver chloride: AgCl), acanthite (silver glance/silver sulphide: Ag_2S) and arsenic-antimony-silver minerals (sulphosalts) (Brumby et al. 2012), and native silver were probably the earliest sources of silver. Acanthite and chlorargyrite can easily be smelted under reducing atmosphere (Craddock 1995; Pernicka 2014).

Since the “dry ores” are rather rare and were probably soon exhausted, the most common ores to refine silver from are lead- or lead-zinc ores like galena (PbS, often found with ZnS: sphalerite), cerussite ($PbCO_3$), anglesite ($PbSO_4$) that contain silver. Galena contains 86.6% of lead and can contain more than 1% of silver. It is easy to separate from the gangue (rock that doesn’t contain metalliferous components) minerals because of its high density.

Other sources for silver are fahlores (copper-arsenic-antimony sulphosalts), sulphuric ores and argentiferous jarosites, as well as electrum (a naturally occurring gold-silver alloy) and pyrite ores (Craddock 1995).

1.2.2 Mines in the Aegean

One of the most important silver mines in ancient Greece to retrieve silver was in Laurion (Attika). The Laurion mines contain galena with relatively high silver amount. It was also found that primarily cerussite and anglesite were mined by the early miners, until these deposits exhausted (Craddock 1995; Photos-Jones and Jones 1994). Two types of galena can be found at Laurion: “pure” galena with very low gold content, and galena with a slight admixture of other auriferous ores. Still, the gold content of both is rather low (Au/Ag below 0.003) (Gale et al. 1980).

Another important mining area was on the island of Siphnos, where today only traces of lead ores are found due to the efficiency of ancient miners. In archaic times, a variety of lead-silver ores, like cerussite, anglesite and argentiferous lead-antimony sulfosalts were exploited. Most of the mines were flooded some time during the 5th century BCE, resulting in a decreasing importance of these deposits. The gold contents of silver retrieved from these deposits ranges between 0.01-0.2% and rarely up to 1% (ratio of Au/Ag $5 \times 10^{-5} – 5 \times 10^{-4}$) (Gale et al. 1980; Gale and Stos-Gale 1981b; Pernicka 1987).

Early mines in Thasos were found to have been important lead-silver sources starting from the early Iron Age until late Byzantine times. The main ore that was smelted was galena which was cupellated in Thasos as well (Hauptmann and Pernicka 1988). Coins were minted in local mints starting not later than 500 BCE (Gale et al. 1988).

Other potential sources for silver since the archaic and classical times in Greece were in Chalkidiki and southern Euboea (Gale et al. 1988). The deposits of mount Pangaion were the most important northern Aegean silver and gold sources (Archibald 2012). Also silver mines in Asia Minor (Altinoluk and Balya Maden) can be considered as silver sources (Higgins 2006; Treister 1996). The deposits in the Rio Tinto area (Spain) were exploited by the Phoenicians and mainly contain jarosite ores (Rovira and Renzi 2017).

1.2.3 Technologies

The extraction of metal from the ore (smelting) requires high temperatures and, depending on the process, a reducing or oxidising atmosphere. Lead can be reduced from galena at temperatures that can be reached in an ordinary hearth, but to separate silver from lead, high temperatures of around 950-1000°C are needed (Craddock 1995).

To receive silver from a lead ore, a process called cupellation is used. The mined mixture of rock and ore is crushed and washed until only the metal-containing fraction is left. It is then smelted to an argentiferous lead bullion. When smelting argentiferous lead ores to argentiferous lead, copper, arsenic, tin, antimony, bismuth and precious metals stay in the metal. Most of the zinc goes into the slag or evaporates (Pernicka 1987). In a second step, the argentiferous lead is placed in an open crucible to melt it. This special crucible is called cupel. It is traditionally made of an absorbing material with low silica content, e.g., bone ash combined with a binder was used by the Romans, in Laurion evidence for clay lined crucibles was found. On the surface of the melt, lead is oxidised to litharge (lead monoxide) and removed mechanically or absorbed by the cupel. Arsenic and antimony evaporate or oxidise, and tin oxidises in the beginning of the cupellation process. Remaining zinc is also easily oxidised, while copper continuously passes into the litharge. In the end of the process, all lead will be oxidised and silver remains in the cupel (Craddock 1995; Gale and Stos-Gale 1981a; Pernicka 1987).

Jarosite ores don't contain lead. To extract silver from jarosites, lead needed to be added and then cupelled as described above.

1.2.4 Elemental composition of silver objects – indicators for ore sources and manufacturing techniques

Depending on their affinity to react with oxygen, small amounts of other elements that were present in the argentiferous lead and in the silver ores are partly remaining in the silver in different amounts. Minor elements that are found in silver derive either from the ores or from the alloying material are copper, lead (from the ore or from the alloying material), gold and bismuth (usually from the ore), and zinc (from the alloying material).

Native silver

The elemental composition of native silver is easily distinguishable from the smelted silver. It contains only small amounts of lead and gold (<0.01%), and high concentrations of volatile and easily oxidizable elements (Hg, As, Sb) up to several per cent. The bismuth concentrations in native silver can reach up to 1%, resulting in high Bi/Pb ratios. If native silver is melted, the chemical composition changes significantly because of the loss of volatile elements (Pernicka 2013, 2014).

Copper

The main alloying element found in silver alloys is usually copper. It is present in the refined silver after cupellation in small amounts typically around 0.2-0.5% (Gale et al. 1980). Copper can be assumed to be added deliberately when it is present in amounts over 1% (Buccolieri et al. 2014). It acts as a hardener in the alloy, which would otherwise be too soft for objects of daily use. With increasing amounts of copper, the colour of the alloy changes slightly towards the yellow spectrum compared to pure silver, and also increases the tendency of the alloy to tarnish (see 1.2.5) (Brepohl 2008). Since copper was usually deliberately alloyed with silver, it cannot serve as an ore tracer.

Lead

Lead in small amounts is usually present in silver retrieved from ores. The lead content in silver from ores that don’t need to be cupelled (chlorargyrite and acanthite) is usually below 0.05%. In the end of the cupellation process, the silver usually still contains amounts of lead between 0.1% up to 1.2% (Pernicka 2014). Lower lead concentrations can be achieved, but silver loss up to 25% can occur at the end of the cupellation process and was unlikely done regularly (Pernicka and Bachmann 1983).

Low lead concentrations indicate a good cupellation process, while higher amounts of lead generally indicate that either the process was less successful or that the lead derived from the alloying material. Since most of the silver is produced from argentiferous lead ores, especially galena (lead sulphide) and cerussite (lead carbonate), lead isotope ratio analysis together with the elemental analysis is a well-established technique to investigate provenance (Pernicka 2014). However, an addition of lead-bronze increases the castability of the alloy and might be intentional. Additionally, silver from jarosite ores needed to be cupelled with added lead. This distorts the informative value of the analytic results, since an unknown percentage of lead of an unknown source was added.

Gold

Gold is often found in silver objects up to several per cent. It behaves in all aspects similar to silver and is often present in the ore. The gold concentration in the refined silver derives directly from the ore, since it is noble and stays in the silver during cupellation (Civici et al. 2007; Greiff 2012). However, the Au/Ag ratio of a single deposit can be widely spread (Pernicka 1987).

Bismuth

The bismuth content of the silver is to a certain extent indicative for the ore deposit it derives from. Different deposits contain different amounts of bismuth. During the cupellation process, bismuth stays in the silver until most of the lead is extracted. Only in the final process phase, bismuth is reduced from the silver. The Bi/Pb ratio was found to be dependent on the initial bismuth content of the ore (L’Héritier et al. 2015).

Zinc

While lead, gold and bismuth contents in silver derive from the ore, zinc most certainly comes from the alloying material. Zinc, if present in the ore, usually evaporates completely during the cupellation process (Craddock 1995; Pernicka and Bachmann 1983). If a significant amount of zinc is present in the final product, it must have either been added - intentionally or unintentionally - as an alloy in combination with copper (brass/“orichalcum”), or the silver was smelted from an ore that doesn’t need to be cupelled. Alloying brass to silver is known to be performed since the 1st century CE by the Romans, where zinc is commonly present in silver objects except from silver coins (Mortimer 1986). before the Roman period brass was probably known and described by ancient writers, but rather rare (Craddock 1978). It was the most precious metal after gold and silver, and recent discoveries of “orichalcum” ingots provide evidence for a Mediterranean trade of the raw material probably from Anatolia in the late 6th century BCE (Caponetti et al. 2017). So far, no evidence for alloying “orichalcum” to silver during this time was found.

1.2.5 Silver corrosion

This study deals with archaeological silver finds that were buried for centuries and corroded during this time. Corrosion in general describes the process of decay by chemical reactions with gases and/or liquids in the environment. Metals tend to turn back to their more stable state as they occur in nature (ores). Only noble metals are excluded from this process (Goffer 2007).

Although pure silver is a precious metal and not much affected by oxidation, it corrodes under the presence of sulphur, bromine or chlorine. Archaeological silver objects are most commonly made of alloys of silver and copper. Copper corrosion crusts are often found on these objects, since copper is a reactive metal and migrates to the surface to form corrosion products. This will also result in a copper depleted surface of the object, once the corrosion products have been removed. The thickness of this layer depends on many variables, such as the environmental conditions, time and alloy composition and can thus not be generalized. Depending on the environment, silver corrodes more or less during burial.

After excavation, silver objects are usually treated in a conservation workshop. Three commonly used techniques to clean corroded silver are chemical, electrochemical and mechanical treatment (Costa 2001; Palomar et al. 2016; Viljus and Viljus 2012). Archaeological silver objects like tarnished silver and objects with thin corrosion layers are usually cleaned chemically. Mechanical cleaning is used when the corrosion layers are very thick, or chemical cleaning proves to be ineffective. Although it is known that some chemical treatments are effective in removing sulphur compounds from the object (Palomar et al. 2016), it results in changes of the alloy composition on the surface (Moreno-Suárez et al. 2016).

After cleaning, the objects are usually coated with a protective layer like wax or polymers, to prevent further corrosion by aggressive gases from the environment[2] (Selwyn 2004). If treated uncoated silver objects are stored in an environment where sulphur compounds are present, it is very likely that a homogenous layer of silver sulphides, also known as tarnish, forms over time. Since H_2S is usually present in small amounts in the air, nearly all silver objects that have not been coated show a layer of Ag_2S on the surface. The tarnish is usually dark grey or black and builds a passivating layer that prevents the bulk object from further corrosion (Goffer 2007; Selwyn 2004).

These factors must be considered when performing surface analysis on silver objects. The analysed finds from Olympia were excavated between 1887 and 1968. Conservation was performed on most of them, but all objects show post-conservation corrosion. There is little to no documentation about the methods used on the silver objects in Olympia.

1.3 X-ray fluorescence spectroscopy (XRF)

XRF is a non-destructive technique that does not require sampling, hence, making it an ideal technique to gather information about archaeological objects. The use of portable instrumentation allows to analyse without moving an object to the laboratory. Since only a short time is needed for each measurement, many readings can be taken quickly. This can give a good overview on the composition

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[2] The most widely used polymer is Paraloid B72, a copolymer of ethyl methacrylate and methyl acrylate, that is applied in a thin film (Down 2015)

and homogeneity of an object or large groups of objects. It can also give information about the manufacturing processes an object went through.

1.3.1 Principles of XRF

For x-ray fluorescence (XRF) spectroscopy, x-rays are used to excite the elements of a sample and detect the characteristic secondary x-rays that are emitted.

To analyse a material, x-rays are focused on a spot[3] of the sample's surface. Electrons from the inner shells of the atoms on the spotted surface[4] are removed, resulting in an electron vacancy. This vacancy is filled by electrons from a higher energy level. During this process, x-rays with a characteristic energy are emitted. The energy is equivalent to the difference between the energy level of the electron and the energy level of the vacancy. The x-ray signal is collected by a detector and processed to a spectrum. The intensity of emission is statistically related to the sample's composition (Bertrand et al. 2012; Ferretti 2014). The gathered information is qualitative (identification of the elements) and semi-quantitative, in some cases even quantitative (determination of the percentage composition).

Although this method is well suited for material analysis, there are some restrictions. For portable XRF without vacuum or helium atmosphere, the lightest detectable element usually is potassium (Z=19), but recent devices are also capable of detecting lower atomic number elements. In vacuum or in a helium atmosphere, even elements with an atomic number as low as 11 (Na) can be detected, whereas the emission lines of light elements are otherwise absorbed by air. It has to be kept in mind that the analytical information of different elements comes from different depths of the sample. Another problem is the fact that only a superficial layer is analysed, making it hard to draw conclusions concerning the bulk composition of a corroded object without removing the corrosion layer (Ferretti 2014).

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[3] The spot size varies with the used instrument.

[4] The depth of the excitation depends on the matrix of the sample, the geometry, the incident beam energy distribution and the characteristic line energy of the analyte.

1.3.2 XRF analysis on archaeological silver

Noble metals are ideal to be analysed non-destructively by surface techniques such as XRF spectroscopy due to their high corrosion resistivity. Because of its relatively low corrosion rate, silver is a particularly suitable material for XRF analysis (Constantinescu et al. 2005). The quantitative evaluation of the elements can be used to gather information about the ore source and type, the period of manufacture and the technologies used.

So far, only few archaic silver objects were analysed by XRF, and none of the silver found in Olympia was archaeometrically studied before. Most previous studies were performed on silver coinage. The most common analytical technique is lead isotope analysis, mainly performed on coins (e.g. Gale et al. (1980, 1988); Pernicka (2013)).

2 Materials and Methods

2.1 Analysed finds

In general, silver finds are quite rare in Olympia, especially compared to the enormous number of bronze objects that were found.

For this study, 35 objects that derive from different excavations in Olympia were analysed. Most of them were excavated in the earlier excavations (1930s until 1960s). The objects that were found in Olympia stayed in Greece, either at the site or at the National Archaeological Museum of Athens[5]. The objects studied in this work are all stored in the New Archaeological Museum in Olympia. All accessible silver-containing objects located at the site were analysed.

The dating of the objects varies from archaic to Byzantine times, with a focus on the archaic period and a gap between the early classical and the Roman period (Fig. 2). Many of these objects have not been published earlier or studied intensively. Although some of the objects are not precisely dated, they were analysed for comparison, and to see if the analysis may give a hint on their manufacturing. The analysed finds can be mainly categorised in two groups: (1)

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[5] The reason for this is the contract of 1874 between Germany and Greece, in which it is regulated that the finds from Olympia belong to the Greek people and therefore stayed in Greece, while the scientific evaluation was reserved to the German archaeologists (Heilmeyer et al. 2012).

objects made of silver and (2) copper or copper alloy helmets with silver decorations.

