NON-DESTRUCTIVE X-RAY FLOURESCENCE ANALYSIS OF EARLY BRONZE AGE METAL ITEMS FROM KALINKAYA-TOPTAŞTEPE: WITH CRITICAL REMARKS ON THE FORMERLY APPLIED ELECTROCHEMICAL CLEANING PROCEDURE

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ABSTRACT

NON-DESTRUCTIVE X-RAY FLOURESCENCE ANALYSIS OF EARLY BRONZE AGE METAL ITEMS FROM KALINKAYA-TOPTAŞTEPE: WITH CRITICAL REMARKS ON THE FORMERLY APPLIED ELECTROCHEMICAL CLEANING PROCEDURE

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This thesis focuses on late Early Bronze Age metal objects from funeral context from the site Kalınkaya-Toptaştepe, dated to the late 4th and 3rd millenium BCE. The site yielded a large number of metal objects from EBA necropolis of the southern slope of Toptaştepe, offering an ideal closed assemblage for an archaeometrical analysis to reveal the metalworking technologies of an early small rural community of Central Anatolia. First archaeometrical analysis applied on these objects, however, revealed unexpectedly high amounts of Zinc, which turned out to be not an intentional alloy, but modern contamination due to the electrochemical cleaning, carried out in the 1970s. A second analysis has carried out after cleaning the metal objects with micro-sandblasting technique, to remove the artificial Zn contamination. The accumulated data provided us with important insights into the metal consumption and alloying traditions of a late EBA village community in Central Anatolia, showing the earliest conscious alloys were being applied in small hamlets of the EBA as well. It has been apparent that any pre-Iron Age metal object, revealing Zn in its chemical composition can not be considered as early brass, but clearly a result of a modern, ill-advised cleaning application.

Keywords: Early Bronze Age, Central Anatolia, Archaeometallurgy, Early metallurgy.

ÖZ

KALINKAYA-TOPTAŞTEPE ERKEN TUNÇ ÇAĞI METAL BULUNTULARININ TAHRİBATSIZ XRF ANALİZİ: ÖNCEDEN UYGULANMIŞ ELEKTROKİMYASAL TEMİZLEME PROSEDÜRÜ ÜZERİNE ELEŞTİREL YORUMLARLA

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Bu tez, bir M.Ö. geç 4. ve 3. binyıl yerleşim yeri olan Kalınkaya-Toptaştepe mezarlık alanının geç Erken Tunç Çağı metal buluntuları üzerinde gerçekleştirilmiş bir çalışmadır. Alan, özellikle Toptaştepe'nin güney yükseltisindeki Erken Tunç Çağı mezarlığında bulunan çok sayıda metal objeler ile Orta Anadolu'nun eski ve küçük bir köy toplumunun metal teknolojileri hakkında önemli bilgiler vermiştir. Bu objeler üzerinde gerçekleştirilen ilk arkeometrik çalışmalarda karşılaşılan beklenmedik Çinko oranları ile karşılaşılmıştır. İkinci analizler, objelerdeki Çinko kontaminasyonu yüzeye herhangi bir zarar vermeden ortadan kaldırmak için mikro-kumlama yöntemi ile temizledikten sonra gerçekleştirilmiştir. Elde edilen sonuçlar, Orta Anadoludaki bir geç Erken Tunç Çağı toplumunun metal kullanımı ve alaşım gelenekleri üzerine önemli bilgiler vermiş, ilk bilinçli metal alaşımların, dönemin küçük yerleşim alanlarında da kullanıldığını göstermiştir. Çalışmanın sonucunda, Demir Çağı öncesi herhangi bir metal buluntu analizinde karşılaşılabilecek Zn oranının, erken bir pirinç olarak değerlendirilmemesi, bunun modern zamanlarda, hatalı bir temizleme çalışmasının sonucu olan bir kontaminasyon olarak görülmesi gerektiği ortaya çıkartılmıştır.

Anahtar kelimeler: Erken Tunç Çağı, Orta Anadolu, Arkeometalurji, Erken metalurji.

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Special thanks to Ben Claasz Coockson, long-time archaeological illustration instructor of Bilkent University, Department of Archaeology, for his unique and tremendous contribution in drawing the entire objects from Kalınkaya-Toptaştepe for this study.

I am very grateful to the Ministry of Culture and Tourism, and the Museum of the Anatolian Civilizations for granting the permission to work on these authentic archaeological objects. Dr. Abdullah Zararsız from the Turkish Atomic Energy Authority, and Latif Özen from the Conservation Laboratory of the Museum of the Anatolian Civilizations made all the technical and spectrometrical analyses available.

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Last, but of course not least, most special thanks go to the most beautiful family one could ever have; my parents Nilüfer and Erkan Geniş, and my sister Asst. Prof. Dr. Ahu Geniş-Gruber. Mere words would never explain the love and gratitude I have for you. Thank you!

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CHAPTER 1:
GENERAL INTRODUCTION

1.1. INTRODUCTION

Despite ever intensified archaeological research in Central Anatolia, our knowledge of settlement strategies, cultural traits, and technological advances in the immediate vicinity of better-known early urban centers of the Early Bronze Age (EBA), such as Alacahöyük or Eskiyapar, remains rather limited. The stunning assemblages of Alacahöyük's famous royal tombs are contrasted by a meager body of well documented finds and features of smaller villages, or rural hamlets. When it comes to the field of archaeometry, one soon realizes that there is a still a huge demand for comprehensive studies that need to be carried out in Central Anatolia.

