Article

New Insights in Metallurgical Manufacturing in the Caucasian Area: The Case Study of Artefacts from the Samshvilde Citadel Ruins (South Georgia)

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Abstract: An archaeometric approach was applied to the study of the hoard found in the Samshvilde fortress, one of the richest areas of archaeological artefacts in Caucasian Georgia, since it is representative of the historical events from the Neolithic period until the most recent epochs. In this context, four coins dated back to the 12th–13th centuries AD to the reign of King Giorgi III, Queen Tamar, and King Giorgi IV of Georgia underwent different analytical methods to collect information about the technological production process, the probable forge location, and their conservation state. Optical microscope observations provided details about the decorations, the stylistic aspects, and a preliminary evaluation of the conservation state. Portable X-ray fluorescence and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy analysis revealed a composition consisting almost exclusively of copper with a lower amount of tin, lead, and silver. Moreover, degradation products (copper chlorides and sulphates) and cuprite patina were identified. The metal-supplying areas could be related to the nearby Bolnisi Mining District, and the forge location could coincide with the hoard location in Samshvilde, but further data and analyses are necessary.

Keywords: characterisation; coins; copper; cuprite; degradation products; metals; Samshvilde

1. Introduction

The history of ancient coins is always strictly connected to the geopolitical, social, religious, and economic evolution of a country or an empire. The first use of copper alloys for coins dates back to the 5th century BC [1,2].

The information about their minting, effigy, circulation, devaluation, and disuse often provides further elements in the archaeological reconstructions [3].

In this regard, archaeological studies are integrated by archaeometric investigations whose effectiveness has been widely demonstrated in the studies regarding other ancient materials such as mortars, marbles, and bronze or obsidian furnishings [4–6]. Archaeometric non-invasive and micro-destructive techniques such as portable X-ray fluorescence, Raman spectroscopy, and scanning electron microscopy represent efficient support for collecting crucial data on the composition and manufacturing processes of the coins [1,7–13].

The archaeometric and archaeological studies on the hoards are fundamental in areas such as the Caucasus, which were considered crossroads until ancient times and often disputed for their strategic geographical position or the richness of their territories.

The Caucasian region is considered a key passage between the Caspian and the Black Seas, respectively on the east for Northern Iran, Central Asia, and via these regions to China, India, the Persian Gulf, and Russia, and on the west towards Greece and neighbouring areas [14]. Moreover, the Transcaucasian region, a very long and large valley cutting the Caucasus into east and west, makes connections between the two sides easier. For these reasons, the area has always been the subject of contention and wars between the various powers in history: Greeks, Persians, Turks, Mongols, Arabians, Armenians, etc.

On the other side, more than 200 deposits, some of them outcropping, including mineral ores of gold, copper, arsenic, antimony, etc., have been listed in Georgia, where, as in the rest of the South Caucasus, the systematic exploitation of metal ores probably started in the 5th millennium BC [15,16]. In this regard, the Georgian Bolnisi gold–copper mining district in the Lesser Caucasus is well-known since prehistory for its mineral deposits; it draws even now from the Cretaceous Madneuli barite–gold–copper–polymetallic (i.e., lead–zinc, pyrite, silver, sulphur) deposit, one of the most extended of the region [17–21] (Figure 1A). According to [22], the oldest metallurgy on Georgian territory has been located in the Bolnisi region, rich in early agricultural settlements, too. This is confirmed by the remnants of ancient copper ore extraction close to Tsitelisopeli and its vicinity [16,22].
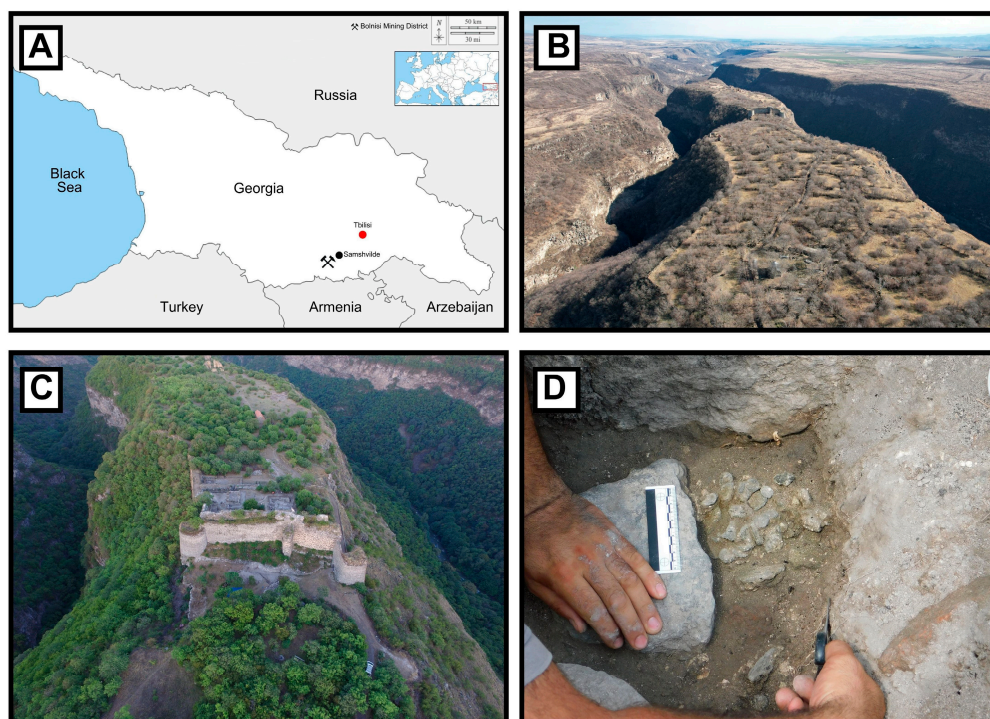
Figure 1. General view of the study area: (**A**) Samshvilde and Bolnisi districts on a Georgia map; (**B**,**C**) a panoramic view of the Samshvilde archaeological site; (**D**) a hoard found in Samshvilde Palace, where the samples come from. Credits: Photos: David Berikashvili.