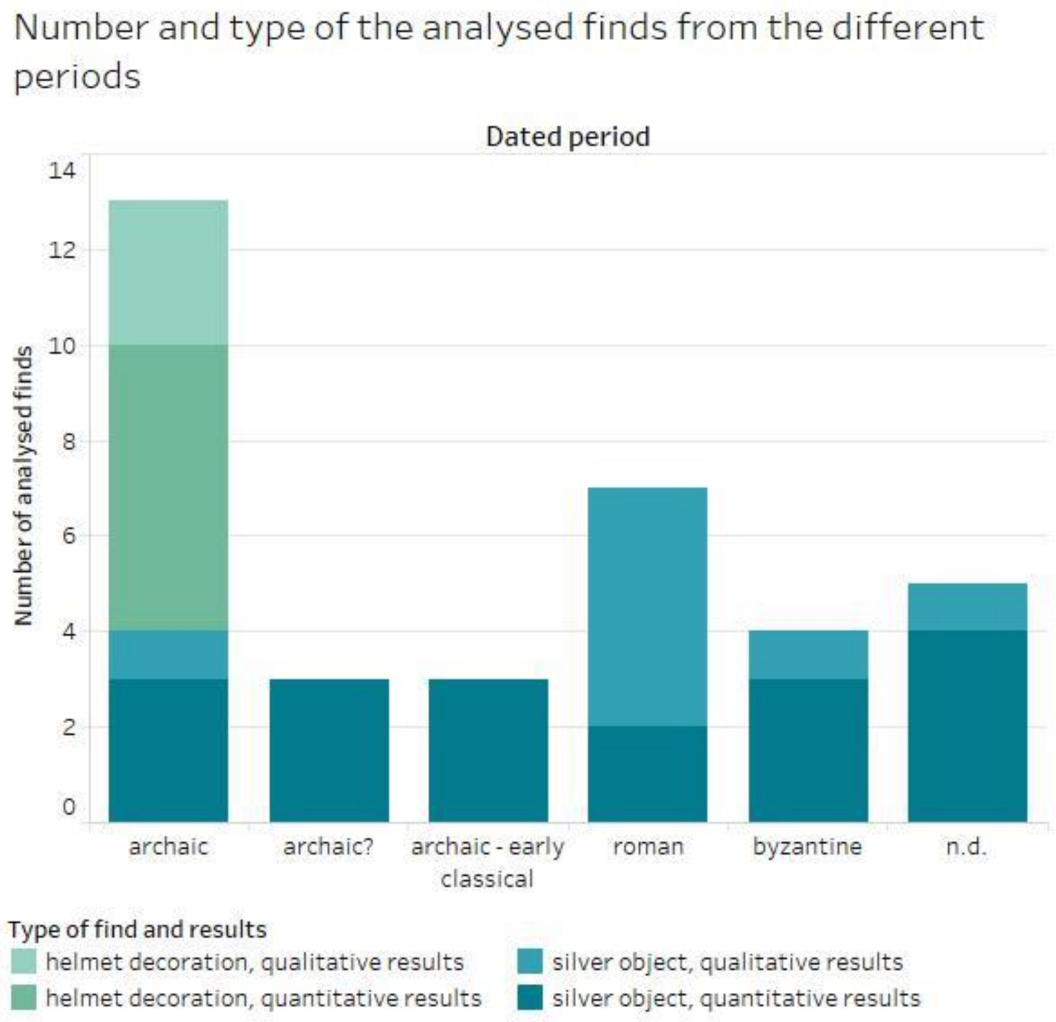

Fig. 2: Overview of the number and dating of finds, and the type of obtained results

2.1.1 Objects made of silver

Table 1 gives an overview of the analysed objects made of silver. This group consists of 27 objects of different shapes and from various times. Mainly the jewellery was published and archaeologically studied (*B3223*, *Br2113a*, *o.Nr.*, *V9*, *V15*, *V17*, *V22*, *V202*, *V203*: Philipp (1981); *V23*: Hitzl (1996); *V232*: Kunze and Schleif (1939), *Met244*: Furtwängler (1890)). A study on the big leaf-like sheet *V14* is in progress by H. Philipp-Koenigs and will probably be published next year[6]. The other objects have not been studied in detail before. Photos of the objects can be found in the appendix.

Table 1: overview of the silver objects

Inventory number	**designation**	**description**	**dating**
		conservation state	
B3223	needle (fragment)	needle with a maximum diameter of approx. 1 mm, bend and broken twice, three notches underneath the missing head	not dated
		glued, coated with black corrosion	
Br2113a	three hair pins	needles with a maximum diameter of ca 1 mm, different lengths (4.5, 7.5 and 10.5 cm), each has a big spherical head and notches right below. The middle-sized one shows more ornaments than the other two.	byzantine (middle of 4th - inclusively 5th century CE)
		all coated with dark grey corrosion, the smallest is broken and glued below the head	
Met233	small chain	chain with triple eyelets (initially), 8 cm long fragment	not dated
		covered with thick, dark, matte corrosion and partially copper corrosion	
Met244	small cross	2 x 1.5 cm, made of a thin rectangular silver sheet, cut to the middle from the edges. The rim is notched, one side is detached and contains a hole	byzantine, 6th century CE[7]
		thick dark corrosion	
o.Nr.	ring	small ring with flattened ring band, widening to the top. The ring head shows a round elevation	roman, 1st half of the 3rd century CE
		strong black corrosion, broken on the bottom	
V9	snake bracelet (partly gilded)	intact snake bracelet with 1¼ helical turns, one snake head on each end placed next to each other, rich point- and line-engravings, in the middle and on the ends decorated with palmettes, partly gilded (only preserved in few areas)	archaic – early classical 2nd half of 6th – 1st half of 5th century BCE
		corrosion in the areas not covered by gilding	
V11	rosette	diameter ca. 1.8 cm, 18 leaves, gilded on one side	archaic?
		little corrosion on the silver, broken and glued	
V12	spoon	13.4 cm long, with a tipped end, two nodes on the handle	roman

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[6] Personal correspondence with Prof. Philipp-Koenigs, who also suggested the dating of this piece to the archaic period.

[7] Chronological ranging suggested with the help of Dr. A. Rettner from the Archäologische Staatssammlung München.

		little corrosion and extremely yellowed coating	
V13	unworked piece of silver	6.75 cm long, up to 0.85 cm height, crack in the middle of the piece, traces of filing on one side (probably original)	not dated[8]
		brown-grey corrosion on the unfiled side, filed side less corroded, yellowed coating	
V14	fragment of a silver sheet (for a shield?)	thin silver sheet in a heart shape, 19.2 x 15.4 cm, small holes for nails and engraved lines on the sides	archaic
		broken in small pieces, glued on a plexiglass support, yellowed coating and corrosion in some areas	
V15	fragment of a snake bracelet	10.9 cm long, flattened piece, u-shaped cross section, snake head symbolised by engraved eyes on one side	archaic - early classical
		dark corrosion, traces of iron corrosion	
V17	ring	one side flat rhombus shaped, the other round and enlarged, inner diameter 1.9 cm	archaic (Etruscan type)
		strong corrosion	
V20	fragment of a hinge	part of a flat sheet with two soldered parts of a hinge and rivet	not dated
		dark grey corrosion	
V22	ring	strongly bent, biggest expansion 2.7 cm, subdivided by several notches, flattened and broadened in the middle with a slightly oval engraved disc soldered on	roman, 3rd century CE
		broken and glued several times, dark grey corrosion	
V23	weight	2.8 x 1.8 x 0.4 cm, with inscription “[Δ]ΙΟΣ”, intentionally cut on one side	archaic-early classical 5th century BCE
		homogenous matte grey corrosion	
V24	“Wulstattasche” (elongated silver bead)[9]	tube with an inner diameter of 1 cm, 1.75 cm long, with three grooved bands, four pearled wires soldered on, the two outer ones being bigger than the inner ones. Filed on one side	archaic?
		little corrosion, some pearls are missing, yellowed coating	
V25	ornamented disc	5.75 cm diameter, with repoussé ornaments, hole in the centre and two holes in the outer area	archaic?
		broken several times, glued to a paper, dull dark corrosion	

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[8] According to the excavation diary, the workplace it was supposedly found next to dates to the archaic period.

[9] The designation derives from the inventory book. The German word „Wulstattasche“ translates to „escutcheon“, which this object was wrongly designated. In this study, the term elongated silver bead is used to prevent confusion.

V26	fragment of an aryballos	upper part and neck fragment, diameter 2.5 cm, engraved concentric circles on the flat top, ornamented band on the rim, lower part with engraved geometric ornaments is not preserved[10]	archaic
		some fragments broken and glued, thin light grey-brown corrosion	
V59	fragments of a fitting	several fragments of a thin silver sheet of unknown use, some holes for nails	not dated
		dark grey corrosion, in some parts with coating metallic, partly glued fragments	
V202	earring	round earring, with round cross section, pair with V 203, closure mechanism with a hook	late roman
		strong corrosion, partly with copper corrosion	
V203	earring	same as V 202, closure opposingly shaped	late roman
V232 (fragment)	fragment of a rosette	rim fragment of a big rosette (V232), length ca. 2 cm, with repoussé ornaments	archaic
		copper corrosion on the edge, surface with grey corrosion, applied on a support made of wax	
V234	pair of earrings	round earrings, with round cross section and flattened front, closure mechanism with a hook	late roman
		strong corrosion, partly with copper and iron corrosion	
V235	earring	round earring, with round cross section and flattened front, closure mechanism not preserved	late roman
		strong corrosion, partly with copper corrosion	
V459	rim fragment of a vessel	3.1 cm long, ca. 1 mm thick fragment, partly deformed	not dated
		very thick grey-purple coloured corrosion layer on both sides, removed or broken off in a small area, edge with a brittle optic revealing the cross-section	

More detailed information is available for some objects:

The three pins of inventory number *Br2113a* represent a very common type of pin that is often found in Olympia. All other pins of this type found in Olympia are made of copper alloy. The three pins were found together in one of the stone-covered graves dating to the byzantine period. They were probably made in one or more local workshops (Philipp 1981).

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[10] Information about the decoration derives from the inventory book. Some small parts of engravings are still visible.

The bracelet *V15* resembles the locally produced bracelet type with snake heads. It does not match perfectly with those made from one of the identified workshops. It may derive from a local workshop in or near Olympia (Philipp 1981).

Bracelet *V9* is a different type, which has similarities with a type that is more common in northern Greece/Macedonia. Differences in V9’s appearance suggest a local production in the Peloponnese, maybe even near/in Olympia. It is stated in publications that it was maybe entirely fire gilded (Philipp 1981).

The late roman earrings *V202, V203, V234* and *V235* all belong to the type with a hook and eye. They have a flattened front where further decoration was soldered on (Philipp 1981).

The analysed fragment *V232* belongs to the big rosette that is stored in the National Archaeologic Museum Athens. Kunze and Schleif (1939) suggest a use of the rosette as a shields’ arm cover decoration. There are other similar finds and this, together with the context, date the object to the archaic period.

It has to be mentioned that quantitative analysis could not be performed on all of these objects for different reasons. First of all, the corrosion on some of the objects was too severe to prepare the area necessary for quantitative analysis without strongly damaging the object. In other cases where a preparation was apparently possible, the analysis showed too much interference of corrosion products. Finally, the limited time the objects were accessible restricted the possibility to analyse all objects quantitatively.

2.1.2 Helmets with silver decoration

All of the observed helmets date to the archaic period. Unlike the silver objects, the helmets from Olympia have been studied intensively and dated more precisely. The majority is made exclusively of copper alloy, but a small group shows ornaments made of silver or rivets coated with silver (Born 2009; Frielinghaus 2011). The analysed helmets date to different times of the archaic period[11].

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[11] All mentioned helmets are published in Frielinghaus (2011). Additional information for the individual helmets can be found in the following literature: B2610 (Kunze 1961; Mallwitz and Herrmann 1980), B2764 and Br1087 (Kunze 1961), B5095 (Pflug 1989), B5316 (Kunze 1967; Mallwitz and Herrmann 1980), B7946 (Kunze 1994), Br4089 (Furtwängler 1890; Kunze 1961)

B2610, B2764, Br1087, Br4089 and M164

These represent the earliest of the analysed helmets dating to a timespan between the 2nd half of the 7th century BCE and the first quarter of the 6th century BCE. Most of them are dated more precisely by Frielinghaus (2011): *B2610* dates to the third quarter of the 7th century BCE, *B2764* to the second half of the 7th – first quarter of the 6th century BCE and *M164* to the 1st quarter of the 6th century BCE. The dating of the nose covers *Br1087* and *Br4089* cannot be further refined. They all belong to the Corinthian type of the second phase and are similar to another group of helmets, the “Myros” group. This helmet type was one of the most popularly manufactured in the archaic period. 600 Corinthian helmets were found in Olympia and thus represent the majority of all 850-1000 helmets found at this site. Corinthian helmets were manufactured all over the Greek world and were also popular beyond its borders. However, there is no evidence for the manufacture abroad. It is suggested by Frielinghaus (2011) that this type of helmets was primarily manufactured in southern mainland Greece or the Peloponnese. There is no hint for the provenance of the analysed helmets. The majority of them have only minor or no decoration at all (Frielinghaus 2011). Three more helmet fragments that might have belonged to the same group (Inventory number *177*, *B2103* and *B3845*) could not be located in the museum storage during the short time of our stay.

The analysed decorations consist of one rivet line along the rim of the helmets. The rivets on the helmets *Br1087*, *B2764* and *M164* are only coated with silver while the ones on the other helmets are entirely made of silver. *B2610* shows also a spiral ornament next to the rivet line and *M164* has two parallel lines of rivets. The nose cover *Br4089* shows an ancient repair, where a bronze sheet was attached below a crack with small bronze rivets.

B5095 and B5179

Both helmets belong to the later Corinthian type, phase III, dating to the late 6th to early 5th century BCE. They show similarities to the “Hermione” group, named after the place where the representative individual was found. There is no hint for places of manufacture for this type of helmets (Frielinghaus 2011). The analysed helmets are the only ones of this type that still have silver decorations present as small palmettes. On *B5095*, one is applied near the eye opening and one near the shoulder. *B5179* has only one palmette near the eye opening.

B5316

Helmet *B5316* represents the most elaborately decorated helmet of the studied group. It is one of the few Illyric helmets found in Olympia, belonging to group IIIA of phase III, dating to the late 6th – early 5th century BCE (Frielinghaus 2011). A horseman is applied on both cheek covers, and the forehead shows two lions fighting a boar. Above the boar, a big rivet is situated to attach a crest. The only similarly decorated helmet found near Olympia is in the British Museum. A third comparable helmet was found in Trebeništa (Republic of Macedonia). This helmet might have been manufactured in the Illyric or Macedonian region (Frielinghaus 2011).

B7946

The Chalkidian helmet *B7946* contains silver eyebrows and a silver rim ornament. The silver on this helmet is completely corroded, visible by the porous and dull lead-grey appearance. It dates to the fourth quarter of the 6th century – first quarter of the 5th century.

2.1.3 Pre-analysis treatment

With few exceptions, the objects are more or less severely corroded. Most of the objects were conserved previously, most probably with EDTA (“Titriplex”), but corroded again during the time of storage.

The elemental ratio (especially minor elements) changes in corrosion layers compared to the initial alloy. This change is further enhanced by previous conservation treatment. Therefore, the measurement spots for the microXRF analysis on corroded objects were mechanically cleaned in an area of ca. 0.5 x 0.5 mm. Some objects that were previously conserved and coated with a protective layer showed a metallic surface. In these cases, no mechanical spot preparation was carried out. Where present, the polymer coating was severely yellowed. The polymer coating was partially removed with cotton swabs and acetone. After the measurements, all prepared spots were coated again with 5% Paraloid B72 in Acetone.

No preparation of the objects was performed for the measurements with the handheld XRF because of the big spot size.

2.2 Experimental

Measurements with a portable handheld XRF and with a portable micro-XRF were performed on site at the museum depot of Olympia.