Involving archaeometry in analysis sure enough sharpens the awareness of any archaeologist for versatile methods, applications and limits to highlight conventionally retrieved archaeological data. However, during this study, another theoretical discussion of previously collected archaeometrical data was not only embarked upon, but rather, they have been tested on hypotheses with an applied spectrographic method on actual archaeological items. An affinity to ancient metal objects made the author, who has been trained as an archaeologist, to sketch a project for non- or minimal invasive spectrographic investigations of pre-classical metal items. Thus, providing an assemblage of Central Anatolian EBA metal items for spectrographic analysis made this research possible.

Kalınkaya-Toptaştepe and the metal items from this site were chosen for two particular reasons. The modest corpus of a total of 45 metal objects from an at least professionally documented burial context, represents an ideal cache of study items and a solid body for an archaeometrical research. That aside, any spectrographic analysis carried out on pre-classical artifacts will sure enough enhance the still very limited archaeometrical database for metal-based artifacts from the periphery of larger, major centers of the EBA in Anatolia at large.

1.2. GENERAL INFORMATION ABOUT KALINKAYA-TOPTAŞTEPE

The prehistoric settlement and cemetery of Kalınkaya-Toptaştepe, with Toptaştepe itself being a natural elevation with ancient occupation traces, is located to the Northeast of the modern village of Kalınkaya, district of Alaca, Çorum province.

The site is located approximately 1300 m. above sea-level, and 3 km. North-East of one of the major sites of Central Anatolia (in later Hittite times known as the "Land of Hatti") in the EBA, Alacahöyük. (see figs. 1, 2, 3)

Fig. 1 - Map of Anatolia, showing the position of Kalınkaya

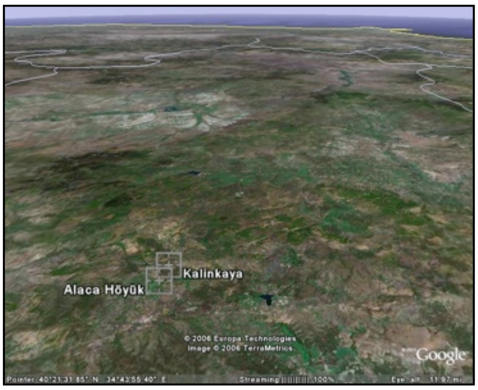

Fig. 2 - Geographical position from Google Earth.

Fig. 3 - A closer view of Kalınkaya on a map.

The first archaeological expedition was carried out in 1948 by Raci Temizer who was then a member of Türk Tarih Kurumu (Turkish Historical Society). In the 1948 expedition, only one ancient tumulus, located to the Northwest of Kalınkaya and Toptaştepe, was excavated. The findings recovered from the tumulus, known to the locals as the "Dedenin Sivrisi" (see fig. 4), were dated to the Late Hellenistic/Roman period (Temizer, 1949).

Until the early 1970s, as a result of this short expedition that run for only a single season in 1948, the vicinity of Kalınkaya was known as place merely yielding late classical remains. No other archaeological survey and/or excavation campaign was conducted until 1971, when authorities were alerted that the local inhabitants of the area illegally started to dig and loot the cemetery on the slope of Toptaştepe, or Taştoptepe as it was occasionally called (see figs. 5, 6).

Fig. 4 - Kalınkaya-Toptaştepe in 1971. Photo taken by Raci Temizer.
Courtesy of the Museum of Anatolian Civilizations.

The news of the looting reached the Museum of Anatolian Civilizations, and its recently appointed director Raci Temizer, who had excavated at Kalınkaya earlier in 1948. Since he knew the place, and was eager to rescue and recover the archaeological heritage of Kalınkaya-Toptaştepe, he immediately appointed a team for a rescue excavation of the site from June to July in 1971. This rescue excavation was launched to prevent further damage and looting caused by the locals. The team included Raci Temizer as the leader of the campaign, architect and illustrator Mahmut Akok, and the archaeology students Aliye Öztan[1], Ahmet Tırpan[2], Levent Zoroğlu[3], and Kathy Ataman from the University of Michigan. The same team was once again on the field in 1973, this time from 10 to 25 July (Zimmermann, 2006a). This two-seasoned expedition revealed the prehistoric phase of Kalınkaya[4], and also brought to light the find and features which are the scope of this thesis.

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[1] Today; Prof. Dr. Aliye Öztan of the University of Ankara. Department of Archaeology.

[2] Today; Prof. Dr. Ahmet Tırpan of Selçuk University, Konya. Department of Archaeology.

[3] Today; Prof. Dr. Levent Zoroğlu of Selçuk University, Konya. Department of Archaeology.

[4] For a comprehensive insight into the settlement history of Kalınkaya, more campaigns would have had to be launched.