All these elements justified the great and heterogeneous abundance of coins in Georgian territories dating back to different and distant historical periods and coming from both local and foreign areas [14,23–26].

Samshvilde was one of the most significant economic, cultural, and political centres of the South Caucasus in the Middle Ages [27] (Figure 1B,C). Due to its convenient and favorable geographic location, it has permanently attracted representatives of various cultures and ethnic groups over the centuries. This explains the multiplicity of the artefacts and items discovered in Samshvilde as a result of archaeological excavations [28–30].

Among them, the coin hoard of the Middle Ages, which includes 285 coins of the 12th–13th centuries and coins cut on behalf of the Georgian kings, is quite important. This hoard also contains Eastern coins placed there because of extensive economic circulation.

The Samshvilde coin hoard was discovered in 2018–2019, when excavations were carried out on the territory of Samshvilde citadel, in particular in trench #60, where ruins of the palace of the 11th–12th centuries resurfaced [30] (Figure 1C,D).

These were covered, in turn, by other ruins and cultural layers of the late Middle Ages. However, it was managed to discover the well-preserved floor level where lime plaster was applied. The excavations confirmed that this part of the palace was entirely burned down: the roof collapsed, and the wooden bearing structure of the roof was entirely placed on the floor.

Fragments of clayware common for the 11th–12th centuries, including pieces of glazed ceramics, glass fragments, and stones, were found after excavations of ruins concentrated at the floor level. Here, the remains of a small, burned wooden box containing the above-mentioned coins were discovered.

The finding of such a hoard as a result of methodical and systematic archaeological excavations occurred rarely, especially if the hoard included coins cut on behalf of various representatives of the royal family. In this regard, the hoard discovered in Samshvilde citadel is unique since it includes coins cut on behalf of the Georgian King Giorgi III (1156–1184), Queen Tamar (1184–1210), and King Giorgi IV Lasha (1210–1223). All three monarchs were representatives of the Bagrationi royal family, and under their rule, the Georgian kingdom reached the pinnacle of its political, cultural, and economic revival. Thus, this period is considered the "Golden Age" in the history of the Georgian kingdom of the Middle Ages, and due to the economic strength of the country, Georgian coins circulated almost throughout the entire Near East.

Moreover, it is worth pointing out that, in addition to the above royal coins, the other three groups were distinguished. Some coins of various rulers bearing a secondary seal constitute the second group [30].

The third and fourth groups include, respectively, coins of Eastern origin, namely, Shirwan Shah's coins, and coins that could not be identified due to a low level of preservation [30].

Thus, the Samshvilde hoard represents a significant archaeological discovery relevant not only for the historical reconstructions of the specific former settlement but also of Georgia in the Middle Ages and a certain part of the Near East.

For this reason, at this stage, the main goal of this research is to define the technological features, the state of conservation of selected coins, potentially the place of cutting, and whether the royal mint was located directly on the Samshvilde former settlement, i.e., in the place where this hoard was discovered. An archaeometric approach was adopted by applying complementary techniques such as a digital optical microscope (DOM), portable X-ray fluorescence, fibre optics reflectance spectroscopy (FORS), and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS).