2.2.1 Handheld XRF

Analysis was performed on the silver objects using a Bruker Tracer III SD set up, with a beam diameter of 4 mm. An Al/Ti filtered (304.8 µm Al plus 25.4 µm Ti) high-energy excitation mode (high voltage set at 40 kV and current of 12 µA) was used for the analysis of minor and trace elements with an atomic number $Z > 22$. The collection time of each measurement was 60 seconds. For the silver objects only qualitative data was gathered. In the case of the gold foil and the bronze chain quantitative data were collected. The data quantification was made using S1PXRF software and the calibration curve for gold and copper alloys, respectively.

In many cases, no full coverage of the window was achieved due to the shape and size of the objects. The measurements took place on the uncleaned objects, resulting in qualitative data only.

2.2.2 Portable microXRF

The micro-probe XRF analysis was carried out using a customized version of an Artax (Bruker AXS) spectrometer. The spectrometer composes of commercial, state-of-the-art hardware components: an X-ray microfocus Rh-anode tube (spot size 50×50 µm, max 50 kV, max 1 mA, 30-W maximum power consumption, Be window 0.2-mm thickness) and a polycapillary X-ray lens as a focusing optical element (IfG) with a focal distance of about 21.2 mm. The X-ray detection chain consists of a thermoelectrically cooled 10-mm2 silicon drift detector (X-Flash, 1000B) with 146 eV FWHM at 10 kcps coupled with a digital signal processor. A color CCD camera (with approximately ×13 times magnification) combined with a dimmable white LED and a spot laser beam assures reproducible positioning of the measuring probe, as well as visualization and documentation of the analyzed area. Three stepping motors coupled with the spectrometer head allow three-dimensional movement for elemental mapping and precise setting of the analysis spot at the focal distance of the polycapillary lens.

The measurement conditions were set at 50 kV, 600 μA (high voltage, current) for the X-ray tube. The samples were measured using filtered and unfiltered excitation; the use of a filter -in this case a composite filter of Ti (23.6 ± 0.2 μm) and Co (17.7 ± 1.3 μm) - improves the detection limits for trace elements, whereas using an unfiltered excitation the detection of light elements down to Silicon (Z=14) is possible. The acquisition time was set depending on the type of analysis; single spots with filter were measured for 100 or 300 s and without filter for 25s. Some area scans were also performed (25 s per step) with a step size of 0.1 mm.

For the quantitative results a homemade software[12] was employed based on the fundamental parameters approach that utilizes an analytical description of the lens transmission efficiency (Kantarelou and Karydas 2016).

The measurement spots were prepared as described above. The objects were placed on a height-adjustable platform, aligning the measurement spot in a 90° angle to the radiation source and the detector (Fig. 3).

Objects that consisted of parts that could have been made of different materials (e.g. the handle and bowl of the spoon) and objects that didn’t need cleaning were analysed on more than one spot.

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[12] Developed at N.C.S.R. „Demokritos“

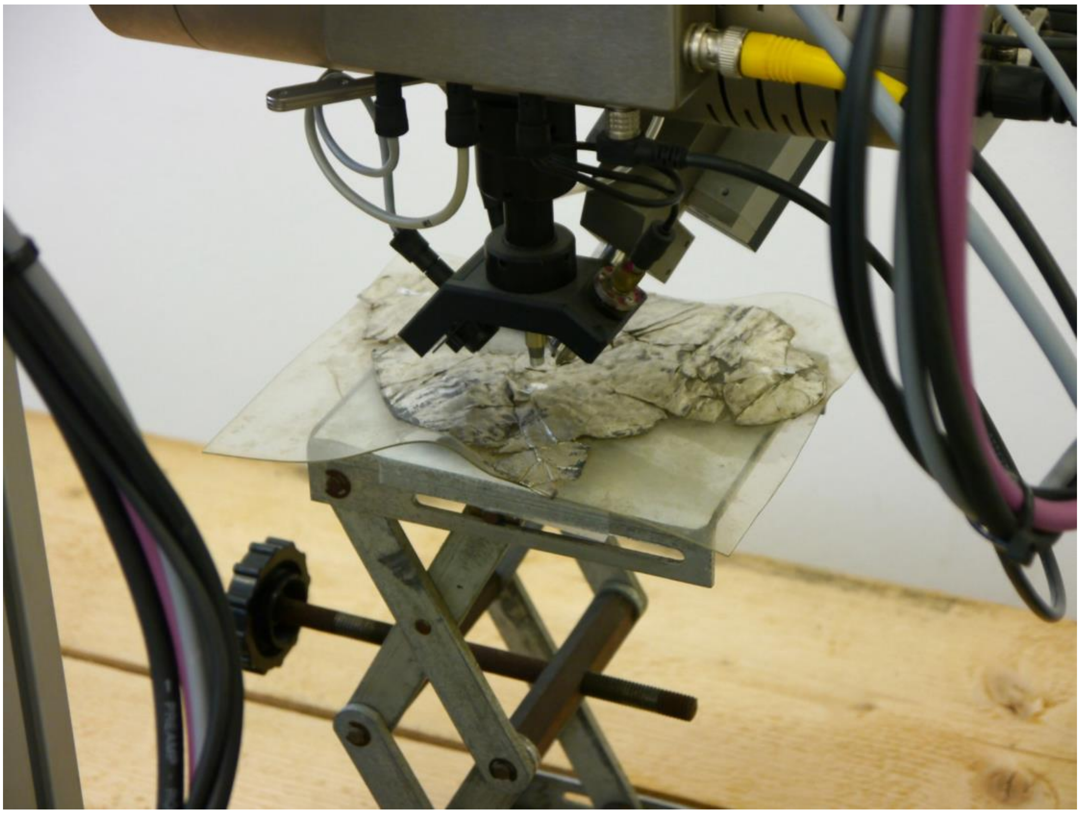

Fig. 3: Example of the experimental setup

3 Results

With the microXRF, quantification of the elemental composition for 53 spots on 24 individual finds was possible. All analysed spots contained silver as the major element between ~78% up to 99.5%. Additionally, copper (0.15% - 21.7%) and gold[13] (0.07% - 2.98%) were present in all measurements. Lead[14] (0.011% – 2.4%) was measured on all except two spots, and bismuth[15] (0.008% – 0.38%) was measured on all except three spots. 33 measured points on 20 objects showed zinc values[16] between 0.017% and 2.61%. A table with all obtained results can be found in the appendix.

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[13] Au: detection limit 78 ppm
[14] Pb: detection limit 71 ppm
[15] Bi: detection limit 69 ppm
[16] Zn: detection limit 100 ppm

In the following description, silver and copper are referred to as major elements, and gold, bismuth, lead and zinc as minor elements.

Quantitative results could be obtained for:

- The decoration of 8 archaic helmets
- 3 archaic objects
- 3 archaic to early classical objects
- 2 roman objects
- 3 byzantine objects (all with the same inventory number)
- 3 objects that are assumed to be archaic, but not certainly (not published, dating based on the excavation diary)
- 4 objects that are neither dated nor mentioned in the excavation diary

The helmet decorations, although also archaic, are discussed separately. They are dated more precisely, and the results differ significantly from the archaic objects.

3.1 Helmet decorations

The majority of the helmet decorations contain less silver than the archaic objects. Only the decorations of *M164, B5179* and parts of *B5316* contain above 97% silver like the archaic objects. The other decorations have silver contents down to 95.6%.

An interesting observation is that of all analysed archaic finds, 4 helmet decorations contain measurable amounts of zinc. Especially the decorations of *Br4089* and parts of *B5316* contain significant values of zinc (over 0.2%).

Four out of seven helmet decorations and the rivet of *B5316* show elevated bismuth values. In fact, the decorations of the helmets *B2610, B5095, Br 4089* and the rivet of *B5316* show the highest analysed bismuth values of all studied finds

3.1.1 B2610

Three spots on different rivets and one spot on the spiral decoration were analysed. The measured bismuth concentrations of all spots (0.285% - 0.382%) represent the highest of all finds. There is a variation between the bismuth values of the different spots, but they are clearly distinguishable as a cluster from all other measured values. Concerning the general composition, all spots group well together, with low lead values in all measurements. The decorations don’t contain any zinc.

3.1.2 B5095

Measurements were performed on both decorations. All spots showed a high percentage of minor elements compared to the archaic objects and compared to B5179. Both decorations are characterised by high Bi (third highest of all finds, 0.21-0.23%) and Pb (third highest of all finds, 0.8-0.9%) values. The Bi/Pb ratio is the lowest of all helmets. Obviously, both decorations are made of the same material.

3.1.3 B5179

Three independent measurements were taken on the same decoration. Variations between the spots are visible. The silver content of all measured spots is the second highest (~98.5%), and the percentage of minor elements is among the lowest compared to the other helmet decorations. Spot 1 and spot 3 show slightly elevated lead values compared to the archaic objects, while on spot 2 and spot 3 traces of zinc (0.034% and 0.038%) are observed.

3.1.4 B5316

Six spots were measured, one on each part of the decoration. The compositions of the decorations differ in some cases severely from each other. All contain zinc in different amounts. Except from the left rider, the Bi/Pb ratios and gold contents of the spots are similar.

Lion and rider on the right side (viewed from the front)

The two measured spots are similar in their composition. Both contain less silver and more copper than the other decorations of *B5316*, but the smallest content of minor elements. They contain the second highest amount of zinc, but the Zn/Cu ratio is low (0.07).

Left lion

The material of the left lion contains the second highest amount of silver (98.2%) and the second highest percentage of minor elements (1.02%) compared to the other decorations of *B5316*. The copper value of 0.77% is very low. The measured spot shows the highest zinc value (0.28%) of this helmets' decorations, resulting in a Zn/Cu ratio of 0.27.

Left rider

The measured spot shows the highest silver content (98.9%) of all helmet decorations. The copper content of 0.156% is the lowest of all measured finds. The Bi/Pb ratio (2.8) is much higher than those of the other decorations of *B5316* (0.4-0.94), and the gold value is elevated. Zinc was measured to be at 0.066%.

Boar

The material of the boar decoration contains little less silver and more copper than the left lion. Higher bismuth and lead values, and a lower zinc content were measured compared to the other decorations.

Rivet

The spot on the rivet has a silver content of 97.5% and a copper content of 1.46%. The percentage of minor elements, in particular of lead and bismuth, is the highest of the *B5316* decorations. Is contains the least zinc and shows the lowest Zn/Cu ratio.

3.1.5 Br1087

One spot on the remains of a rivets' silver coating was measured. Because of the difficulties of reaching the spot, the results should be considered semi-quantitative, only.

The silver content is among the lowest (80.4%) and the copper content among the highest (17.63%) of all measured finds. The concentration of minor elements (2.02%) including the zinc content (0.76%) is the highest of all archaic finds. It shows an elevated gold and lead content. The Bi/Pb ratio is relatively low, similar to some of *B5316* decorations.

3.1.6 Br4089

On this fragment, three spots on different rivets were measured. All show high percentages of minor elements and the highest gold content compared to the other archaic finds. In all spots, zinc was measured between 0.22 and 0.42%, representing the second highest zinc content of the helmet decorations. The

Bi/Pb ratios are among the highest of all finds. All spots show very low lead values (below 0.014%) and high bismuth and gold values.

3.1.7 M164

Three spots on different silver coated rivets were measured. All contain between 97% and 98.2% silver. The quantity of minor elements in general (0.146% - 0.163%), and the gold content in particular, is the lowest of all measured finds. On one spot, the values of bismuth and lead lay below the detection limit. The values for both elements in the other analysed spots are similarly low (Bi below 0.025% and Pb below 0.017%). Minimal quantities of zinc (up to 0.05%) were measured.

3.2 Objects

3.2.1 Archaic objects V14, V26 and V232

All archaic objects have a very high silver content of 96.9% up to 99.5% and a copper content below 2.06%. They contain only few amounts of minor elements and no zinc. Two groups can be identified: pure silver and alloyed silver.

V14 (leaf-like sheet)

In all three measured spots, the silver content is the highest of all measured finds (99.5%) and almost no impurities are present. The copper quantities (<0.21%) are so low that certainly no copper was added deliberately. The material can be addressed as “pure silver”.

V26 (aryballos)

One spot was measured on the top part and one on the bottom part of the object. The two parts differ in their composition. The bottom part (s2 in Fig. 6) is quite similar to *V14* in its composition (“pure” silver, no added copper), but with a little higher gold content (0.361%). The top part (s1 in Fig. 6) contains significantly less bismuth and more copper, gold and lead than the bottom. It shows the highest copper (2%), gold (0.81%) and lead (0.188%) content, and the lowest bismuth content (0.012%) of all archaic objects. The Bi/Pb ratio is much lower than the one for the top and *V14*.

V232 (fragment of an ornamented disc)

The measured spot shows a high silver content of 98.7% and 0.65% copper. Except from the lower gold value (0.64%), the minor elemental composition of *V232* is similar to the top part of *V26*.

3.2.2 Objects uncertainly dated to the archaic period V11, V24 and V25

The three objects that were found in context with archaic layers show big differences in their compositions.

V11 (small rosette)

Concerning the silver, copper and lead values, the measured spot of *V11* fits in the range of the archaic objects. No zinc is present. However, the percentage of minor elements is higher. This shows in the high bismuth and gold content, and the Bi/Pb ratio.

V24 (elongated bead-like object)

The measured spot contains 97.3% silver and only 0.36% copper. The percentage of other components is high, within the range of the Roman and Byzantine objects. An outstandingly high gold content of 2.2%, representing the third highest measured gold content of all finds is observed. Minimal amounts of zinc (0.07%) are present. The Zn/Cu ratio thus is relatively high but should not be considered valid.

V25 (ornamented disc)

The measured spot on *V25* shows the lowest silver and the highest Cu content of all measured finds (77.9% Ag, 21.7% Cu), while the percentage of minor elements is among the lowest. Zinc is present with 0.219%, but the Zn/Cu ratio is very low. The values for bismuth and lead lie below the detection limit.

3.2.3 Archaic to early classical objects V9, V15 and V23

The three objects dating to the archaic to early classical period are characterised by a silver content lower than the archaic objects, between 94.3% and 97.8%, and a higher copper content of 1.61% to 5.2%. The quantity of minor elements is slightly higher than the “pure silver” (up to 0.5%), but still very low compared to the other finds. The Bi/Pb ratios are lower than those of the archaic pure silver, but higher than those of the archaic alloys. All objects of this group contain zinc in small amounts (below 0.12%).

V9 (snake bracelet)

One spot on the bracelet was measured. Its lead content is between the archaic objects, the bismuth and gold content are slightly lower. It shows the highest zinc value (0.12%) and the highest Zn/Cu ratio of 0.05 of the archaic-early classical objects.

V15 (snake bracelet)

The measured spot on the second snake bracelet of a different type shows the lowest silver and the highest copper values of this group. The lead (0.190%) and bismuth (0.057%) value are higher, and the gold value (0.191%) is lower than those of the other objects of this group. Zinc was measured in a small quantity (0.065%).

V23 (weight)

The spot on V23 shows the highest silver and the lowest copper content of this group. The Bi/Pb ratio is similar to the two bracelets, but a higher gold value (0.4%) was measured. The small amount of zinc (0.017%) can be neglected.

3.2.4 Roman objects V12 and V202

The two Roman objects show a wider range in the silver (88.2 – 93.9%) and in the copper (3.46 – 10.65%) content, as well as a higher minor element percentage than the earlier objects. Especially the lead content is higher, but below 0.55%. The zinc values differ between 0.05% and 0.59%.

V12 (spoon)

A spot on the handle and on the bowl were measured and clearly show that different materials were used for the two parts.