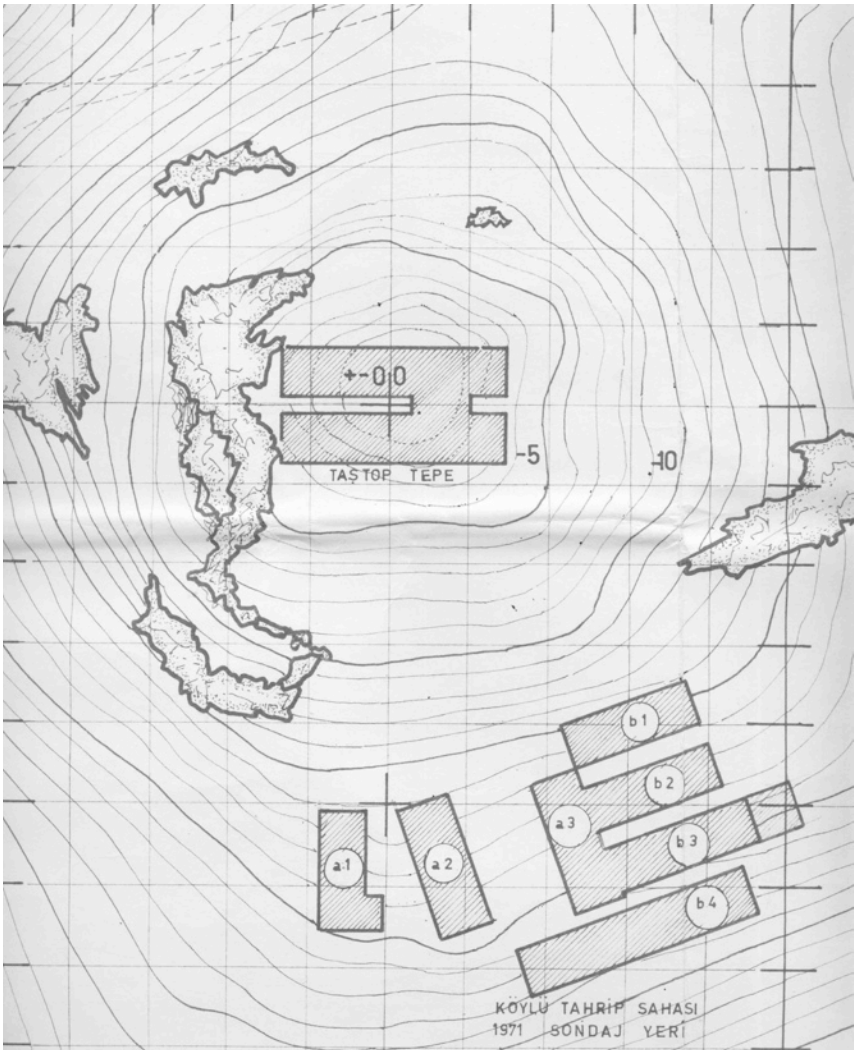

Fig. 5 - Topographical map of Kalınkaya-Toptaştepe in 1971.
Trenches, a1-a3 and b1-b4, corresponding to the location of the EBA cemetery.
Courtesy of the Museum of the Anatolian Civilizations.

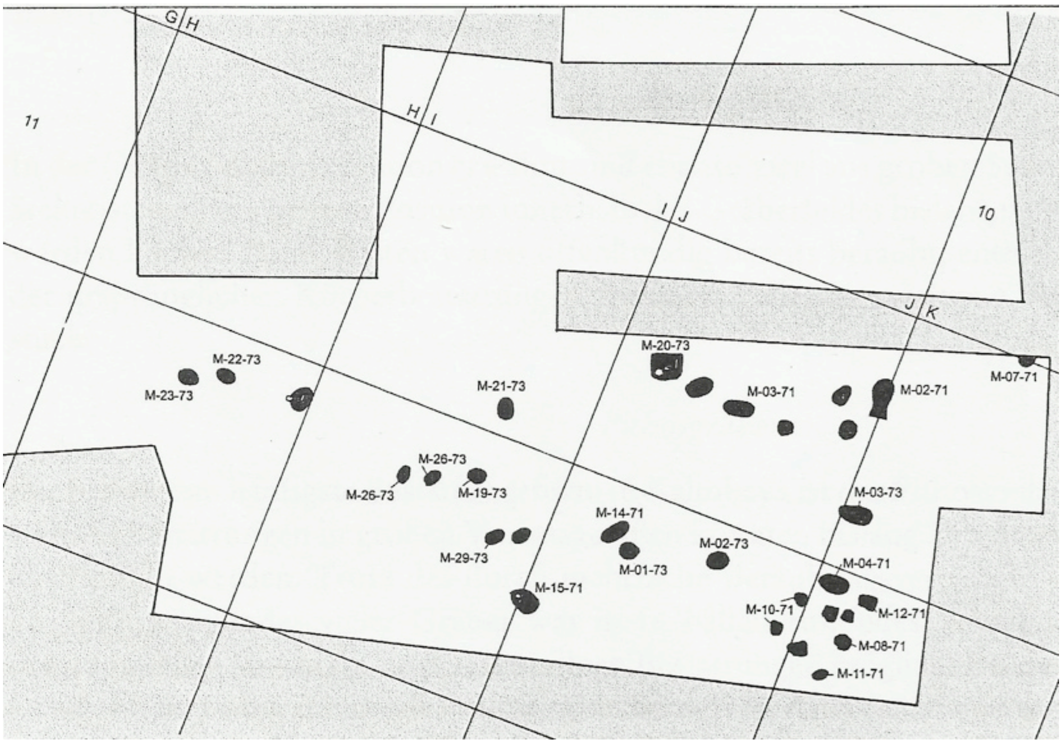

Fig. 6 - Map and list of grave numbers and their positions at b3 trench.
Image is taken from Zimmermann, 2007a.

Unfortunately, the results of the Kalınkaya excavations were never published. Excavation diaries, photo printouts and slides are besides the original artifacts the primary sources. The only other sources are the brief reports (or better paragraphs) on the Kalınkaya expedition, authored by Prof. Dr. Machteld J. Mellink for three consecutive years in the “Archaeology in Asia Minor” series published in the American Journal of Archaeology (Mellink, 1972; 1973; 1974).

No other archaeological study was carried out on Kalınkaya until 2005, when Asst. Prof. Dr. Thomas Zimmermann from Bilkent University initiated a project on Kalınkaya and started to study on the objects that were stored in the Ankara Museum of Anatolian Civilizations depot.

The documentation and findings from the 1971 and 1973 expeditions revealed a prehistoric impact from the Chalcolithic to the Middle Bronze Ages (4th to early 2nd millennium BCE), with the major occupation phase restricted to the EBA (3rd millennium BCE). Following the excavation diaries, prehistoric occupation of the site has been divided into four stages: Stratum A is dated to the Chalcolithic era; Stratum B is dated to the EBA, here divided into two sub-phases. Stratum C is presumably a transitional layer where a successive changeover from the Early to Middle Bronze Age was attested. The final occupation phase[5], only known from surface findings, coincides with the Old Hittite Period, namely the 17th century BCE (Zimmermann, 2006a).