2. Materials and Methods

The archaeologists of the University of Georgia, working in the Samshvilde fortress since 2012, divided the citadel area into 99 trenches (5 × 5 m each). Among them, trenches no. 59, no. 60, no. 66, no. 67, no. 68, and no. 69 are rather relevant because of the findings discovered dated back to the high-late medieval centuries (11th–13th centuries) and Islamic, pre-Islamic, and Ottoman objects in stratigraphic continuity [31].

The coins investigated are representative of different historical periods: they were cut on behalf of King Giorgi III (1156–1184), Queen Tamar (1184–1210), and King Giorgi IV Lasha (1210–1223), well-known in Georgian numismatics. The coins come from trench no. 60 [30].

Table 1 synthetises the main information about the artefacts, and Figure 2 shows the coins and their stylistic details both on the obverse and reverse sides.

Table 1. Coins investigated and main archaeological information. "Depth" indicates the depth of finding of the coins from the present ground surface.

Artefact	Description	Age	Discovery Data	Trench/Square	Depth (m)
A-532	Copper Coin Weight 4.03 g	King Giorgi III (1156–1184)	2017	60/C-3	1.22
B-783	Copper Coin Weight 1.53 g	Queen Tamar (1184–1210)	2018	60/C-2	1.15
C-1047	Copper Coin Weight 35.3 g	King Giorgi IV Lasha (1210–1223)	2018	60/C-2	1.15
D-360	Copper Slab Weight 24.02 g	Middle Ages	2017	60/B-2	1.15

Figure 2. Artefacts investigated shown in both views: obverse and reverse. (**A**) Coin A-532; (**B**) Coin B-783; (**C**) Coin C-1047; (**D**) Slab D-360.

Great importance is linked to the fact that, in addition to coins, a copper slab (D-360) was found in the Samshvilde hoard. The slab seems to have been placed in a special mould and prepared for cutting coins. The discovery of the copper slab and the semi-finished copper plates suggests that most of the coins included in the hoard were probably cut in the medieval city of Samshvilde. To confirm or disprove this hypothesis, the compositions of the three royal coins and the slab were determined and compared.

The artefacts underwent complementary analytical methods to define their chemical features, probable variations in the productive technological process over time, and to evaluate their conservation state.

The samples were previously observed by a portable digital optical microscope (DOM) in order to characterise the decorations and individuate the probable areas affected by degradation phenomena. A digital microscope Dino-Lite AM4113TFVW (Taiwan) was used with the following technical characteristics: resolution 1.3 megapixels; magnification 10×, 50×, 200×; illumination, 4 UV light emitting diodes (LED) with 400 nm+ emission; integrated white 4LED; one colour CMOS sensor; manual calibration; and a measuring accuracy of approximately 3 µm.

Single-spot analyses for each sample were performed using fibre optics reflectance spectroscopy (FORS), a spectroscopic technique that analyses the light reflected from a surface illuminated with visible light and near-infrared radiation.

The FORS measurements were carried out in the spectral range 380–1050 nm by using a tungsten lamp (BPS101 Tungsten Halogen Light Source with a spectral output of 350 to 2600 nm) (BeWTek Inc., Plainsboro, NJ, USA) as the source and the grating Qmini Broadcom as the detector. The FORS spectrometer also provides colorimetric analyses of the investigated surface.

Optical fibre bundles were used both to drive the light on the surface under analysis and to collect the reflected radiation. The measuring head geometry was $45°/0°$. The probe, in contact with the surface, was a fibre holder, which, at the same time, guarantees a soft contact and permits obtaining the best distance from the surface. This allows for maximising the signal and maintaining the measuring area shielded from undesired external light. The analysed area was 2 mm^2, and each acquired spectrum was the average of 128 scans (measurement time: 0.04 s). As a reference, a B&WTek inc. white plate (99%) was used. For each sample, three measurements were acquired on the same area, repositioning the fibre, in order to verify the significance of the recorded values.

Portable X-ray fluorescence, being a non-invasive analysis, was performed directly on the coins, providing preliminary compositional information on a "wide" surface of about 2.5 mm^2, detecting possible degradation products or the presence of soil contamination elements. X-ray fluorescence spectroscopy using portable instrumentation (AMPTEK XRF spectrometer) (Bedford, MA, USA) was carried out both on the obverse and reverse (Side A and Side B) of the artefacts, and the XRF spectra were collected through a spectrometer with a miniature X-ray tube system (Mini-X—Amptek). It includes the X-ray tube (maximum voltage of 40 kV, maximum current of 0.2 mA, Rh target, 1 or 2 mm collimator), power supply, control electronics, and USB communication for remote control; a silicon drift detector (X-123SDD—Amptek) with an FWHM energy resolution of 125 to 140 ev @ 5.9 Kev Mn Kα (depends on peak time and temperature); an energy detection range from 1 Kev to 40 Kev; a maximum count of up to 5.6 105 cps; XRF measurements have been acquired using the factory provided data DPPMCA Display and Acquisition software (Bedford, MA, USA) and subsequently the spectra were processed and graphically provided by Origin Pro 8.5 (Northampton, MA, USA). The detector's primary beam and axis formed an angle of 0 and 40 degrees, respectively, perpendicular to the surface of the sample. The measurement parameters for the four samples are as follows: tube voltage, 35 kV; current, 80 μa; and acquisition time, 60 s. No filter was applied between the X-ray tube and the sample, and the distance between the sample and detector was about 1 cm. The configuration parameters were selected to ensure a good spectral signal and an optimal signal-to-noise ratio (SNR).

Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) was applied to obtain more detailed morphological and chemical data. The artefacts were previously coated with a thin and highly conductive graphite film. An ultra-high-resolution SEM (ZEISS CrossBeam 350 equipment) (Oberkochen, Germany) coupled with an EDS—EDAX OCTANE Elite Plus—silicon drift type detector was used.

The SEM images were acquired with backscattered electrons (BSE); the chemical composition is expressed in elements (weight %).

3. Results and Discussion

3.1. DOM Observations and FORS Spectroscopy

Dino-Lite AM4113T enabled observing the details of the surface of the samples in terms of iconography and alterations (Figure 3).

Sample A-532 shows traces of dark incrustation, especially at the centre of the incision on the obverse side, whereas the reverse one is better preserved (Figure 3A). Coins B-783 and C-1047 are affected by greenish encrustations on both sides (Figure 3B,C).
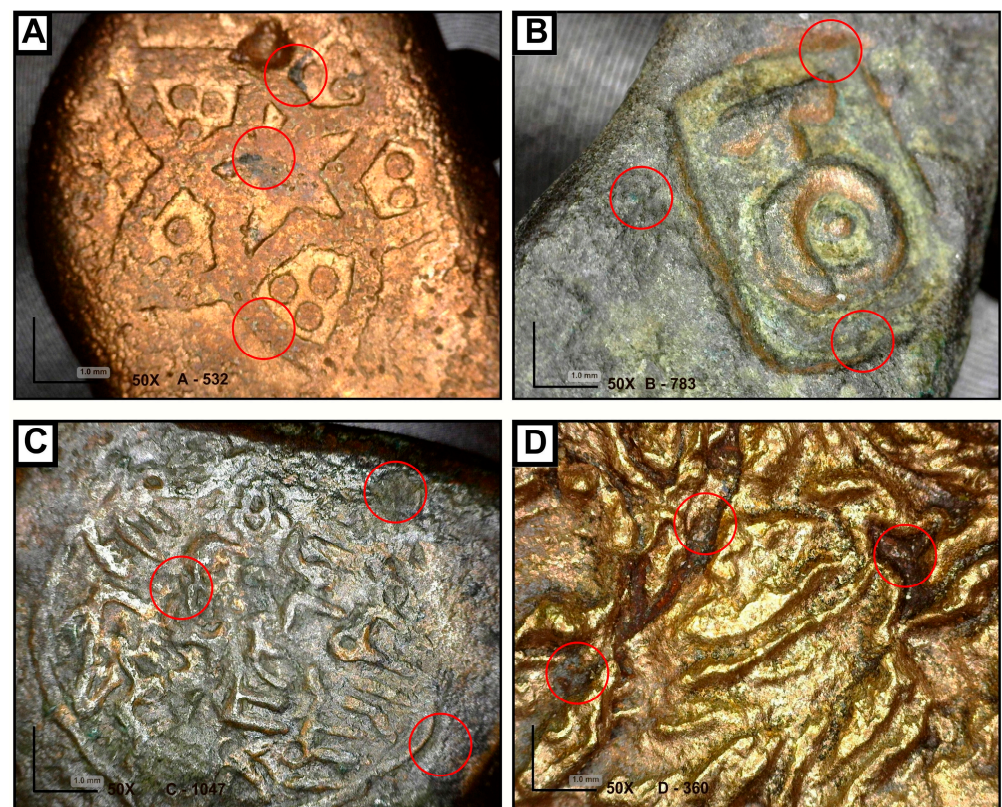
Figure 3. DOM observations of the artefacts at 50X: (**A**) A-532 obverse view; (**B**) B-783 obverse view; (**C**) C-1047 reverse view; (**D**) D-360 reverse view. The red circles indicate the areas analysed by FORS.

Sample D-360, not being a coin but probably a scrap, does not show recognisable iconography. The surface of the reverse side is deeply and irregularly incised, with both blackish and reddish traces of incrustations (probably related to the interaction with the soil in the burial stage) inside the "chisellings" (Figure 3D). The obverse side is rather smooth and cleaner than the reverse one.