The bowl contains the least silver and the most copper of the Roman objects, while at the same time, it shows the lowest percentage of minor elements. The gold value (0.6%) is the lowest of the Roman objects, and the Bi/Pb ratio the highest (0.125). Both values are very similar to two of the Byzantine objects. Contrary to the handle, it only contains a very small quantity of zinc (0.049%).

The handle is made of an alloy containing 93.3% silver and 4.62% copper. It contains a higher percentage of minor elements than the bowl. The higher gold content (0.85%) and the lower Bi/Pb ratio compared to the bowl are more similar to the large Byzantine needle. The zinc content of 0.59%, and a Zn/Cu ratio of 0.12 are relatively high.

V202 (earring)

The earring has a high silver (93.9%) and a low copper (3.46%) content. The percentage of minor elements is the highest of the Roman objects, and only slightly lower than the Byzantine objects. The bismuth and lead value are the lowest of the Roman objects, while the gold content (1.93%) is among the three highest of all measured finds. Zinc is present (0.36%) in the alloy.

3.2.5 Byzantine objects Br2113a

Because of their different compositions, the three pins are dealt with as three independent objects. At least two spots were measured on each pin, one on the head and one on the needle. All pins contain above 3.26% copper, with most values much higher. The percentages of minor elements vary greatly among the pins but are generally the highest of all finds. The bismuth values for the middle and the small pin are higher than those of the other objects. Zinc is present in amounts of more than 1.27%.

Large pin

The head and the needle contain a similar amount of silver (90.4%), but the head contains 1% less copper and 1% more zinc. The values of the other elements are similar. The gold and Bi/Pb values of the large pin differ from those of the middle and small pin.

Middle-sized pin

The head and needle of this pin differ significantly in the elemental composition: The silver content of head (94%) is 4.5% higher than the one of the needle and the copper content of the head (~3.3%) is 3.75% lower than the one of the head. The difference shows also in the zinc content, which is 2.34% in the needle and 1.5% in the head. The Zn/Cu ratio thus differs between 0.32 (head) and 0.24 (needle). The gold and Bi/Pb values of head and needle, and those of both values of the small needle, are similar.

Small pin

One spot on the head and two spots on the needle were analysed. Although both measurements on the needle were performed in the same area, the results differ in the silver and copper concentration.

Except from spot sn2, the head and needle show similar amounts of silver (~83%) and copper (~13%). Spot sn2 contains less silver (77.9%) and more copper (18.37%). The lead, bismuth and gold values of all three measured spots are in the same range and similar to the middle-sized pin. The zinc values are the highest of all measured finds (~2.5%), and the Zn/Cu ratios are similar to those of the large pins needle.

3.2.6 Undated objects B3223, V13, V20 and V59

The four undated objects were measured to find possible similarities to certainly dated objects. The results show that none of the objects can be clearly matched to one of the dated groups.

B3223 (needle fragment)

The spot on *B3223* contains 90.5% silver and 6.46% copper. The concentration of minor elements is high (3.03%). These values, as well as those for bismuth and gold are similar to the byzantine pins. However, big differences are found in the much lower zinc (0.07%) and the much higher lead (2.4%) value. The lead concentration is the highest of all measured finds.

V13 (raw material/lump)

Three spots and two areas were measured on this object. All contain 96.5% - 97.4% silver and 0.45% - 0.86% copper, and a generally high percentage of minor elements (between 1.7% and 3%). The results of the single measurements show a wide distribution for the minor elements. All have the highest percentages of gold (between 1.68% and 2.98%) of all finds. The bismuth values differ significantly between the measurements. Spot s2 shows the highest bismuth value of the measured objects, only three helmets have higher amounts of bismuth. On the contrary, area c2 shows the lowest measurable bismuth value of all measured finds. The other spots and areas have relatively low bismuth values (0.02-0.03%). The lead values are similar in all spots, resulting in a wide range of Bi/Pb ratios within the material.

V20 (hinge)

The measured spot on *V20* has a silver content of 93.5% and a copper content of 4.36%. The percentage of minor elements is among the higher of the measured finds. It shows the second highest lead content (1.8%), while bismuth is below the detection limit. The gold value is in the higher range and small amounts on zinc are present (0.066%).

V59 (sheet fragment)

One spot was measured on a fragment of *V59*. It has a silver content of 98.4% and a copper content of 1.05%. The lead and gold values are in the same range as those of the archaic objects, but the bismuth content is much higher (0.08%). The Bi/Pb ratio is the second highest of the objects.

3.2.7 Objects made of different material (V11 golden side, Met233)

Quantitative results for the golden side of *V11* showed that it consists of a gold-silver alloy (60.01% gold, 37.84% silver) with traces of copper (0.69%) and zinc (0.56%).

The small chain *Met233* is strongly corroded. Analysis showed that it consists of a bronze alloy. A tin content of 61.94% and a copper content of 31.09% were measured, representing the corrosion layer depleted in copper. Additionally, arsenic (2.32%), antimony (1.35%), lead (1.31%), iron (0.97%), bismuth (0.52%), zirconium (0.17%), nickel (0.11%) and manganese (0.08%) were measured.

3.3 Qualitative results

Only qualitative results could be obtained with the handheld XRF because of the corrosion present. The detected elements for the finds that no quantitative data were gathered are shown in Table 2. The big spot size made it impossible to measure the ornaments on the helmets, which are smaller than the window of the machine. For some objects, no quantitative data could be obtained neither with the micro-XRF because of corrosion products.

Table 2: Qualitative results obtained from the handheld-XRF and the portable micro-XRF (additional information gained only with the portable micro-XRF marked in yellow)

Inv. number	comments	Ag	Cu	Zn	Pb	Au	Bi	Fe	Br	Cl	Ca	S	As	Ni	Sb	Sn	Cr	Sr	Zr	Rb
Met 244		x	x	x	x	x	x	x	x	x	x	x							x	
o.Nr.		x	x	x	x	x		x	x	x	x	x	x						x	
V17		x	x	x	x	x	x	x	x	x	x			x					x	x
V203		x	x	x	x	x	x	x	x		x						x		x	
V22		x	x	x	x	x	x													
V234	broken one	x	x	x	x	x		x												
V234	intact	x	x	x	x	x		x												
V235		x	x	x	x	x		x												
V459	partly on clean silver	x	x	x	x	x	x	x	x											
V459	only on corrosion	x	x	x	x	x		x	x											
Br1087		x	x	x	x	x	x	x	x	x	x								x	x
B2764		x	x	x	x	x	x	x	x	x	x						x	x	x	x
B7946		x	x		x			x	x	x	x								x	

4 Discussion

This study is the first systematic analysis of the silver objects from Olympia. Some conclusions regarding specific aspects can be drawn by comparing the quantitative results among each other. It should however be kept in mind that the amount of obtained data and analysed finds is not representative.

The qualitative results reveal that mostly iron, chlorine and bromine, but also calcium are present in the corrosion layers. The general information that copper, zinc, lead, gold and bismuth are present in the alloys besides silver are too vague to serve as an information source.

4.1 Observations

The quantitative results of the XRF analysis of the objects show a correlation between the copper content and the period of manufacture. A general trend indicates that the copper content increased between the archaic/early classical and the Roman/Byzantine period, except from a few exceptions (*Br4089* and *V15*). The ratio of major versus minor elements is also related to the dating of the objects: between the archaic and early classical period, the percentage of major elements (copper and silver) is much higher, and the percentage of minor elements (lead, gold, bismuth and zinc) lower than in the Roman and Byzantine period (Fig. 4), indicating a different manufacturing process or different silver sources in in the Roman and Byzantine period.

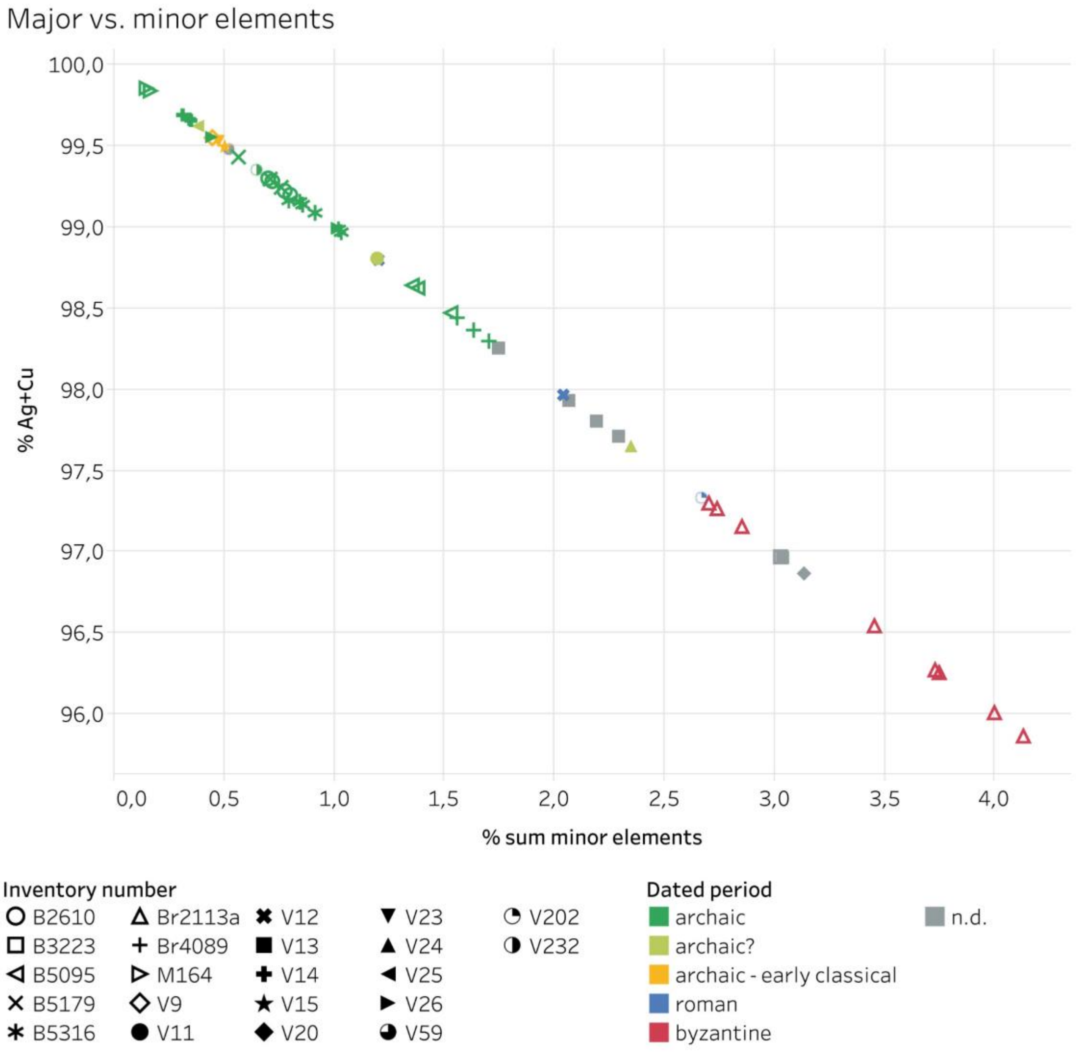

Fig. 4: Major and minor element content of all analysed finds

The material of *V14*, the bottom of *V26*, *V232*, *B5179* and left rider and left lion of *B5316* have more than 98.2% silver and less than 1% copper and can thus be seen as pure silver. *V13* and *V24*, although containing less silver, contain similarly low amounts of copper and can be included in this group. All other analysed finds are made of alloyed silver.

4.1.1 Minor elements

Following, the results obtained for the different elements are discussed.

Table 3 shows the expected minor element composition in the refined silver deriving from the different silver ores. These values must be looked at carefully, since the information represents metal of the direct product from an ore. It does not consider recycling or impurities that may occur during the smelting process. The lead values of silver deriving from cerussite, anglesite and jarosite correspond to those of galena, since cupellation is needed for all three ores.

No statement can be made concerning the possible presence of tin in small amounts because of the overlapping with the silver lines.

Table 3: overview of the elemental composition of silver retrieved from different ores after (Craddock 1995; Gale et al. 1980; Pernicka 2013; Pernicka and Bachmann 1983)

silver origin	**Pb**	**Au**	**Bi**	**comments**
native silver	very low, <0.01%	can be very low (<0.01%), but not necessarily	up to 1%	often amounts of (volatile) elements in the final product (As, Sb, Hg)
chlorargyrite (AgCl), acanthite (Ag_2S)	<0.05%	<0.5%	“low” (no exact values, varying between deposits)	
galena (PbS)	0.1-1% (values down to 0.05% possible)	0.01-0.1%	0.1-1%	needs to be cupelled
cerussite ($PbCO_3$), anglesite ($PbSO_4$)	0.1-1%	>0.1%	differing between deposits	needs to be cupelled
jarosites	0.1-1%	can be very high (up to 16%)	differing between deposits	needs to be cupelled by addition of lead

Lead

Silver that derives from cupelled ores usually contains lead in amounts of 0.1%-1% (Craddock 1995). In some cases values as low as 0.05% were observed (Pernicka 2013). It is known that low values could be achieved with cupellation, but this probably went along with a silver loss of up to 25% (Pernicka and Bachmann 1983). Lower lead values are expected in the final product when the silver derives from ores that don’t require cupellation, like acanthite and chlorargyrite (Craddock 1995). Fig. 5 shows the lead and bismuth content of the analysed finds. The comparison of the lead and bismuth content gives information about the efficacy of the cupellation process. The Bi/Pb ratio can lead to a discrimination of the ore source (see below).