The archaeological objects matching the context of this thesis, however, come exclusively from the EBA occupation horizon, more precisely the cemetery on the Southern slope of Toptaştepe (see fig. 5). Since no absolute dating technique was applied at the time of the excavations, they are categorized according to conventional archaeological methods; in our case through typological comparison.

A Chalcolithic phase precedes the EBA funeral area, including nine burials (M-4-73, M-5-73, M-21-73, M-22-73, M-23-73, M-27-73, M-28-73, M-29-73, M-31-73). All are inhumed male and female adults, with the exception of M-23-73 which was determined as an infants burial (Zimmermann, 2007a). No strict orientation is seen, as the burials are seen to be aligned randomly. Considering this, and the absence of ceremonial or votive, or any offerings at all in these burials, it can be said that the first inhabitants of Kalınkaya had at least no archaeologically traceable funeral gift custom.

The EBA burials, which yielded the metal findings discussed in this thesis, vary in style and associated finds. Two intramural burials (M-A-71, M-B-71) from the mound itself had no associable grave goods (see fig. 6). Extramural burials include cist graves, pithos burials, and simple flat earth graves (Zimmermann, 2007a; 2007b).

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[5] Stratum D.

Two crude cist graves were extremely damaged or badly preserved. Inhumations were found inside, but these cist graves were not given burial numbers. Pithoi are seen to be the most popular burial custom of the period, with 42 inhumations placed in jars (M-01-71, M-02-71, M-8-71, M-10-71, M-16-71, M-2-73, M-3-73, M-6-73, M-7-73, M-9-73, M-10-73, M-13-73, M-14-73, M-15-73, M-8-73, M-11-73, M-12-73, M-13-73, M-16-73, M-17-73, M-18-73, M-24-73, M-25-73, M-26-73, M-30-73). Although most of them were severely disturbed, 14 pithoi have associated grave goods (first 14 in order from the list above, from M-01-71 to M-15-73).

Three simple flat earth graves (M-20-73, M-1-73, M-C-73), especially the wealthy burial M-20-73, which is the grave of a young woman[6], likewise yielded notable grave goods. M-1-73 and M-C-73 were heavily damaged as a result of looting, so it is likely that many associated goods were lost. Still, a bronze axe and bronze bull statuette were recovered from these graves. Considering the amount and content of these graves, it is possible to say that the simple flat earth graves were used for higher ranked individuals of the EBA society of Kalınkaya (Zimmermann, 2007a; 2007b).

Apart from the ceremonial items mentioned above, the range of metal objects retrieved from the burials consist of jewelry, weapons, and tools. Cast, drilled, and polished jewelry accessories (2 rings, and 16 bracelets) of Kalınkaya-Toptaştepe, represents typological and technical similarities with neighboring sites like Resuloğlu (Zimmermann, 2006a). Thus, it is safe to say that the craftsmen of not only a singular site, but the artisans of this EBA region were following the same technique, whether they were the members of different workshops, or the very same artisans of the same tradition. Regional similarity in terms of typological matters is likewise seen with weapons as well, with for example, the broad triangular flange and beveled edges observed on daggers representing another regional phenomenon

[6] Anthropological analyses done by renowned physical anthropologist Prof. Dr. John Lawrence Angel (Zimmermann, 2007a).

that frequently exists in the Central, as well as the Western Anatolian EBA (Zimmermann, 2006a). While typologically analyzing the weapons recovered from the burials of Kalınkaya, it should also be noted that the combined technique of tongue-and-rivet hafting used on these daggers has a widespread spatial and chronological distribution in Anatolia (Stronach, 1957).

According to the acknowledged, but unfinished work of Stronach, these riveted daggers are generally dated to the 3rd millennium BCE. Since the jewelry findings of the site highly resemble their contemporary counterparts recovered from Resuloğlu, a site dated to the EBA-III period, hence the late 3rd millennium BCE (Yıldırım & Ediz, 2005; Yıldırım, 2006); the finds of Kalınkaya-Toptaştepe should until further notice be tentatively dated to the late 3rd millennium BCE, at least until we have a firm, dendrochronological and radiocarbon-based chronological framework for EBA Central Anatolia, which we do not have for the time being[7].

The excavations at Kalınkaya-Toptaştepe produced pottery and stone artefacts as well. However, this study deals with metal based artefacts, namely copper-based artefacts. The origins of the source for copper comes in mind, where three possibilities stand forward as the conceivable answer to such question.

1.2.1. THE PEOPLE OF KALINKAYA IN THE EARLY BRONZE AGE

When one starts to discuss about the EBA Central Anatolia and the development of not only artisanship, but the difference in social stratification and life reflected in the archaeological record, recovered especially from the cemeteries and domestic architecture, a question immediately arises: Who were these people?

The 3rd millennium BCE in Anatolia is one of the most innovative and progressive periods in the history of the peninsula. This is the time when Early Bronze Age starts,

[7] For a recent account on chronological problems, refer to Bertram, 2008.

expanding until the beginning of the 2nd millennium BCE. At this time, a pre-Indo European group of people, Hattians, were inhabiting this developing parts of Anatolia, namely Central Anatolia; whose name is known through Hittite sources (Klinger, 1996; Bryce, 1999; Alp, 2002). Hattians were not a society of Indo European origin, unlike their successors in Central Anatolia, the famous Hittites, as we know from the their language, which is easily recognizable with the extensive use of prefixes (Akurgal, 1990). The evidence for the language of the Hattians, “Hattili” as named by the later Hittites[8], is found in the Hittite archives, which are predominantly cultic or religious in character (Bryce, 1999). The profound Hattian influence on later Hittite culture and metal technology is well reflected in the archaeological record, particularly from major Hattian foci like Alacahöyük, Eskiyapar, and Horoztepe, and the case that many Hattian expressions were later on adopted in Hittite language (Koşay, 1938; Akurgal, 1992).