The observations by DOM enabled selecting the most suitable areas for the FORS analyses, namely, where the alterations seemed to be more visible. The spectra were acquired in the region from 380 to 1100nm on three sample areas for each coin to obtain the first identification of the main corrosion products and patina composition. The results show quite different spectral features for the A-532 and D-360 finds (Figure 4A) than the FORS spectra collected on the B-783 and C-1047 surfaces (Figure 4B).
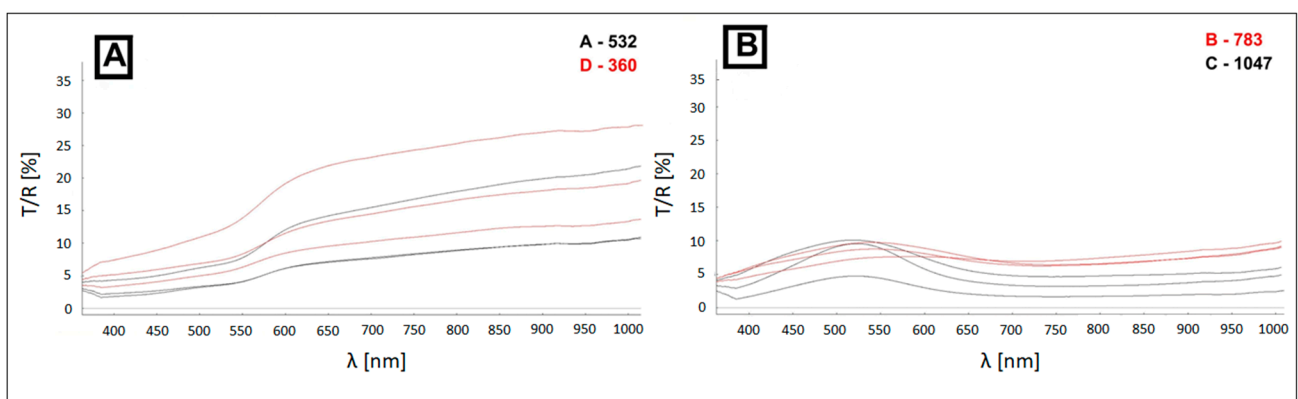

Figure 4. FORS spectra acquired on three different areas of the patina surface: (**A**) A-532, D-360; (**B**) B-783, C-1047. (T/R = Transmittance/Reflectance; λ = wavelength).

The spectral curves of B-783 and C-1047 achieve a reflectance maximum at 520–540 nm and large absorption bands in the range of 650–1000 nm attributable to basic copper sulphate (e.g., brochantite—$Cu_4(SO_4)(OH)_6$) and copper chloride (e.g., nantokite—$CuCl$) [32].

The FORS spectra of A-532 and D-360 show a broad absorption band in the 400–580 nm region, attributable to Cu_2O (Cuprite), characterised by a quite different spectral behaviour from that of other copper compounds [32].

3.2. Portable X-ray Fluorescence and SEM-EDS

The XRF analyses were conducted on both sides of the samples, and the spectra obtained were overall superimposable (Figure 5; Table 2). Table 2 is a qualitative synthesis of the relative abundances of the elements evaluated on the basis of the peak intensities. The spectra reveal copper (Cu) as the main element of the alloy constituting both coins and the slab, followed by lead (Pb), and tin only in D-360. In addition, the other elements are all in very low quantities: the coins B-783 and C-1047 show a similar composition consisting of silicon (Si), calcium (Ca), iron (Fe), nickel (Ni), and arsenic (As); in addition to these, there are also antimony (Sb) and chromium (Cr) in D-360, whereas silver was identified only in A-532.
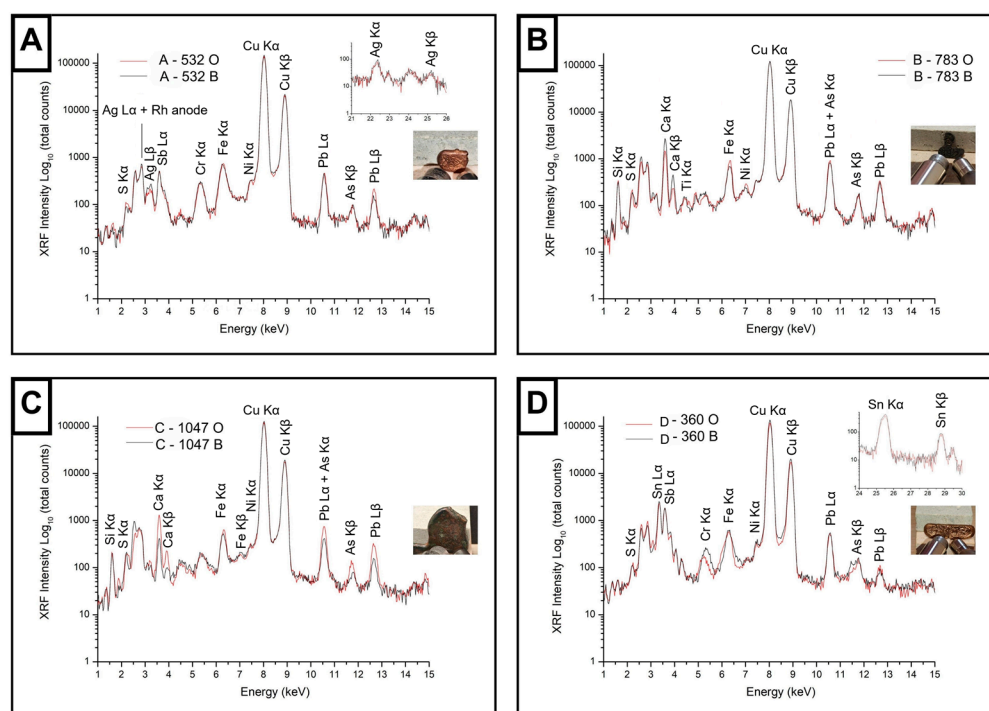