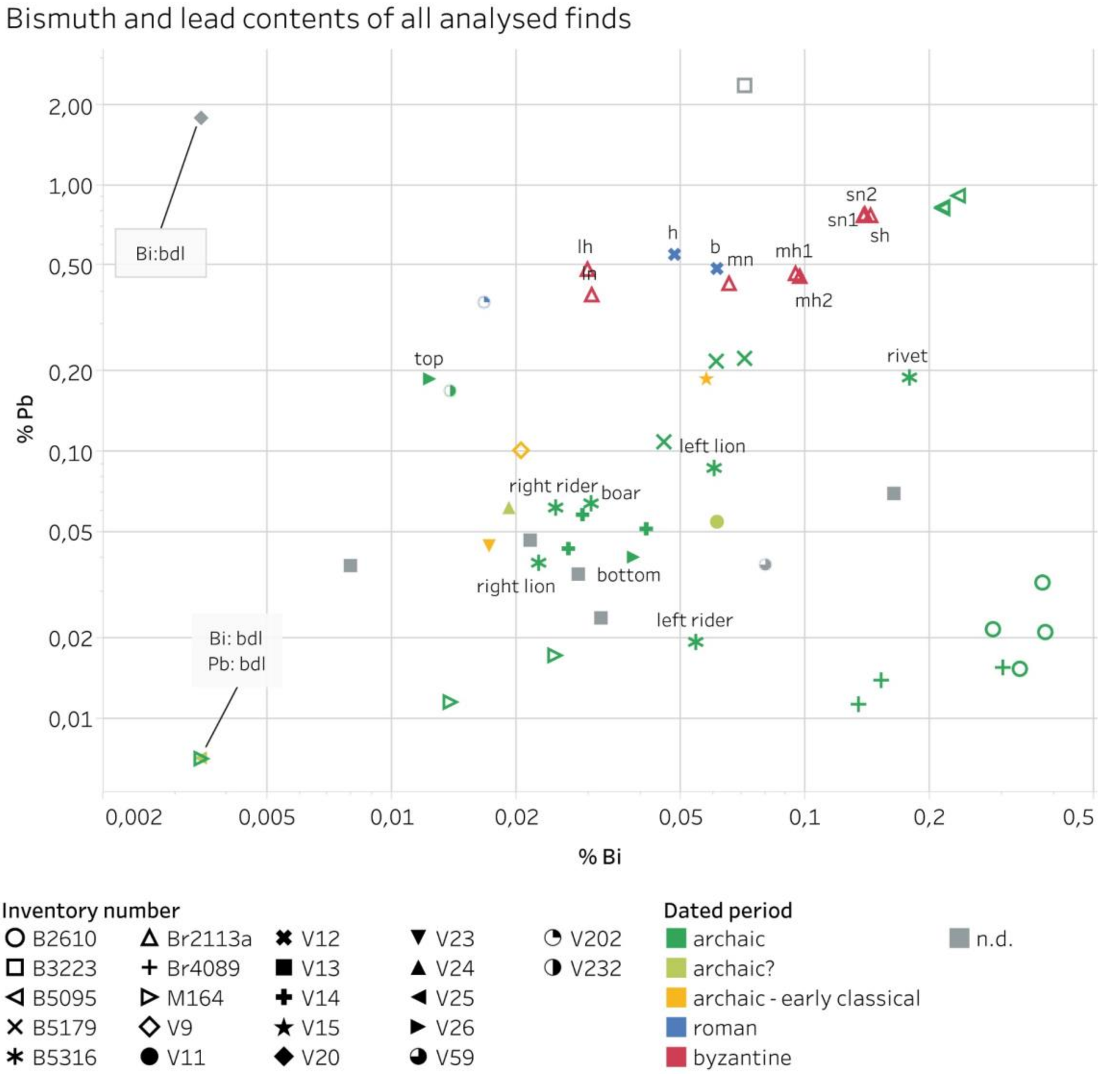

Fig. 5: Bismuth and lead content of the finds (logarithmic scales)

B3223 and *V20* have the highest lead contents of all finds, and the values are above the percentage commonly found in silver after cupellation. It can be assumed that the majority of the lead in these two objects derives from the alloying material. An explanation would be the addition of lead bronze. Since the Bi/Pb ratio is distorted by the added lead, it is not informative.

Although the lead values for *B5095* and *Br3112a* are elevated compared to the other finds, lead was probably not intentionally added (concentrations below 1% are well possible to remain in the silver after the cupellation process). It is likely that it represents residues from the cupellation process, which is in these cases also supported by the relatively high Bi content.

The lead contents of *B2610*, left rider and right lion of *B5316*, *Br4089*, *M164*, *V11*, *V13*, *V14*, *V23*, *V25* and *V59* are extremely low (<0.05%) and lay beneath the commonly suggested percentage that is present after the cupellation process. This might indicate the use of ores that don't need to be cupelled. Another possible explanation is the recycling of silver, leading to an oxidation and elimination of lead during re-melting, or the use of native silver. The analysed spots on *B2610*, *B5316*, *M164*, *V14* and *V59* were not mechanically cleaned. A decrease of lead in the surface layer in these spots may be due to previous conservation treatment, as shown by Moreno-Suárez et al. (2016).

The other objects showing lead values between 0.05% and 1% probably derive from ores that were cupelled.

Bismuth

The bismuth content in the silver derives from the ore. If the silver derives from a lead-bearing ore and was cupelled, the bismuth content decreases in the end of the cupellation process. With longer duration of the process, more bismuth is oxidised and thus extracted along with lead. The bismuth and lead contents can thus give information about the efficiency of the cupellation process.

L'Héritier et al. (2015) proved that the Bi/Pb ratio increases with a higher initial bismuth content of the ore. This ratio can be distorted by the addition of lead or copper, the remelting or the mixing of different materials. Still, it is to some extent possible to discriminate between different ore sources, even more effectively when combined with the gold content (see below).

Six to eight groups and several single spots not belonging to any of the groups can be identified when looking at the Bi/Pb ratio and the gold content (Fig. 6). However, it is not sure if these groups indeed represent different deposits.

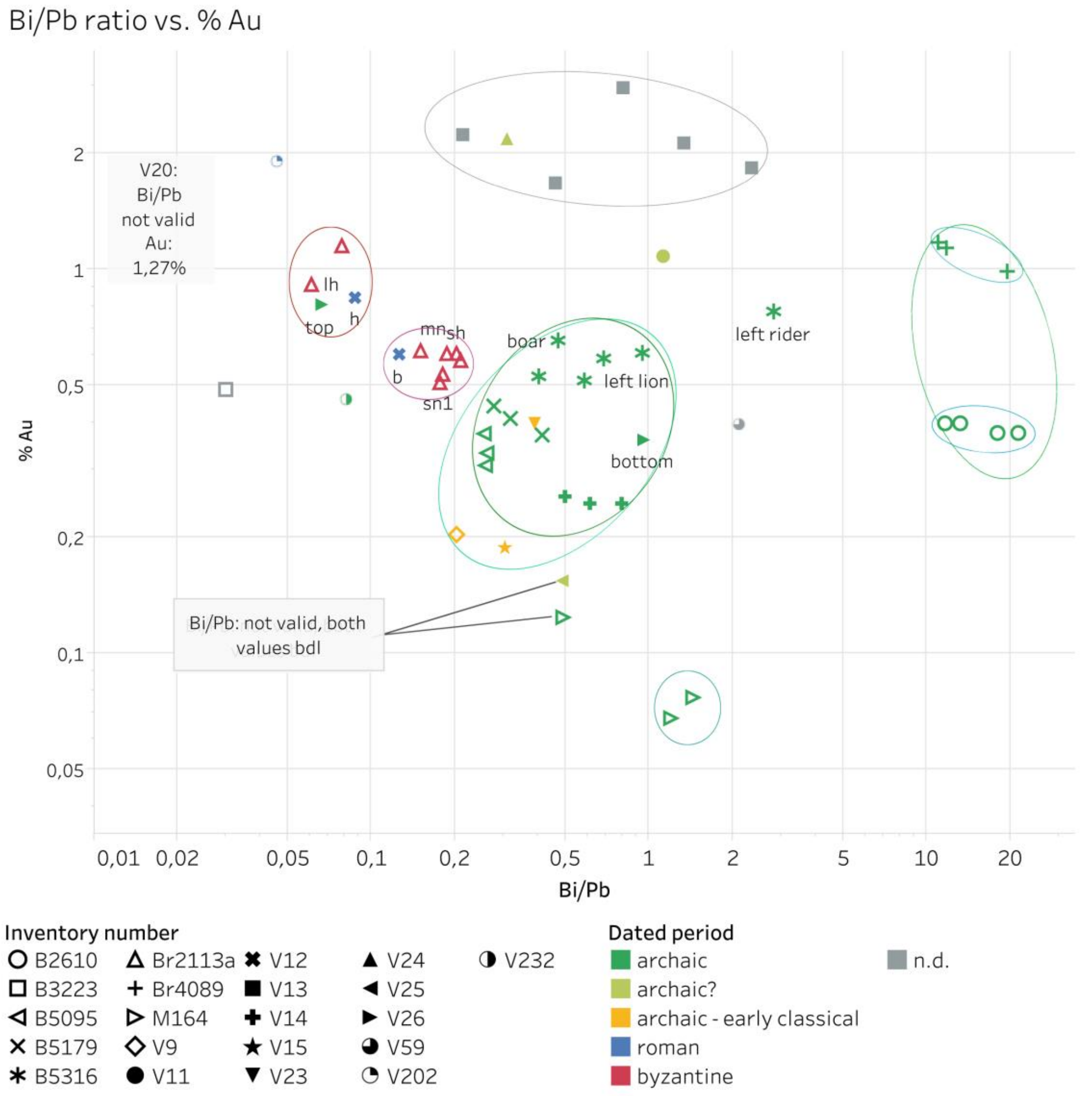

Fig. 6: identified groups regarding the Bi/Pb ratio and gold content (logarithmic scales)

Gold

Three clusters can be identified regarding the gold content. The decorations of M164 contain the least amounts of gold and are clearly separated from the other finds. *V13*, *V24* and *V202* contain much higher gold values than all the other finds and form the second cluster. The values for the other finds cannot be further differentiated and represent the third cluster.

Silver that derives from galena usually contains 0.01% - 0.1% gold. Only the material of *M164* falls within this range but has a lead content that is lower than commonly found in silver deriving from cupellation. Explanations for this are discussed in the chapter dealing with Lead. Another source might be native silver, but none of the additionally expected (volatile) elements were observed. This does not necessarily exclude native silver as a source, since the volatile elements would evaporate, and other elements oxidise partly during melting.

It is uncertain if and how the gold content is increased when the duration of the cupellation process is very long in order to receive lead values down to 0.05% as observed for many finds. Silver loss up to 25% has been reported (Pernicka 2014). No study investigating if a gold loss occurs along with the silver loss was published so far. Since gold is more noble than silver, no oxidation should take place, leading to an elevated gold content and a higher Au/Ag ratio.

Higher gold contents, as observed on most of the archaic finds, all archaic-early classical finds (except from *V26* top), *V59*, *B3223* and *V25* are typical for silver retrieved from chlorargyrite and acanthite (up to 0.5%) and the oxidised lead ores cerussite and anglesite[17].

The materials of *Br4089, B5316*, *V232,* as well as the Roman, Byzantine and the other undated finds have gold values above 0.5%. The gold values above 0.5% could be explained by recycling of silver which was once gilded. High gold contents can also derive from jarosite ores (Craddock 1995). These must be refined by cupellation with added lead, leading to a higher lead content than found in *V13, Br4089* and the left rider of *B5316*, making it unlikely for these to derive from jarosite ores.

Table 4 shows an overview of the characteristic patterns of the finds and an attempt to define the ore type that was used to retrieve the silver. If not mentioned explicitly, the lead and gold values lay within the known range of the indicated ore type. In all cases, recycling of the material must be taken in account as a possible distraction of the elemental pattern. Lead values down to 0.05% are assumed to be possibly reached by cupellation.

Table 4: elemental characteristics and possible ore types used for the different finds

Inv. number	**characteristics**	**possible ore type used**
B 3223	intentionally added lead, gold <0.5%	all possible
Br2113a	elevated lead, elevated bismuth, gold >0.5%	cupelled lead ore, jarosites
V9	gold <0.2%	cerussite, anglesite, acanthite, chlorargyrite, galena
V11	lead <0.05%, gold >0.5%	acanthite, chlorargyrite, highly refined lead ores

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[17] no distinct value for the maximum gold content for silver retrieved from these ores was found

Inv. number	characteristics	possible ore type used
V12 handle	gold >0.5%	cupelled lead ore, jarosites
V12 bowl	gold >0.5%	cupelled lead ore, jarosites
V13	pure silver, high gold content, lead <0.05%	acanthite, chlorargyrite, highly refined lead ores
V14	pure silver, lead <0.05%, gold <0.3%	acanthite, chlorargyrite, highly refined lead ores
V15	gold <0.2%	cerussite, anglesite, acanthite, chlorargyrite, galena
V20	intentionally added lead, gold >0.5%	cerussite, anglesite, jarosites
V23	lead <0.05%, gold <0.5%	acanthite, chlorargyrite, highly refined lead ores
V24	pure silver, high gold content	cerussite, anglesite, jarosites
V25	lead below detection limit	acanthite, chlorargyrite, native silver
V26 top	gold >0.5%	cerussite, anglesite, jarosites
V26 bottom	pure silver, gold <0.5%	cerussite, anglesite
V59	lead <0.05%, gold <0.5%	acanthite, chlorargyrite, highly refined lead ores
V202	gold >0.5%	cerussite, anglesite, jarosites
V232	pure silver, gold <0.5%	cerussite, anglesite, acanthite, chlorargyrite
B2610	lead <0.05%, gold <0.5%	acanthite, chlorargyrite, highly refined galena
B5095	elevated lead, elevated bismuth, gold <0.5%	cerussite, anglesite
B5179	pure silver, gold >0.5%, Bi/Pb similar to B5095	cerussite, anglesite
B5316 boar		cupelled lead ore
B5316 right lion	lead <0.05%	acanthite, chlorargyrite, or recycled
B5316 right rider		cupelled lead ore
B5316 left lion	pure silver	cupelled lead ore
B5316 left rider	pure silver, lead <0.05%	acanthite, chlorargyrite, highly refined lead ores
B5316 rivet	gold >0.5%	cerussite, anglesite, jarosites
Br4089	lead <0.05%	acanthite, chlorargyrite, highly refined galena
M164	lead <0.05%, lowest gold content	highly refined lead ores, native silver

Au/Ag ratios for provenance discrimination

The Au/Ag ratio does not change during smelting of silver and thus derives directly form the ore. Fig. 7 shows the Au/Ag ratios of all analysed finds. However, it is not clear in what way the ratio is distorted (see above).

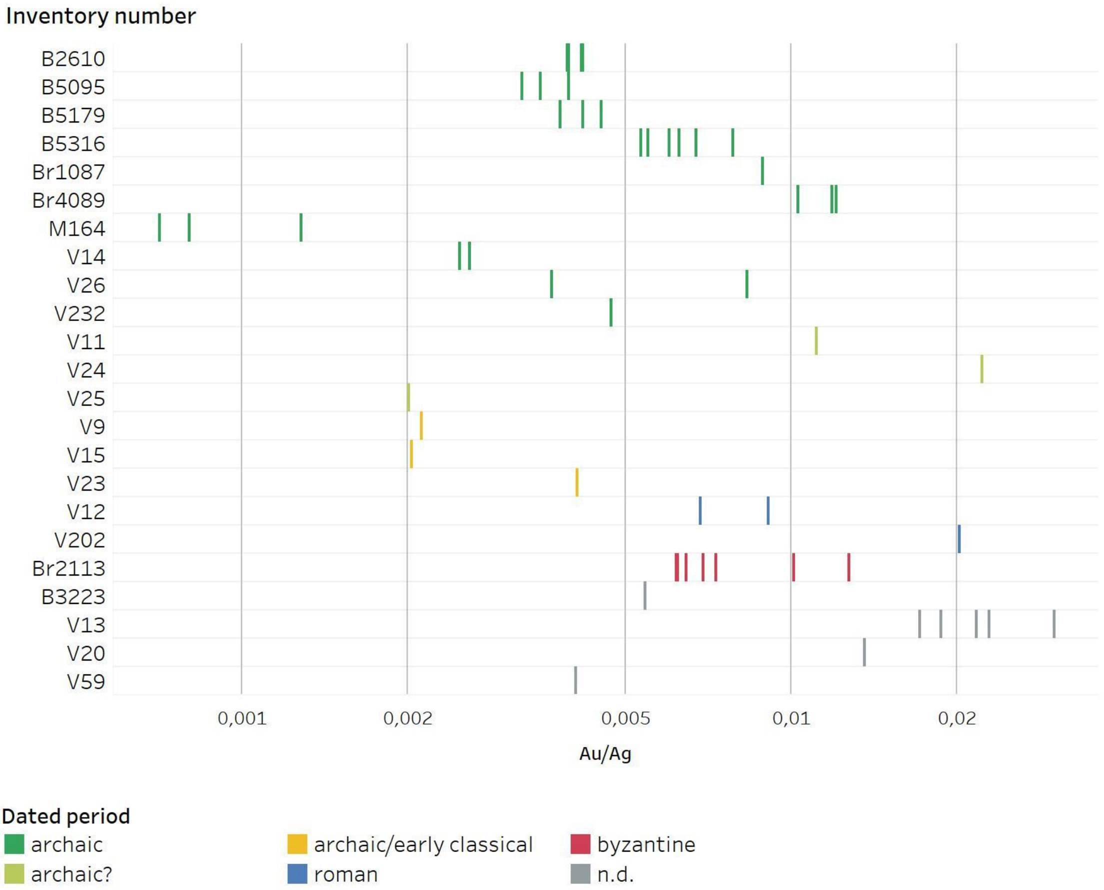

Fig. 7: Comparison of the Au/Ag ratios of all analysed finds

When comparing the obtained Au/Ag ratios to the plot (Fig. 8) generated by Pernicka (1987), it is evident that the ratios of the measured finds from Olympia are all in the higher range of this plot. If the parameters for the calculations are correct and not distorted by a change in the Au/Ag ratio, the ore sources for *B2610, B5095, B5179, V14, V23, V26* and *V232* can be narrowed down to Chalkidiki, Pangaion and Siphnos. The gold values of *B5316* are too high to derive from Pangaion, but are typical for Siphnos and Chalkidiki.