Even though it is argued that Hattians were not of Indo European origin, their ethnicity, origins and whereabouts remain unknown, although linguistic hints might point to a Northwest Caucasian affiliation. What we know is that Hattians were predominantly active in the EBA Central Anatolia, with their extensive skill and artisanship on metalworking technologies, and was wiped off the scene as written on the cuneiform tablet of the legendary founder king of the Hittites, Anitta[9], recovered from Kültepe-Kaniš (Alp, 2002).

1.3. POSSIBLE RAW MATERIAL SOURCES

Since an absolute provenance analysis, like Lead Isotope Analysis, has not yet been carried out on the Kalınkaya-Toptaştepe finds, we do not necessarily have a concrete, positive knowledge of where the raw material for the copper-based artifacts came

[8] The official language of the Hittites was called Nešite, belonging to the Indo European language family; although Akkadian was also used by Hittite scribes, mostly for trade records (Bryce, 1999; Alp, 2002).

[9] “... then came the King of Hatti.. I have defeated him as well...” (Anitta Tablet: 14-15; Alp, 2002)

from. However, three prehistoric copper mines in the region have been detected during extensive surveys in the 1990s, and are reasonably close to the site. Derekütüğün, Üçoluk, and Çağşak (see fig. 7) are three substantial sources of Cu, that are highly possibly the source(s) of supply for Cu, not only for Kalınkaya but also for the Bronze Age Central Anatolia at large.

Fig. 7 – Possible raw material sources for Kalınkaya-Toptaştepe's metal objects.

The ancient copper mine at Derekütüğün, located at 900-1000 m. elevation at 1 km east of modern village of Derekütüğün, near Bayat, Çorum is a spot which has proved to be active in the EBA (see fig. 8). Radiocarbon dating was performed in 2009 by a team of specialists led by Prof. Dr. Ünsal Yalçın from the University of Bochum-Ruhr, confirming that the mine was in use since the 3rd millennium BCE. Moreover, a small schematic figurine with typical EBA features from the galley testifies to human activity since in this period[10]. The copper slags recovered from the nearby classical period settlement (Wagner & Öztunalı, 2000) shows that this copper mine was not only used during prehistoric times, but also in historical periods. Although we do know that the mine was active then and in use since the 3rd millennium BCE[11], it is about 78 km. away from the site, which makes it the farthest mine in relation to the Alaca district that could have be used as a copper source to supply the Kalınkaya community.

Fig. 8 – Distance between the site and Derekütüğün mine, approx. 78 km.

Traces of copper have also been found at 900-930 m. elevation to the north of modern Üçoluk village near Sungurlu. Üçoluk mine is about 49 km as the bird flies

[10] Personal communication with Prof. Dr. Ünsal Yalçın. The results has not yet been published.

[11] *ibid.*

away from Kalınkaya-Toptaştepe (see fig. 9). However, no clear archaeological evidence that would testify to pre-classical exploitation has been observed here at Üçoluk, although the area is believed to have served as a raw material source during prehistoric times, not by mining probably collecting nodules from the surface (Wagner & Öztunalı, 2000).

Fig. 9 – Distance between the site and Üçoluk mine, approx. 49 km.

Finally, a small copper-ore mine is found a few hundred meters west of modern Çağşak village, at 1090 m. elevation (see fig. 10). This mine is the closest one to Kalınkaya-Toptaştepe at only 31 km. as the bird flies from the site. Small-flaked ore waste recovered on the slope of the ancient mine suggest that the site was a raw material source of an unknown, presumably prehistoric age. Hazelnut-sized slag fragments show evidence for ancient metallurgical activities on site (Wagner &

Öztunalı, 2000); however, no absolute dating has yet been carried out on these slags to identify their period and composition.

Fig. 10 – Distance between the site and Çağşak mine, approx. 31 km.

Due to their relative proximity to Kalınkaya, these three briefly sketched resources should be considered as the most reasonable candidates to supply a small rural settlement like Kalınkaya with necessary unprocessed, raw copper.

Prior to dealing with the major issue and subject of this study, a brief look at the previous endeavors concerning the archaeometrical research in the region might be helpful.

1.4 PREVIOUS ARCHAEOMETALLURGICAL STUDIES CARRIED OUT IN CENTRAL ANATOLIA

Central Anatolia in the EBA (ca. 3000-1950 BCE) is known as a dynamic arena for social and technological innovations, witnessing crucial trends in early urbanization processes and masterly accomplishments in metal production techniques (Sagona & Zimansky, 2009). Well attested, especially in the second half of the 3rd millennium BCE, are long distance commercial relationships with Mesopotamia and presumably also the Caucasian regions, allowing the transfer of goods, ideas and technologies (Jettmar, 1971; Muhly, 1985). Most prominent examples for the latter are the royal tombs of Alacahöyük, dated to the final quarter of the 3rd millennium BCE[12], which yielded evidence for fascinating alloying and crafting techniques, comprising the skilful utilization and combination of copper, silver, gold, and some of the earliest, maybe the earliest larger iron artefacts in the ancient world[13].

Several pioneering studies on the archaeometrical dimension of these groundbreaking innovations were conducted in the 1930's by Dr. Stefan Przeworski, applied to several metal artifacts from Alacahöyük by Dr. Edgar Meyer in 1937 and peaked in Prof. Dr. Ufuk Esin's spectrographical account on Anatolian metal artefacts (Koşay, 1938; Przeworski, 1939; Esin, 1969).