Figure 5. XRF spectra of the coins and the slab: O = obverse side, R = reverse side. The spectra were reported on a Log_{10} scale to improve the low-intensity values' readability. The images show the moment of the acquisition: (**A**) A-532; (**B**) B-783; (**C**) C-1047; (**D**) D-360.

Table 2. Intensity values of the Kα or Lα characteristic lines for the chemical elements for each of the metallic finds investigated via XRF analysis. The total counts collected under the same measurement conditions (35 kV, 80 microA, 40 s, 1 cm work distance) are reported. (* not identifiable for the trace element due to the overlap of the energy lines of the tin present in the alloy in high percentage.)

Artefact	Sn Kα	Ag Kα	Sb Lα	Cr Kα	Si Kα	Ca Kα	Fe Kα	Ni Kα	Cu Kα	Pb Kα	As Kβ
A-532	-	95	495	288	-	-	731	354	148,428	465	110
B-783	-	-	-	-	343	1500	943	358	124,186	943	197
C-1047	-	-	-	-	212	1309	651	329	119,440	753	139
D-360	422	-	*	266	-	-	657	362	135,999	554	184

SEM-EDS areal analyses were carried out on each sample, both on altered and unaltered zones, in order to determine the morphological features and the main composition of the coins and to identify any other traces of secondary products (Figure 6; Table 3).
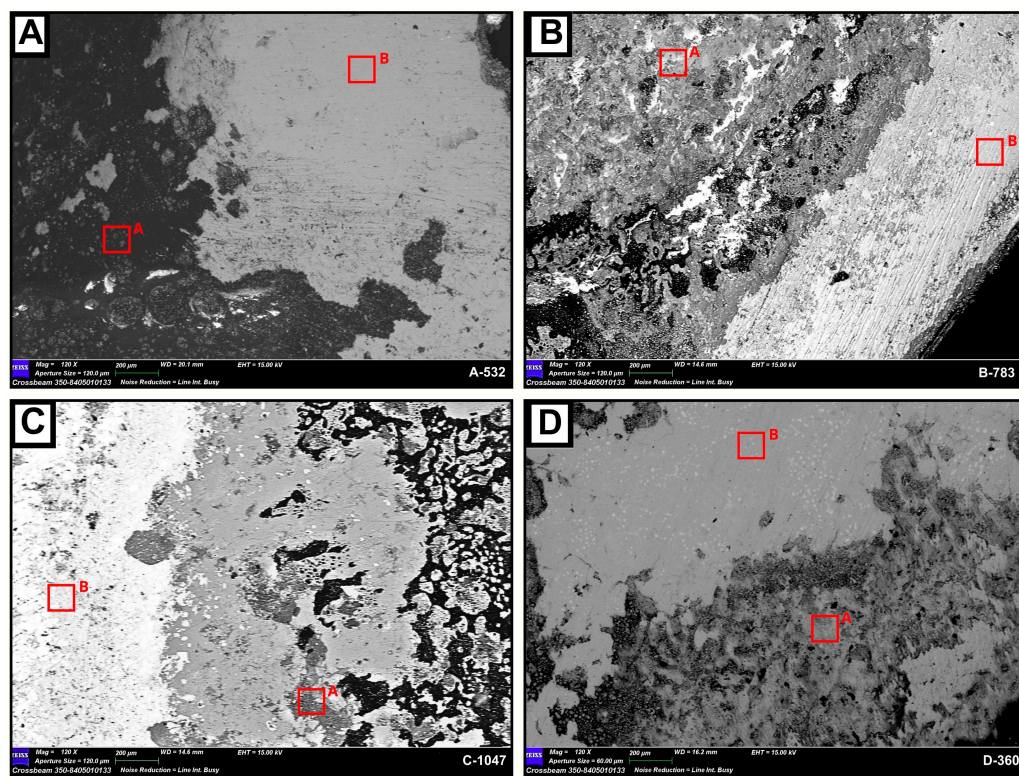
Figure 6. SEM microphotographs of the samples. The red squares indicate the altered (A) and unaltered (B) areas analysed. (**A**) A-532; (**B**) B-783; (**C**) C-1047; (**D**) D-360.