The material of *V9* and *V15* might derive from Chalkidiki, Pangaion, Siphnos or Euboea. For *M164*, a provenance from Balya in Asia Minor is also possible. The mines in Altinoluk, although a potential ore source for *M164*, were proven to be exploited in the 3rd century BCE and can therefore be excluded (Treister 1996).

The silver of *Br4089* has the highest gold content of the archaic finds. The only overlap with a deposit listed by Pernicka (1987) is with Chalkidiki.

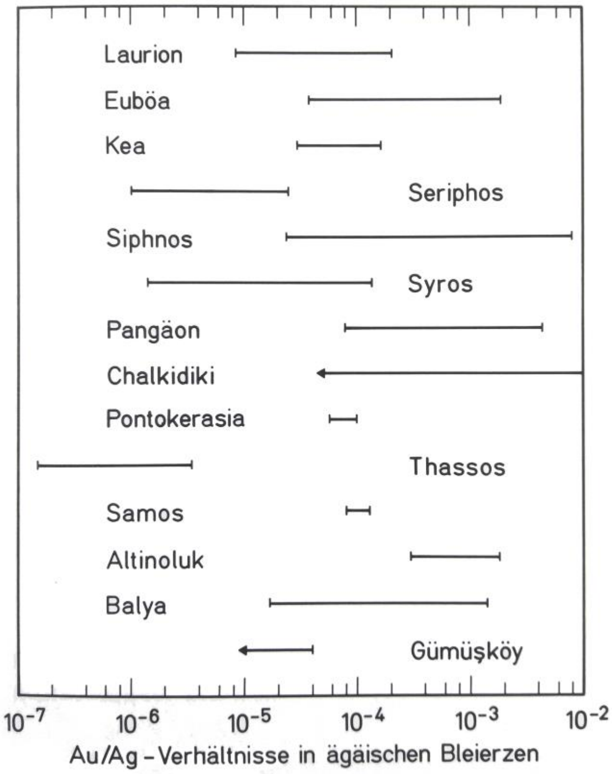

Fig. 8: plot showing the Au/Ag ratios observed in Aegean lead deposits (Pernicka 1987)

Additionally, a provenance from Spain (Rio Tinto) or other deposits that were known in the Greek world outside the Aegean is possible, as well as traded silver from the Near East. For objects from the Roman and Byzantine period, uncertainly dated and undated objects, there are too many possible ore sources to find a match.

Zinc

Fig. 9 presents the Zn/Cu ratio and the zinc content of all objects. For the objects *V14*, *V26* and *V59*, the values lay below the detection limit (bdl, 0.01%).

Fig. 9: Zn/Cu ratio and zinc content of all finds

In the materials of *B5316* right side decorations, *M164*, *V9*, *V12* bowl, *V15*, *V20*, *V24* and *V25*, zinc is present but the Zn/Cu ratio is too low to indicate an intentional addition of brass. Mortimer (1986) assumes that the Zn/Cu ratio stays relatively constant through melting. Commonly used brass alloys contain often zinc percentages above 20%, but also as low as 9%, explaining a smaller Zn/Cu ratio in the silver alloy. However, it is possible that brass was present in the alloying material. An explanation for the elevated zinc content could be the use of scrap metal as an alloying material, that contained small amounts of brass. It is also possible that zinc did not completely evaporate during the smelting of argentiferous lead-zinc ores. Finally, the enrichment of zinc in the surface during burial was observed and could explain the elevated zinc values (Mortimer 1986).

The higher (above 0.2%) zinc values and a Zn/Cu ratio of 0.09-0.32 (similar to brass) make it assumable that brass was added as an alloying material to the silver of *B2113a*, *Br4089*, *B5316* left lion, the handle of *V12* and *V202*.

These observations are especially surprising for the archaic helmets *B5316* and *Br4089*, since the addition of brass to silver is until now known to be performed since the first century CE. So far, no evidence for an earlier silver alloy with brass was found. This may be due to the scarce elemental analysis of silver objects (previous analyses mostly dealt with coins).

Although the left lion of *B5316* shows a Zn/Cu ratio similar to brass, the copper content is so low that it is unlikely that brass was added. The zinc value is possibly elevated due to surface enrichment.

4.1.2 Comparison of the decorations belonging to the same helmet type

Although dating also to the archaic period, the helmets are discussed separately because of their obviously different chemical composition compared to the archaic objects. The compositions of the decorations of the individual helmets are internally consistent, with the exception of *B5316*. Fig. 10 shows the gold content and Bi/Pb ratios of the different helmet decorations indicating the type of helmet they are attached to. No correlation between the chronological classification and composition could be observed.

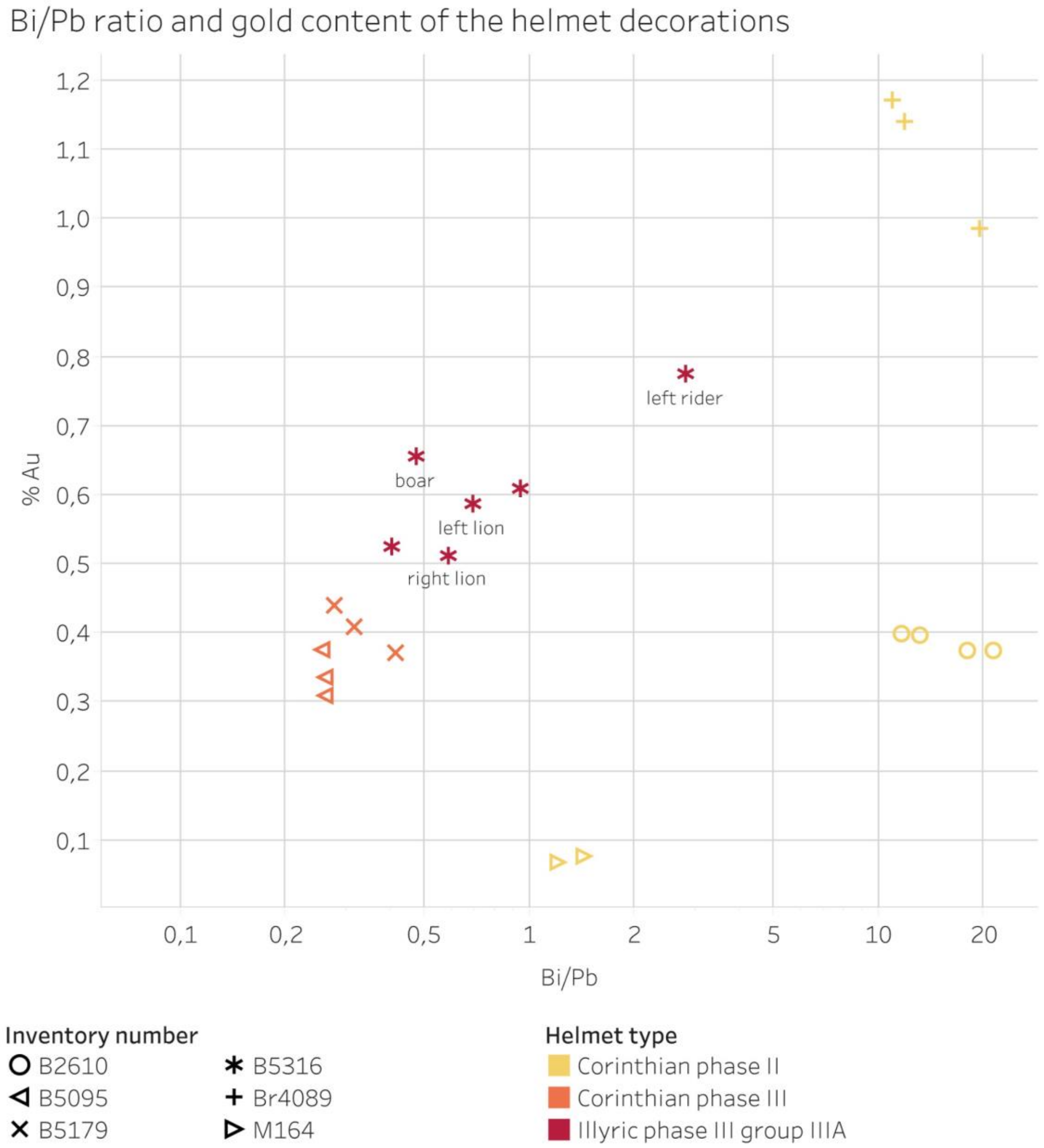

Fig. 10: Bi/Pb ratio and gold content of the helmet decorations (Bi/Pb ratio on logarithmic scale)

Corinthian phase II helmets

B2610, *Br4089* and *M164* belong to the same helmet type but their decorations show significant differences in their composition.

The Bi/Pb ratio and gold content of *M164* differ to such an extend from the other two helmets, that it can be safely assumed they derive from a different deposit.

The decorations of *Br4089* and *B2610* all show very high Bi/Pb ratios. The gold values of *Br4089* are higher than those of *B2610*, and consistent among the decorations of each helmet. The separation by the extremely high Bi/Pb ratio makes it reasonable to assume at least the rivets of one helmet derive from the same deposit, respectively. Despite the big difference in the gold content, it cannot be excluded that the silver for both helmets derives from the same deposit (see above). It is however sure that the silver was alloyed with different materials, showing through the zinc content of *Br4089*.

An explanation for the difference between the compositions of the decorations could be a different origin within the Greek world of the helmets, that were brought to the sanctuary as offerings. This interpretation is contradictive to the hypothesis of local production mentioned by Frielinghaus (2011), at least for the analysed helmets.

Corinthian phase III helmets

A rather different picture is found when looking at the decorations of the Corinthian type phase III helmets. The silver compositions indicate the use of the same raw material. The Bi/Pb ratios of the decorations of both helmets are similar, but the generally lower lead and bismuth concentrations indicate a better refinement of the silver used for *B5179*. *B5095* was probably alloyed with copper, while pure silver was used for *B5179*.

Illyric helmet phase III group IIIA

B5316 is the only helmet analysed of the Illyric type. Born (2009) was not sure if the material was actually silver or tin and suggested a thin foil-silvering of the decorations, that was supposedly still present on some parts. The results of the XRF analysis show only silver in the analysed spots. However, analysis was performed only where the surface was already appearing metallic (except from the rivet, where no metallic surface was present) and it is possible that only the “silvering” was analysed.

Differently from the decorations on the other helmets, those of B5316 are not consistent in their composition. The different decorations are distinguished from each other.

The left rider is made of pure silver. The higher Bi/Pb ratio combined with the higher gold value compared to the other decorations raise the assumption that the silver derives from a different source.

The other decorations are possibly made of a material deriving from the same deposit. They show differences in their copper content: right rider and lion are clearly made of an alloy containing copper amounts that are considered high enough to be added deliberately. The left lion is made of pure silver. Boar and rivet have copper values that could derive either from the ore or from an addition of copper. The Bi/Pb ratios and the gold content for the left lion, right lion and rider, as well as the boar are similar in their composition and could indicate the same ore source.

Right rider and lion show the same elevated zinc content and Zn/Cu ratios. It can be assumed that the same alloying material was used. It is questionable if the zinc value and Zn/Cu ratio of the left lion should be regarded as (traces of) brass. So far, no evidence for the deliberate addition of brass was observed, and the low copper content does not support an intentional addition of an alloying material. It might derive from a crucible in which brass was melted before, or it represents a surface enrichment in zinc due to corrosion. Additional analysis would be necessary to solve this uncertainty.

The higher bismuth and lead values of the rivet indicate a less successful cupellation process. The, although slightly elevated, Bi/Pb ratio and similar gold content make it reasonable to believe that it was made of the same ore, but in a different batch as the other four decorations. The lower zinc value of the rivet supports this hypothesis.

4.1.3 Observations on the compositions of the objects from different periods

In addition to the general observations for all finds, the compositions of the objects show correlations with the time of manufacture. The lead content correlates similar to the major/minor element ratio: archaic and archaic-early classical objects have a lower lead content than roman and byzantine objects (Fig. 11). This suggests the hypothesis of a less careful cupellation process in later times.

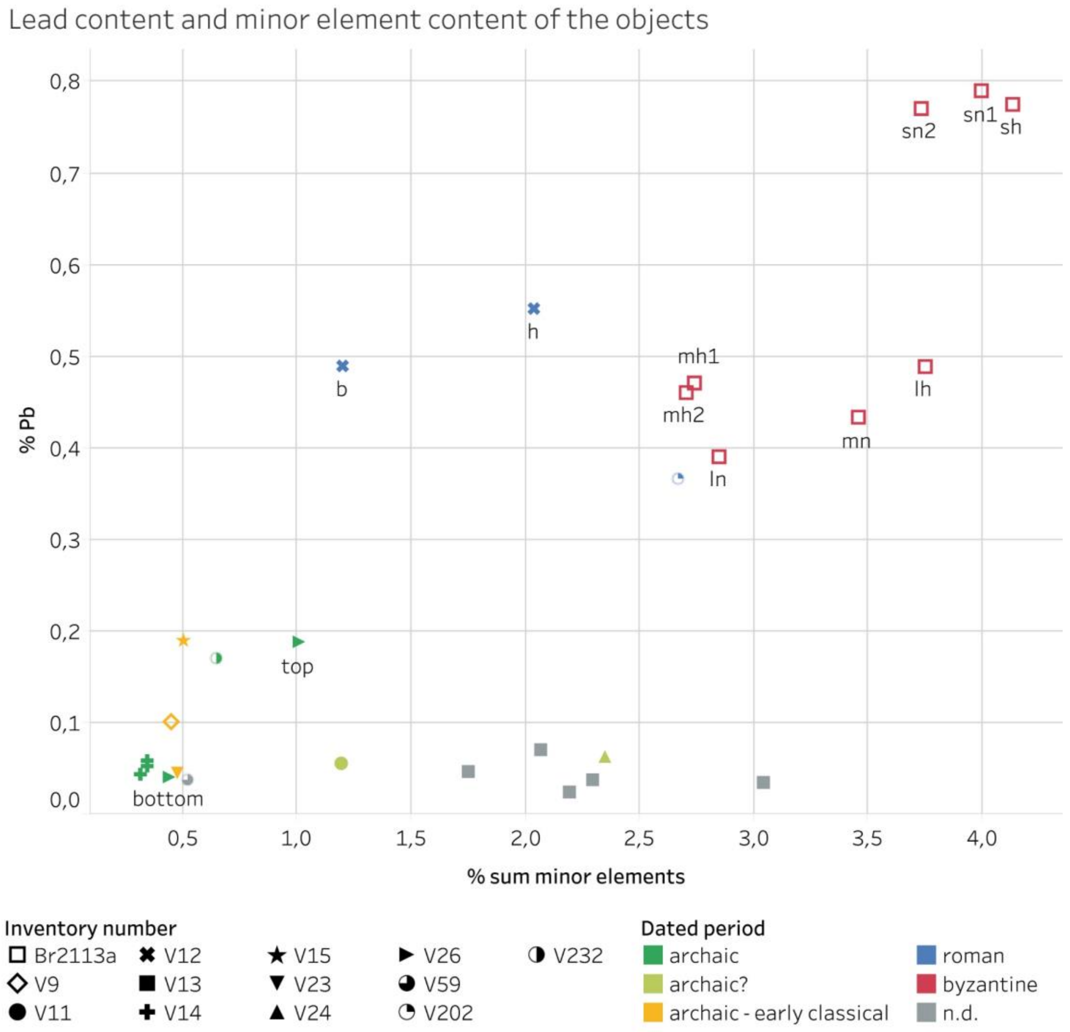

Fig. 11: Lead content and minor element content of the objects

An even stronger relation is found between the zinc content and the time of manufacture (Fig. 9): While archaic objects don’t contain any zinc at all, objects of the archaic-early classical period show small amounts of zinc (up to 0.12%). Roman objects show a greater variety in their zinc content, between 0.05% - 0.59%, and the Byzantine objects all contain more than 1.27% zinc. The Zn/Cu ratios suggest an intentional addition of brass starting in the Roman period. This is in accordance with Mortimer (1986), who found that a deliberate addition of brass to silver was performed since the 1st century CE. The bismuth and gold values show no correlation with time.