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[12] Samples for most recent C-14 dates presented by Prof. Dr. Ünsal Yalçın in a recent lecture delivered on March 24, 2011 in the Museum of the Anatolian Civilizations in Ankara, were retrieved from wooden residues in socketed metal items from Alacahöyük, stored in the museum vaults for more than 60 years. The results testified to a extremely early date for some of the burials in the first half of the 3rd millennium BCE. However more analysis on uncontaminated items from this site should be carried out to verify this early date.

[13] In the same lecture (see footnote 12) Prof. Dr. Ünsal Yalçın, Bochum, confronted us with stunning new discovieries on the metal objects from the Alaca burials, retrieved with the help of semi-quantitative XRF analysis. It was revealed that most the zoomorphic standards were additionally coated with copper-based alloys, previous to finishing them with gold and silver applications. Moreover, the "gold vessels" from the distinguished graves obviously turned out to be silver items, only plated with a thin layer of gold. One now eagerly waits for a comprehensive publication of these fascinating results.

The following decades brought only a few major contributions, dealing with issues concerning metal production and consumption, including Pre-Classical Central Anatolia, such as Prof. Dr. Prentiss de Jesus' work, with some more analysis results of EBA metal items (De Jesus, 1980). Lastly, there is Prof. Dr. Aslıhan Yener's in-depth account on the technical and social dimensions of the "domestication of metals" (hence the title), albeit mainly focusing on her research in the Taurus region (Yener, 2000).

That aside, Prof. Dr. Andreas Müller-Karpe focused comprehensively, though exclusively on the archaeological aspects of metalwork in early Anatolia (Müller-Karpe, 1994).

However, a recent re-evaluation of metal objects from Tarsus, once analyzed in the scope of Prof. Dr. Ufuk Esin's comprehensive study (Esin, 1969), revealed profound differences between the old and new datasets, hence reinforcing the need for new analyses series, especially more recent spectographic investigations to refocus on developments in metal consumption and alloying traditions in the 3rd millennium BCE (Özbal & Kuruçayırlı, 2005).

In recent times, archaeometrical analyses targeting the metallurgy of Central Anatolia in Bronze Age, were pursued at a much reduced pace. No larger studies were conducted or published in recent years. Thus, the production and alloying traditions in larger parts of Bronze Age Anatolia, especially the rural foci in the vicinity of early urban centres like Alacahöyük still remain largely obscure. Although an enormous bulk of metal objects from Central Anatolian Bronze Age findspots is stored in the museums of Çorum, Çankırı and Yozgat, very little, if anything is known about their elemental composition, in terms of what raw materials the communities utilized and combined to produce metal tools, weapons, vessels and jewellery items (Zimmermann, 2007c; Zimmermann & Yıldırım, 2009). Thus, this study tries to be one small jigsaw piece in the effort to highlight metalwork in prehistoric Central Anatolia from an archaeometrical point of view.

1.5 ELECTROCHEMICAL REDUCTION METHOD USED IN KALINKAYA-TOPTAŞTEPE METAL ITEMS IN BETWEEN 1971-1973: WITH CRITICAL REMARKS

Initial X-ray Flourescence (XRF) analyses on the metal objects that have been recovered from the prehistoric layers of Kalınkaya-Toptaştepe, were carried out in 2006, in the Museum of Anatolian Civilizations, by a group led by Asst. Prof. Dr. Thomas Zimmermann. A puzzling, yet substantial amount of Zn accounted in most objects forced the group to halt the study, since no Zn is to be expected in metal-based objects from a 3rd millennium BCE Central Anatolian context, considering the mining technologies of the time and the results of previous studies of the earlier archaeological expeditions in the region (De Jesus, 1980; Pernicka, 1995; Yener, 2000)[14].

The possible reason of the Zn contamination were discussed by the team, and it has been concluded that at some point after the artifacts were excavated and archived, but most probably between 1971 and 1972[15], an electrochemical reduction method was implemented on the objects recovered from the site in 1971. Since the observed Zn contamination obviously only stuck to the surface of the objects without penetrating them, such a coarse electrochemical cleaning procedure is the only scientific explanation for this phenomenon.

[14] The only other pre-Middle Bronze Age object containing substantial amount of Zn is a macehead, tentatively dated to the EBA from the Sadberk Hanım Museum collection (Anlağan & Bilgi, 1989). However, the suspicion arises that a similar electrochemical cleaning procedure was applied since no other metal objects from the 3rd millennium BCE are known to contain such high amounts of Zn.

[15] Metal artefacts with blank, patina-free surfaces come exclusively from the 1971 rescue campaign; the small number of items retrieved in 1973 all have a thick, crystalline patina.

In this reduction method, the nascent hydrogen acts as the reducing agent, which causes the chemical reaction. However, while generating the nascent hydrogen, the use of Zn and caustic soda were involved into the process, which leads to an electrochemical reaction. An enameled container filled with acid was used to contain the objects inside, and heated, where heat promoted chemical action to hasten the process and obtain the results in a quicker way. The last step is to apply the electrical DC current inside the container that diffracts the patina off the surface of the metals (Plenderleith & Werner, 1979).

This method cleans the patina off the surface to reveal the object’s original surface structure and color, which was clearly the major objective at that time. However, the use of Zn -in the form of coarse powder- is crucial here, since a certain quantity of Zn remaining largely inactive owing to the formation of a film of oxychloride and carbonate (Plenderleith & Werner, 1979). This thin layer and/or fragments of Zn can not be seen by the naked eye, however it becomes clearly evident with the help of spectrometry, which was necessarily not applied by the Kalınkaya excavation team in early 1970s. A general concern might have been to produce clean, presentable objects for the display cases in the relevant museums. Certainly, the metal objects excavated at Kalınkaya-Toptaştepe were probably not the only ones being subject to this treatment in this specific period.