All the artefacts in the original fraction are almost homogeneous, as suggested by SEM images. The coins show a content of copper exceeding 80%; in detail, it reaches high values between 89 and 95% in coins, whereas it is lower (~83%) in the slab. After copper, lead is the most common element, with amounts generally lower than 2.5%; in SEM microphotographs, it appears as typically clearer random droplets finely dispersed in the copper alloy [33]. These structures are almost frequent because of the immiscibility of the two metals in each other during the melting process [33]. Moreover, lead improves the fluidity of the alloy in the melt, making the copper alloys easier to cast, especially in the minting process [33].

Slab D-360 diversifies from other samples because of the highest amount firstly of tin (Sn) and then silver (Ag). Tin is about 10% in D-360, whereas it does not exceed 1% in the other samples. The addition of tin to copper reduces the melting point of the alloy and improves its mechanical properties [5]. Silver reaches 1.6% in the slab, but it is under 1% in the coins.

The differences between the altered and unaltered areas are evident both morphologically and compositionally in all the samples. The degraded ones have an almost powdery appearance, and the distinction between the lead-clearer domains typical of the unaltered part is lost. The amounts of copper decrease significantly, and secondarily also lead, silver, and tin.

Oxygen is present on the surface of all samples, with significantly higher values in the altered areas. It could be related to the major roughness of the surface because of the degradation processes, but it could indicate the formation of copper oxides, such as cuprite and tenorite, considered the main alterations compounds in alloys like these studied and previously identified in the FORS spectra. In particular, the primary patina is composed of

cuprite (Cu_2O), while the patina associated with soil corrosion is mainly formed by tenorite (CuO) [34].

Table 3. Elemental EDS analysis (major elements in weight %) of the altered and unaltered areas of the artefacts. The compositional values indicate the mean of three analyses and the associated error. (Ox = oxygen).

Artefact	Mg	Al	Si	S	Cl	Ca	Fe	Cu	Ag	Sn	Pb	Ox	TOT
A-532													
Altered Area	-	0.4 0.1	12.2 0.49	0.2 0.02	0.2 0.04	-	1.9 0.23	61.3 0.91	0.5 0.13	-	1.8 0.85	21.5 2.08	100
Unaltered Area	-	-	0.6 0.1	-	-	-	-	90.9 1.22	0.8 0.35	0.5 0.21	2.4 0.19	4.8 1.09	100
B-783													
Altered Area	0.3 0.1	0.1 0.01	15 0.20	0.4 0.1	1.4 0.1	1.2 0.06	-	56.6 0.42	-	-	1.9 0.66	23.1 1.33	100
Unaltered Area	-	0.1 0.06	0.2 0.07	-	0.2 0.08	-	-	94.9 1.06	0.2 0.09	0.3 0.17	2.3 0.73	1.8 0.9	100
C-1047													
Altered Area	-	0.4 0.1	1 0.32	1.2 0.11	0.1 0.04	0.3 0.05	-	52.3 0.91	-	-	-	44.7 2.45	100
Unaltered Area	-	0.4 0.03	0.6 0.3	-	0.7 0.12	-	-	89.3 0.96	0.9 0.4	1.0 0.14	0.9 0.13	6.2 1.77	100
D-360													
Altered Area	-	0.3 0.1	3 0.25	-	-	-	6.7 0.43	74.5 0.85	1.5 0.45	7.5 0.70	-	6.5 1.89	100
Unaltered Area	-	-	0.4 0.1	-	-	-	-	83.7 0.5	1.6 0.69	10 0.79	1.1 0.45	3.2 1.03	100

Other elements are related to the interactions between the alloy of the artefacts and the burial environments; generally, they are more abundant in the degraded points and tend to decrease in the unaltered parts. Some of them, such as aluminium, silicon, magnesium, iron, and calcium, could represent the soil deposits accumulated on the findings during the burial stage [9,11,35,36]. The presence, instead, of low amounts of sulphur and chlorine could indicate the first phases of the degradation processes and the consequent formation of minerals such as brochantite [$Cu_4(SO_4)(OH)_6$] and especially nantokite (CuCl), common in many copper-based alloys and known as "bronze disease" [37], consistent with the results obtained by the FORS analysis. However, this process seems to affect the artefacts marginally, both because of the rather low amount of elements detected and since the surfaces of the samples still preserve the original aspect with a limited extension of the greenish powdery spots [36,38] typical of this degradation form.