Archaic objects

Two different materials can be identified for the archaic objects: pure silver (*V14* and *V232*) and alloyed silver. Both are combined in the aryballos *V26*. The Bi/Pb ratios of *V14* and the bottom of *V26* are similar, and higher than those of *V232* and the top of *V26*. The different materials might represent two (or three) different ore sources. The higher gold content of *V26* top could indicate a different ore source than for *V232*, on the other hand, the difference is within the possible variation of one deposit.

Archaic-early classical objects

Both bracelets *V9* and *V15*, although of a different type, show similarities in their minor element composition. The Bi/Pb ratio and the gold content might indicate a common ore source and therefore support the manufacture in one workshop. *V23*, although it shows a similar Bi/Pb ratio as the bracelets, has a higher gold content and falls within the cluster of the archaic objects and helmet decorations (Fig. 6).

Roman objects

A higher lead content (above 0.37%) than in previous periods in all analysed spots is observed. The lead values are below 0.55%, indicating that no lead was added deliberately. The Zn/Cu ratios indicate a deliberate addition of brass in the material of the spoon handle and the earring. Spoon handle and bowl material are either made of two different ores or the different compositions derive from the alloying material. The latter is less probable when comparing the results with the Byzantine pins.

Byzantine objects

The lead content is similar or higher than of the Roman objects, but within the range that is normal for cupelled silver (all values below 0.8%). The Zn/Cu ratios indicates an intentional addition of brass in all alloys.

Different compositions of needle and head are observed for the large and mid-sized pin. It is possible that the silver used for head and needle was the same but alloyed with different types of copper alloys, respectively. The head of the large pin contains less copper and more zinc than the needle. The different compositions of head and needle (higher zinc content of the head) of the mid-sized pin is inverted when compared to the large pin. Unlike the other two pins, head and needle of the small pin seem to be made of the same material. The pattern of lead, gold and bismuth resembles the mid-sized pin, while the Zn/Cu ratio indicate the usage of the same alloying material as the large pins needle.

The lead and gold content, as well as the Bi/Pb ratios of all pins are similar to both parts of the spoon. The data form two groups that could represent two different raw materials: one for the large pin, similar to the spoon handle (*V12*) and *V26* top, and one for the small and mid-sized pin, similar to the bowl of the spoon *V12*. The Bi/Pb ratio is found not to be dependent on the Zn/Cu ratio and the alteration of the Bi/Pb ratio by the alloying material is thus excluded.

4.2 Comparison of the helmet decorations and the archaic objects

By comparing the results from the helmet decorations and the archaic objects, differences in the material compositions become evident.

The most obvious difference is the measurable zinc content in the silver decorations of four helmets, while none of the archaic objects contains zinc above the detection limit of the instrumentation. The high zinc contents of *Br4089* and parts of *B5316* raise the question if zinc was deliberately added to the silver alloy. This would contradict the finds of Mortimer (1986) and imply that brass was already added to silver in the archaic period.

Fig. 12 shows that although the Bi/Pb values of *V14* and *V26* bottom, and 5 of the decorations of *B5316* are similar, the gold content differs between these objects. The partly very large ranges of Au/Ag ratios within one deposit (Pernicka 1987) suggest that the difference between the helmet decorations and the silver sheet lays within the range of one deposit. No information about the range of the Bi/Pb ratio within a single deposit could be found. Therefore, it is not possible to state if *V14* and *V26* bottom, *B5095* and *B5197*, and *B5316* (without left rider) are different groups or variations within one deposit.

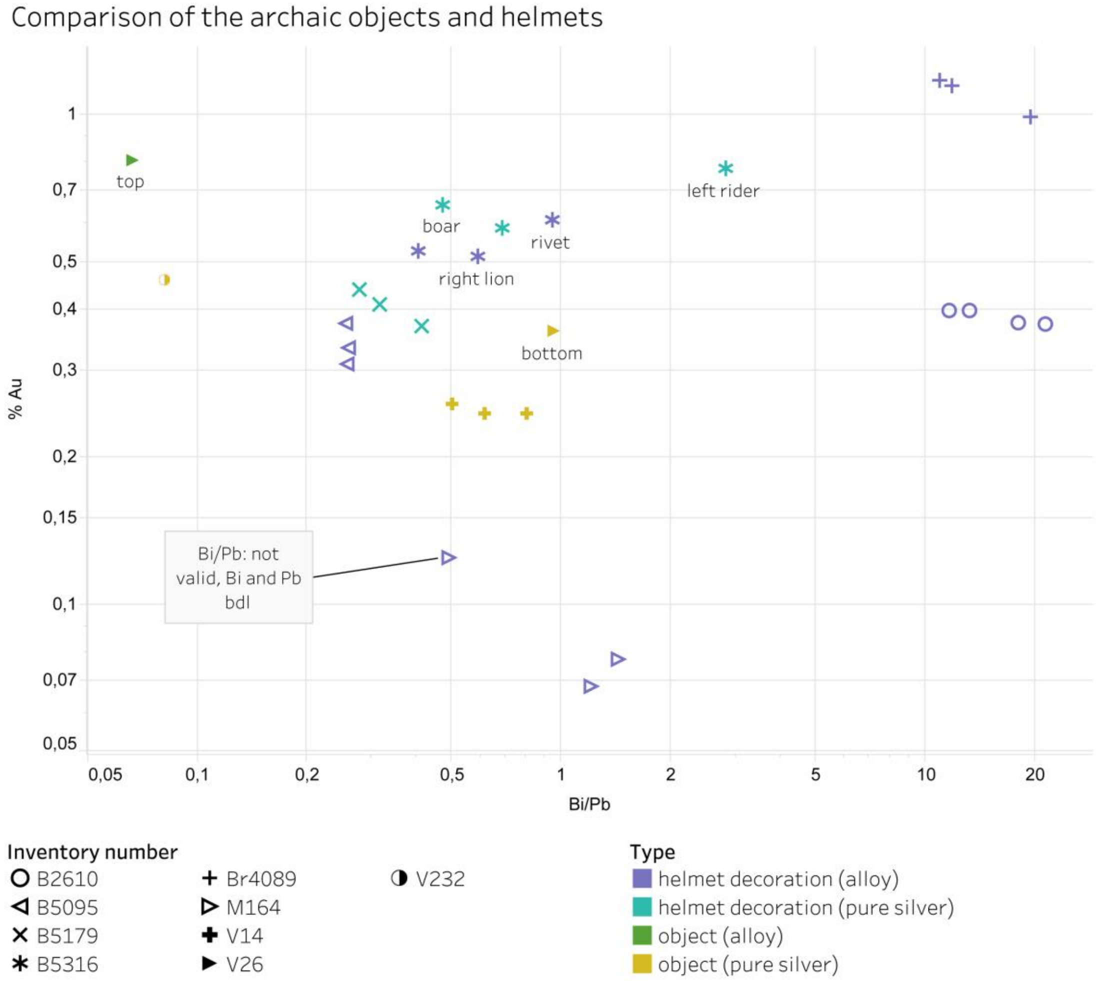

Fig. 12: Comparison of the Bi/Pb ratio and gold content of the archaic finds

B2610, left rider of *B5316, Br4089*, *M164*, *V232* and *V26* top show such big differences, respectively, that they are clearly separable and probably represent individual ore sources (regarding the possibility of a single deposit for *B2610* and *Br4089* see above). It is possible that *V232* and *V26* top derive from the same source.

4.3 Uncertainly dated and undated objects

The analysis of the gilded side of *V11* revealed no mercury, meaning it was not fire gilded as stated in the inventory book. Fire gilding was first applied during the first century BCE and mentioned by Pliny in the 1st century CE (Anheuser 1997; Oddy 1981). A technique that was commonly used before was the application of thin gold foil. This would be in accordance with the proposed dating from the excavation context. However, regarding the quantitative results of the silver, no match with one of the archaic clusters is found, and the dating to the archaic period of *V11* is not supported.

The material of *V13* resembles the elongated bead *V24*, with the difference that no zinc was measured in *V13*. The low copper, bismuth and lead values indicate a careful cupellation process. It is disputable if this material is “pure” silver, but quite certainly no copper was added. The extremely high gold values suggest a different ore source that was used for the silver compared to the other objects. The inhomogeneities within the material cannot be explained conclusively. Since gold and silver have a complete miscibility, no segregation takes place when the melted material cools down. One suggestion is that different materials were melted together and did not mix thoroughly.

Except from the presence of zinc, *V24* shows great similarities to the raw material *V13* and might consist of the same material. The dating of *V24* to the archaic period cannot be supported by comparing it to the other analysed archaic finds.

Although the minor elemental composition of *V25* is similar to the one of *M164*, the high copper content makes this material completely different from all the other examined finds. The dating of *V25* to the archaic period is not supported by the data, especially because of the low silver content.

V59 could not be associated with any other measurement.

Although none of the uncertainly dated objects’ composition is similar to the dated objects, some of them might be archaic anyway. The same can be considered for the undated objects. A reason for a different composition can be a different source of raw material. The number of objects that were analysed is too small to cover all possibly exploited ore sources. The uncertainly dated and undated objects could have been produced from sources that were not used for the identified groups of archaic objects, but date to the same period.

5 Conclusions

35 silver containing finds from Olympia were analysed for this study. The quantitative results of the XRF-analysis for 24 finds revealed correlations between the composition and the period of manufacture: more copper was added, and more impurities in the form of minor elements (Au, Bi, Pb, Zn) were found in finds from the Roman and Byzantine period. The archaic and early

classical finds show high silver contents above 95.5% and up to 99.5%. Only in the group of archaic finds, silver without deliberately added copper was observed. All other analysed materials were made of alloys. The zinc content in the objects from the Roman and Byzantine times indicates the addition of brass as an alloying material to the silver. Based on the quantitative results for the minor elements, suggestions for the types of ores used to smelt the silver can be made. A cluster of 2 archaic objects and 3 archaic helmets could be identified based on the Bi/Pb ratio and the gold content. The decorations of 3 other helmets, although also dating to the archaic period, differ significantly in their composition from this cluster, and the silver probably derives from 2 or 3 other sources. Whether or not the compositions of two other archaic objects results from one or two different sources for the silver is not evident. The helmet decorations of the individual helmets (except from *B5316*) are consistent in their composition. Whether or not zinc in the form of brass was deliberately added to the silver of two helmets remains unclear. A deliberate addition would contradict the recent literature that date the first alloying of brass to silver to the first century CE. Further investigations (on other finds) would be necessary to gain knowledge in this field. It is uncertain if the objects from the archaic-early classical period are similar enough in their composition to derive from the same source. If this is the case, they all can be included in the identified cluster for the archaic finds.

The results do not allow a conclusive dating of the so far undated objects. It is noteworthy that the compositions of these objects don’t correlate with any of the identified clusters. They must thus be seen as individual groups that can’t be associated with the dated objects. However, the raw material (*V13*) and the elongated bead (*V24*) show such great similarities that they are possibly made of the same material.

Qualitative analysis, although faster and less labour intensive, have proven to be without informative value when it comes to silver finds.

6 Perspectives

This study is the first analysis of silver objects in Olympia, in a sanctuary-related context and for archaic, non-coin finds in general.

For further research, the analysis of the remaining silver objects from Olympia that are partly stored in the National Archaeological Museum in Athens could widen the dataset provided in this study and give a more holistic overview on the material. Additional lead isotope analysis could complement this work and may help tracing the deposits the silver derives from.

A study of the silver from other decorated helmets (for example: a late Corinthian helmet from Olympia in the National Museum Athens (Inv. Number 15183, mentioned by Born 2009), other Illyric helmets in the British Museum (Hockey et al. 1992) and in Trebeništa, a nose cover with silver decoration from Delphi (Frielinghaus 2007) and a decorated phase I Illyric helmet mentioned by Pflug (1988)) is highly recommended. The comparison with other archaic finds as it was done in this study should be included where possible. This might reveal locally preferred ore/raw material sources and give information about correlations with the silver of helmets from Olympia. It could also clarify the question if brass was already deliberately added to silver in the archaic period.

This study might be a starting point for a broader comparison of silver objects from sanctuaries all over the ancient Greek world to identify possible connections between them.