Today, we think and analyze from a profoundly different, and definitely a more scientific and materialistic approach. Doing that, we clearly see the defects and mistakes of the so-called restoration methods that were in previously in fashion, such as this one. This method of electrochemical reduction may wipe the “ugly-looking” patina off the surface. However, the particles of Zn powder stick to the surface (and even the object’s subsurface if it has cracks on) that may easily obstruct future spectrographic analysis in terms of getting genuine data for the object’s original chemical composition, as happened in 2006. Far worse, an object with an exposed “original” surface is extremely sensitive to modern contaminants, which may result in a slow but continuous damaging of the object’s surface, and, as worst case scenario, an irreversible loss of material substance.

Therefore, these “out-fashioned” methods have been abandoned by contemporary scholars and alternative, more substantial and “non-destructive” methods are preferred for restoration and conservation efforts.

CHAPTER 2:

MATERIALS AND METHOD

2.1 MATERIALS

The materials that have been analyzed for this thesis study are original metal objects from the EBA context of the prehistoric site of Kalınkaya-Toptaştepe, district of Alaca, province of Çorum. Only metal objects, of which 45 out of 48 could be retrieved for this study, were scrutinized, while other inorganic materials such as pottery or stone have not been included.

These objects were excavated in 1971 and 1973 by a group of scholars, led by Raci Temizer, but not published until 2005, when Asst. Prof. Dr. Thomas Zimmermann of Bilkent University took the initiative and published the findings from domestic and funeral contexts for the first time (Zimmermann, 2006a). However, as indicated in the previous chapter, the ill-advised electrochemical reduction method applied created problems for further archaeometrical analyses. For that reason, a two-step approach was developed to reveal the original chemical composition of the artefacts: cleaning the artificial Zn contamination off the surface, followed by multiple, semi-quantitative non-destructive XRF scannings.

The materials of this study consist of three groups in general, which are pins (17 in number[16]), a ring[17], bracelets (15 in number), tools (3 in number), weapons (5 in number), statuettes (2 in number), and an abstract ceremonial standard.

[16] Two pins (KK 62-73, and KK 75-73) could not be analyzed in this study, since they were not available within the collection that has been brought into the laboratory from the museum depot.

[17] Another ring (KK 67-73) could not be analyzed either, since it also was not available.

The list of materials for this study are as follows[18]:

PINS

1. Pin with pyramidal head (KK 37-71)
2. Pin with spherical head (KK 73-71)
3. Club-headed pin (KK 78-71)
4. Pin with spherical head (KK 84-71)
5. Fragment of pin with spherical head (KK 105-71)
6. Pin with spherical head (KK 106-71)
7. Pin with spherical head (KK 107-71)
8. Macehead, or wart-headed pin (KK 109-71)
9. Pin with spherical head (KK 111-71)
10. Thistle-headed pin (KK 112-71)
11. Pin with spherical head (KK 116-71)
12. Pin with spherical head (KK 126-71)
13. Pin with spherical head (KK 147-71)
14. Long pin (KK 22-73)
15. Pin with spherical head (KK 49-73)
16. Long club-headed pin (KK 60-73)
17. Club-headed pin (KK 65-73)

[18] For a more detailed and illustrated list of materials, please refer to the Chapter 4.

RING

18. Small ring (KK 61-73)

BRACELETS

19. Bracelet (KK 48-71)

20. Fragmented bracelet (KK 48-71)

21. Bracelet (KK 96-71)

22. Small bracelet (KK 97-71)

23. Bracelet (KK 101-71)

24. Bracelet (KK 103-71)

25. Bracelet (KK 104-71)

26. Bracelet (KK 114-71)

27. Small bracelet (KK 117-71)

28. Bracelet (KK 121-71)

29. Bracelet (KK 122-71)

30. Bracelet (KK 123-71)

31. Bracelet (KK 124-71)

32. Bracelet (KK 125-71)

33. Bracelet (KK 63-73)

34. Bracelet (KK 64-73)

TOOLS

35. Crude shafthole axe-type bronze sheet (KK 70-71)

36. Awl, truncator, or tweezer (KK 82-71)

37. Hook-butted axe-hammer (12-73)

WEAPONS

38. Tanged dagger (KK 57-71)

39. Tanged dagger (KK 71-71)

40. Tanged dagger (KK 87-71)

41. Tanged dagger (KK 115-71)

42. Macehead (KK 56-71)

STATUETTES

43. Crude bull statuette (KK 100-71)

44. Bull statuette (KK 33-1-72)

STANDART

45. Ceremonial standart (KK 19-71)

2.2. TECHNICAL METHOD OF THE STUDY: X-RAY FLOURESCENCE

As indicated earlier in Chapter 1, one the major objectives of this study was to reveal the alloying traditions, hence the use of metallic compounds in a small hamlet of the EBA Central Anatolia. Another aim of the study was to further clarify the results of the object's chemical composition after removing the Zn contamination from the surface. Therefore, a non-destructive, semi-quantitative spectrometrical method is an appropriate approach to answer our research objectives questions adequately. The choice for using Portable X-ray Flourescence (P-XRF) device is explained as follows:

First and foremost; P-XRF is a non-destructive method within the realm of spectrographic approaches. For anyone who is active in archaeology, by contributing to the efforts of bringing the story of the past to date, and to carry it to the future generations, a non-destructive research method is of crucial importance. No archaeologist would ever think of destroying, or permanently damaging an ancient object, just to receive an exact measurement or whatever precise numeric data. Instead, the objects can wait some more years for a new non-destructive technology to appear, since they have been waiting for thousands of years to see the daylight, they have all the rights to survive for tomorrow. XRF can easily be a preferred way for such study not only because of being a non-destructive method; it proved to be reliable, requires no sample preparation, the handling is rather easy, it covers all the necessary elements for EBA metal items, and it has an user-friendly data treatment software, allowing a rapid application, delivering immediate, solid results to the researcher. This software and technological compatibility of P-XRF is continuously developing and getting easier by each progression in models, and by new generation of devices.