Silver is present in minimal amounts in all the samples. It could be considered an impurity of the copper alloy and not an intentional addition. The presence of silver is documented in the same geological district [17,21]. Furthermore, archaeological sources [24,26] exclude the voluntary addition of silver to the coins because of the "silver crisis": Mongol invasions, coeval with the minting of the coins studied, generated a great political and economic instability aggravated by the looting with which the Mongols plundered the Georgian region of the most precious objects, including many of silver. Thus, the use of silver for coinage in that period was drastically reduced until it was completely stopped. On the other side, this situation caused a rapid increase in the exploitation of the abundant copper mines of the district, such that the production was so large that some pieces of metal were not transformed into blanks but were struck directly [14].

Antimony, arsenic, chromium, and nickel were determined only by XRF and not by SEM-EDS. Antimony has seen a long history of use from the 5th millennium BC onwards, first in metallurgy as a natural alloying element in copper alloys [39]. These elements frequently coexist with copper ores [40]. In addition, [16] talks clearly about the Georgian copper ores with antimony and arsenic.

The chemical compositions determined by XRF and SEM-EDS are considered complementary. In fact, some elements (antimony, chromium, nickel, and arsenic) are revealed only by XRF, just like others (aluminium, silicon, silver, chlorine, and sulphur) are revealed only by SEM-EDS.

This difference can be correlated with the diverse detection limit/sensitivity of the instruments versus lighter elements such as aluminium and silicon; in addition, the detail of the areas analysed changes from XRF (where it is wider, so more general) to the more detailed SEM-EDS. In addition, the spatial information obtained with XRF is not averaged in the sense of the irradiated area, which is wider, but also on the volume investigated, as the X-ray penetrates way deeper inside the sample compared to the electron beam in SEM-EDS, which gives back almost exclusively data related to the surface. Thus, XRF can provide a more general analysis covering a wider area (also in depth) that can be studied in detail (in terms of both morphology and composition of the surface) by means of SEM-EDS [41–44].

Overall, the composition of the three coins is rather comparable, whereas the slab D-360 diverges, especially in the amounts of the main metals (copper, silver, and tin). This could be related to the different processes of minting undergone by the artefacts: the coins would have finished the manufacturing process, whereas the copper slab represents the rest of the mould still to work or an incomplete coin. This could open at least two hypotheses to develop in the next studies: the coins and the slab come from different forge centres; or, if the forge is the same, the changes in the composition are related to the minting process "interrupted" in D-360 and completed in the three coins.

Anyway, the archaeometric data collected so far, although preliminary, represent valid support for the archaeological reconstructions of the Samshvilde site. These data will be increased, foreseeing more analyses, especially on trace elements and isotopes, and more samples of coins and slabs for better discriminating the probable provenance of copper artefacts and relative raw materials.

4. Conclusions

Three coins and one slab coming from the hoard of the Samshvilde archaeological site were analysed to determine their composition, the conservation state, and finally the probable forge centre.

The artefacts consist of a main copper-based alloy with minor amounts of lead and silver; just scrap D-360 shows a different composition than the coins considering the addition of tin during the minting. The techniques applied are complementary because they allow for identifying various elements thanks to the diverse setting of the instrumental conditions. Some elements in very low amounts, such as chromium and nickel, as well as silver, can be interpreted as impurities probably linked to the ore deposits of the raw materials. Considering the geology of the area and the archaeological sources, this could probably be identifiable in the nearby Bolnisi mining district.

The presence of silicon, calcium, aluminium, and iron is evidence of the interaction between the artefacts and the burial soil. Furthermore, the joint application of DOM, FORS, and EDS provided information about the conservation state of the findings, revealing the presence of the cuprite superficial patina and, especially, that coins are affected by a beginning of degradation, as suggested by the traces mainly of copper chlorides and sulphates such as nantokite and brochantite.

Overall, this work represents a further improvement in the archaeometric research of the ancient Caucasian metallurgy, one of the most ancient in the world. The presence of numerous ore deposits and the consequent great availability of raw materials in the area

make it necessary to deepen the studies about the characterisation of the archaeological artefacts, increasing both the number of findings and scraps to investigate and the analyses to carry out (e.g., trace elements or isotopes) to better discriminate the possible forges or the deposit ores used as supplying areas for the metals.

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Conflicts of Interest: Maria Francesca Alberghina and Salvatore Schiavone are associates of S.T.Art-Test company. The paper reflects the views of the scientists and not the company.

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