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8 Appendix

List of the inventory number, German designation and English translation of the objects

Inventory number	German designation (as in inventory book)	English translation
B3223	Silbernadel Fragment	silver needle (fragment)
Br2113 a	3 Haarnadeln versilbert	three silvered hair pins
Met233	Kettchen	small chain
Met244	kleines Silberkreuz	small silver cross
o.Nr.	Ring (Silber?)	ring (silver?)
V9	Schlangenarmreif teils feuervergoldet	snake bracelet, partly gilded
V11	Silberrosette, feuervergoldet	silver rosette, fire gilded
V12	Silberlöffelchen	small silver spoon
V13	Unbearbeitetes Stück Silber	unworked piece of silver
V14	Fragment eines Silberblechbeschlages (Schildzeichen?)	fragment of a silver sheet (for a shield?)
V15 = B2630	Fragment eines Schlangenarmreifes	fragment of a snake-bracelet
V17	Silberring	silver ring
V20	Fragment eines Silberscharniers	fragment of a silver hinge
V22	Silberner Fingerring	silver finger ring
V23	Silbernes Gewicht	silver weight
V24	Silberne Wulstattasche	silver “escutcheon“, here referred to as: elongated silver bead
V25	Scheibe aus Silberblech	disc made of silver sheet
V26	Hals eines silbernen Aryballos	fragment of a silver aryballos
V59	Fragmente eines silbernen Beschlagbleches	fragments of a silver sheet fitting
V202, V203	silberne Ohrringe	silver earrings
V232	Fragment einer silbernen Rosette, gehört zu V232	fragment of a silver rosette, belonging to V232
V234	silberne Ohrringe	silver earrings
V235	silberner Ohrring	silver earring
V459	Randfragment von Gefäß	rim fragment of a vessel

Quantitative results of the objects

Inventory number	spot number	Ag	sd Ag	Cu	sd Cu	Au	sd Au	Zn	sd Zn	Pb	sd Pb	Bi	sd Bi	other detected elements	Bi/Pb	sum Ag+Cu	sum other	Zn/ Zn+Cu	Au/Ag
B 3223		90,5	0,2	6,46	0,02	0,49	0,01	0,069	0,003	2,40	0,01	0,071	0,004	Cl, Ca, Zr, Br	0,030	96,97	3,027	0,010	0,0054
Br2113a large head	lh	90,5	0,4	5,75	0,04	0,91	0,01	2,31	0,02	0,49	0,01	0,03	0,01	Ca, Fe, Ni, Zr	0,061	96,25	3,745	0,287	0,0100
Br2113a large needle	ln	90,4	0,3	6,78	0,04	1,16	0,01	1,27	0,02	0,39	0,01	0,030	0,005	Ca, Fe, Ni, Zr	0,077	97,15	2,848	0,158	0,0126
Br2113a mid-size head	mh1	94,0	0,4	3,26	0,03	0,60	0,01	1,57	0,02	0,47	0,01	0,09	0,01	Ca, Fe, Ni, Zr	0,201	97,26	2,735	0,324	0,0064
Br2113a mid-size head	mh2	93,9	0,2	3,38	0,02	0,58	0,01	1,56	0,01	0,46	0,01	0,097	0,004	Ca, Fe, Ni, Zr	0,210	97,30	2,702	0,316	0,0062
Br2113a mid-size needle	mn	89,4	0,2	7,12	0,02	0,62	0,01	2,34	0,01	0,43	0,01	0,065	0,003	Ca, Fe, Ni, Zr	0,150	96,55	3,454	0,247	0,0069
Br2113a small head	sh	83,3	0,2	12,56	0,03	0,605	0,007	2,61	0,01	0,78	0,01	0,144	0,004	Ca, Fe, Ni, Br, Zr	0,185	95,87	4,131	0,172	0,0072
Br2113a small needle	sn1	82,7	0,2	13,35	0,03	0,509	0,007	2,56	0,01	0,79	0,01	0,139	0,004	Ca, Fe, Ni, Br, Zr	0,176	96,01	3,995	0,161	0,0061
Br2113a small needle	sn2	77,9	0,2	18,37	0,04	0,54	0,01	2,28	0,01	0,77	0,01	0,138	0,004	Ca, Fe, Ni, Br, Zr	0,179	96,27	3,728	0,110	0,0068
V9		97,2	0,2	2,31	0,01	0,205	0,004	0,120	0,003	0,102	0,003	0,020	0,002	Cl, Ca, Fe, Ni, Br, Zr	0,201	99,55	0,447	0,049	0,0021
V11		97,0	0,2	1,81	0,01	1,08	0,01			0,054	0,003	0,061	0,003	Fe, Br, Zr	1,124	98,81	1,195	0,000	0,0110
V12 handle	h	93,3	0,2	4,62	0,02	0,85	0,01	0,59	0,010	0,55	0,01	0,048	0,003	Cl, Ca, Fe, Ni, Zr	0,088	97,96	2,039	0,114	0,0090
V12 bowl	b	88,2	0,2	10,65	0,03	0,60	0,01	0,049	0,003	0,49	0,01	0,061	0,003	Cl, Ca, Fe, Ni, Zr	0,125	98,80	1,201		0,0068
V13	c1	97,4	0,2	0,86	0,01	1,68	0,01			0,047	0,003	0,022	0,003	Fe, Ni, Br	0,460	98,25	1,749		0,0170
V13	c2	97,0	0,2	0,72	0,01	2,25	0,01			0,037	0,003	0,008	0,001	Fe, Ni, Br	0,213	97,71	2,295		0,0227
V13	s1	97,0	0,2	0,80	0,01	2,14	0,01			0,024	0,003	0,032	0,003	Fe, Ni, Br	1,336	97,80	2,196		0,0216
V13	s2	97,2	0,2	0,72	0,01	1,84	0,01			0,070	0,003	0,16	0,01	Fe, Ni, Br	2,351	97,93	2,070		0,0185
V13	s3	96,5	0,2	0,45	0,01	2,98	0,01			0,035	0,003	0,028	0,003	Fe, Ni, Br	0,809	96,96	3,040		0,0299
V14	s1	99,5	0,2	0,185	0,004	0,246	0,004	0,005	0,001	0,052	0,002	0,041	0,003	Cl, Ca, Fe, Ni, Zr	0,798	99,66	0,344	0,026	0,0025
V14	s2	99,4	0,2	0,209	0,004	0,257	0,004	0,005	0,001	0,058	0,002	0,029	0,002	Cl, Ca, Fe, Ni, Zr	0,500	99,65	0,349	0,023	0,0026
V14	s3	99,5	0,2	0,173	0,004	0,246	0,004			0,044	0,002	0,027	0,002	Cl, Ca, Fe, Ni, Zr	0,613	99,68	0,316		0,0025
V15		94,3	0,2	5,20	0,02	0,191	0,004	0,065	0,002	0,190	0,004	0,057	0,003	Cl, Ca, Fe, Ni, Br, Zr	0,301	99,50	0,503	0,012	0,0020
V20		92,5	0,2	4,36	0,02	1,27	0,01	0,066	0,003	1,80	0,01	bdl		Cl, Ca, Fe, Ni, Br, Zr		96,87	3,133	0,015	0,0135
V23		97,9	0,2	1,61	0,01	0,398	0,005	0,017	0,002	0,044	0,002	0,017	0,002	Ca, Fe, Ni, Br, Zr	0,389	99,52	0,476	0,010	0,0040
V24		97,3	0,2	0,356	0,01	2,20	0,01	0,070	0,003	0,062	0,003	0,019	0,003	Cl, Ca, Fe, Ni, Br, Zr	0,309	97,65	2,347	0,164	0,0221
V25		77,9	0,2	21,7	0,04	0,155	0,001	0,219	0,004	bdl		bdl		Cl, Ca, Fe, Br, Zr		99,62	0,385	0,010	0,0020
V26 top	s1	96,9	0,2	2,06	0,01	0,81	0,01	0,005	0,002	0,188	0,004	0,012	0,002	Cl, Ca, Fe, Ni, Br, Zr	0,066	98,99	1,012	0,002	0,0083
V26 bottom	s2	99,3	0,2	0,249	0,005	0,361	0,005	0,005	0,001	0,040	0,002	0,039	0,003	Cl, Ca, Fe, Ni, Br, Zr	0,953	99,55	0,445	0,020	0,0036
V59		98,4	0,2	1,05	0,01	0,397	0,005	0,005	0,001	0,038	0,002	0,080	0,003	Cl, Ca, Fe, Ni, Br, Zr	2,097	99,48	0,520	0,005	0,0040
V202		93,9	0,2	3,46	0,02	1,92	0,01	0,36	0,01	0,367	0,005	0,017	0,003	Cl, Ca, Cr, Fe, Ni, Br,	0,045	97,33	2,666	0,095	0,0201
V232		98,7	0,2	0,65	0,01	0,461	0,005			0,171	0,003	0,014	0,002	Cl, Ca, Fe, Ni, Br, Zr	0,081	99,35	0,646		0,0046

Quantitative results of the helmet decorations

Inventory number	Dating (approx.)	spot number	Ag	sd Ag	Cu	sd Cu	Au	sd Au	Zn	sd Zn	Pb	sd Pb	Bi	sd Bi	other detected elements	Bi/Pb	sum Ag+Cu	sum other	Zn/ Zn+Cu	Au/Ag
B2610	650-625 BCE	s1	95,9	0,2	3,32	0,02	0,374	0,005			0,021	0,002	0,382	0,005	Cl, Ca, Zr	18,019	99,22	0,778		0,0039
B2610	650-625 BCE	s2	96,0	0,2	3,21	0,01	0,398	0,005			0,032	0,002	0,374	0,005	Cl, Ca, Zr	11,592	99,20	0,805		0,0041
B2610	650-625 BCE	s3	96,1	0,2	3,13	0,01	0,374	0,005			0,015	0,002	0,330	0,004	Cl, Ca, Zr	21,405	99,28	0,719		0,0039
B2610	650-625 BCE	s4a	96,4	0,2	2,90	0,01	0,397	0,005			0,022	0,002	0,285	0,004	Cl, Ca, Zr	13,153	99,30	0,704		0,0041
B5095	525-475 BCE	s1	96,2	0,2	2,37	0,01	0,335	0,004			0,83	0,01	0,214	0,004	Cl, Zr, Fe, Br	0,259	98,62	1,375		0,0035
B5095	525-475 BCE	s3	95,7	0,2	2,79	0,01	0,375	0,005			0,92	0,01	0,234	0,004	Cl, Ca, Zr, Fe	0,254	98,47	1,528		0,0039
B5095	525-475 BCE	s5	96,5	0,2	2,19	0,01	0,310	0,004			0,831	0,006	0,214	0,004	Cl, Ca, Fe, Br, Zr	0,257	98,65	1,354		0,0032
B5179	525-475 BCE	s1	98,6	0,2	0,66	0,01	0,410	0,005			0,226	0,004	0,071	0,003	Cl, Ca, Cr, Fe, Br, Zr	0,314	99,29	0,706		0,0041
B5179	525-475 BCE	s2	98,5	0,2	0,94	0,01	0,372	0,005	0,038	0,002	0,110	0,003	0,045	0,003	Cl, Ca, Ti, Cr, Fe, As, Br, Zr	0,412	99,43	0,565	0,039	0,0038
B5179	525-475 BCE	s3	98,1	0,2	1,13	0,01	0,441	0,005	0,034	0,002	0,220	0,006	0,061	0,003	Cl, Ca, Cr, Fe, Br, Zr	0,276	99,24	0,757	0,029	0,0045
B5316	550-525 BCE	boar	98,0	0,2	1,10	0,01	0,65	0,01	0,111	0,003	0,064	0,003	0,030	0,002	Cl, Ca, Cr, Fe, Ni, Br, Rb, Zr	0,472	99,14	0,861	0,092	0,0066
B5316	550-525 BCE	lion right	96,3	0,2	2,88	0,01	0,51	0,01	0,219	0,004	0,039	0,002	0,023	0,002	Cl, Ca, Fe, Ni, Br, Rb, Zr	0,587	99,16	0,793	0,071	0,0053
B5316	550-525 BCE	lion left	98,2	0,2	0,77	0,01	0,59	0,01	0,285	0,004	0,088	0,003	0,060	0,003	Cl, Ca, Fe, Br, Rb, Zr	0,688	98,98	1,019	0,271	0,0059
B5316	550-525 BCE	rivet	97,5	0,2	1,46	0,01	0,61	0,01	0,057	0,002	0,190	0,004	0,179	0,004	Cl, Ca, Fe, Br, Rb, Zr	0,942	98,97	1,034	0,038	0,0062
B5316	550-525 BCE	rider right	96,0	0,2	3,16	0,02	0,53	0,01	0,235	0,004	0,062	0,003	0,025	0,002	Cl, Ca, Fe, Br, Rb, Zr	0,403	99,15	0,847	0,069	0,0054
B5316	550-525 BCE	rider left	98,9	0,2	0,156	0,004	0,77	0,01	0,066	0,003	0,019	0,002	0,054	0,003	Cl, Ca, Fe, Br, Rb, Zr	2,815	99,09	0,915	0,298	0,0078
Br1087	650- BCE		80,4	0,2	17,63	0,03	0,71	0,01	0,76	0,01	0,38	0,01	0,16	0,004	Cl, Ca, Fe, Br, Rb, Zr	0,426	97,99	2,015	0,041	0,0088
Br4089	650- BCE	s1	96,4	0,2	2,06	0,01	1,17	0,01	0,225	0	0,014	0	0,153	0,003	Cl, Ca, Fe, Br, Rb, Zr	10,954	98,44	1,563	0,098	0,0120
Br4089	650- BCE	s2	95,8	0,2	2,45	0,01	1,14	0,01	0,42	0,01	0,011	0,002	0,135	0,003	Cl, Ca, Fe, Br, Rb, Zr	11,853	98,29	1,706	0,146	0,0118
Br4089	650- BCE	s3	95,6	0,2	2,77	0,01	0,98	0,01	0,334	0,01	0,015	0,002	0,302	0,004	Cl, Ca, Fe, Br, Rb, Zr	19,475	98,36	1,636	0,108	0,0102
M164	600-575 BCE	s1	98,2	0,2	1,68	0,01	0,125	0,003	0,025	0,002	bdl		bdl		Cl, Ca, Fe, Zr		99,84		0,015	0,0013
M164	600-575 BCE	s2	97,0	0,2	2,81	0,01	0,077	0,003	0,044	0,002	0,017	0,002	0,025	0,002	Cl, Ca, Fe, Zr	1,428	99,84	0,163	0,015	0,0008
M164	600-575 BCE	s3	97,3	0,2	2,58	0,01	0,068	0,003	0,053	0,002	0,012	0,002	0,014	0,002	Cl, Ca, Fe, Zr	1,197	99,85	0,146	0,020	0,0007

Analysed spots on the helmets

1: Analysed spots on B2610

2: Analysed decorations on B5095

3: Analysed decoration on B5179

4: Analysed spots on Br1087

5: Analysed spots on Br4089

6: Analysed spots on M164

7: Analysed spot (qualitative) on B2764

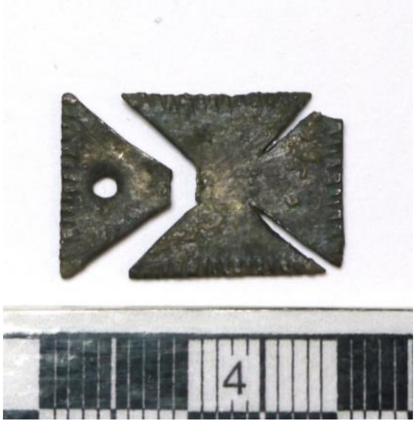
8: Analysed spots on B5316 (left lion, rivet, boar and right lion)

9: Analysed spot on the left rider on B5316

10: Analysed spot on the right rider on B5316

Overview of the analysed objects

11: B3223



12: Met244

13: Br2113a

14: Met233

15: o.Nr.

16: V9

17: V11 silver side

18: V11 golden side

19: V12

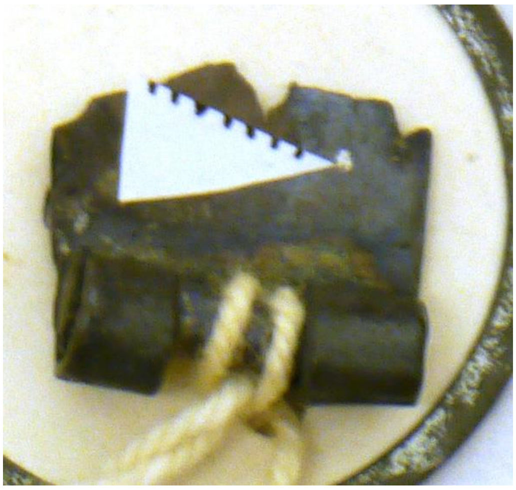
21: V13 back (measured on this side only)

20: V13 front

22: V14

23: V15

24: V17



25: V20

26: V22

27: V23 front

28: V23 back

29: V24

30: V25

31: V26 bottom

32: V26 top

33: Overview of V59

34: Analysed spot on V59

35: V202

36: V203

37: V232

38: V234

39: V235

40: V459 front

41: V459 back