2.2.1 PRODUCTION OF THE RESULTS BY USING XRF

X-rays are produced when high speed electrons collide with the object. Therefore, the X-ray Fluourescence setup inevitably contains a source for electrons, a high accelerating voltage, and -naturally- the metal object that is being studied on. The tube contains two electrodes; one anode as the ground potential, and a cathode, for the high negative potential (see fig. 11). In XRF, characteristic X-rays are being generated to irradiate a substance. These irradiated X-rays force inner-shell electrons to the outer shell, and outer shell electrons move in to fill the spaces. During this process, flourescent X-rays are being generated as electromagnetic waves (Cullity, 2001). By using the intensity of each X-ray energy, in terms of the number of photons, the analysis gives quantitative results, as was used in this study by a calibration curve.

The energy that is set free during the excitement of the substance which provokes the electrons to “jump shell” is unique and typical for every light and heavy matter on our planet, and therefore reveals the elementary composition of a specific natural or manmade item.

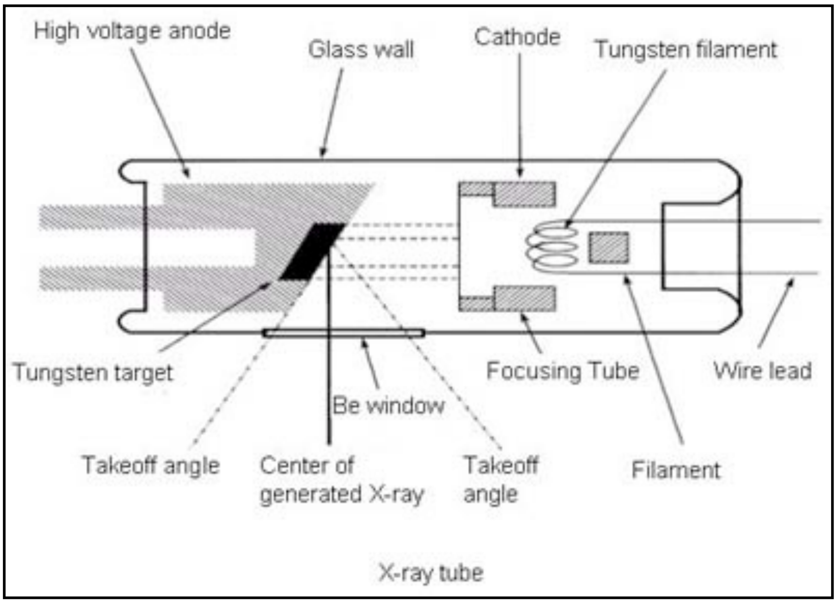

Fig. 11 - Schematic view of a X-ray tube.

Courtesy of SII Nano Technology, Inc.

2.3 XRF DEVICE

This study has been carried out in the Conservation and Restoration Laboratory of the Museum of Anatolian Civilizations, Ankara; the archaeological objects that have been studied in this thesis are either being stored in the depot, or on permanent display. The most recently bought XRF device, the A-2000 Rhino model (also known as Omega Xpress) of Innov-X Systems was used for this study. It is one state-of-the-art portable XRF devices of the world today, and is currently the most advanced portable XRF device, not only in Ankara laboratories, but in Turkey as well (see fig. 12).

Fig. 12 - The XRF device used for this study. Innov-X Systems Model A-2000 Rhino.

Courtesy of Innov-X Systems, Inc.

The technical specifications of the device are as follows:

Weight: 1,6 kg. including battery weight.

Excitation source: X-ray tube - Ag anode 10-40 keV, 5-100 μA, up to 5 filter positions.

Detector: Ultra high resolution Silicon Draft Detector; < 165eV Resolution.

Analysis diameter: 13 mm., circular.

Operating environment: Temperature -10ºC to 45ºC, Humidity: 10% to 90% RH.

The device stores a minimum of 20,000 test results with spectra, works on an Intel 416 MHZ processor and has a 128 MB of cache memory. The software, operating on a Microsoft Windows Embedded CE, includes standard elements package, and precious metals package, that have met all our needs to recover the EBA alloys. Software mode was set to "alloy analytical analysis".

The device we have used also has a P4000F FastID Analysis Package, that allows researcher to compare the spectral signatures in calculating the alloys and chemical compounds. The package also has a feature of Pass/Fail test. Another additional feature is the SB1 Smart Beam, which optimizes rays in both automatic and manual modes, for more sensitive measurements, which can be used in "analytical analysis" mode of the device.

The device was used in September 28, 2010, when the entire XRF tests were carried out in the Conservation and Restoration Laboratory of the Museum of Anatolian Civilizations, with an official permission issued by the Ministry of Culture and Tourism.

2.3.1. CALIBRATION OF THE XRF DEVICE

The portable XRF (P-XRF) device that was used in this study, with its technical specifications given above, had been calibrated, according to the standards of European Union (EU) Commission Joint Research Center Institute for Reference Materials and Measurements[19]. Calibration was done by the trained technical staff of the Innov-X Co. Following the calibration, a test was carried out to test the accurance of the device by Latif Özen and Mahmut Aydın, from the Restoration and Conservation Laboratory of the Museum of the Anatolian Civilizations.

Certified Reference Material (CRM) used for the calibration was BCR 691, recommended CRM for ancient alloys by European Commission (Ingelbrecht et.al., 2001), which was made available as a set of five alloys[20] in the form of polished discs with diameter of 35. mm., and 2 mm. thickness.

To test the accuracy of the device calibration, the results of the two certified reference materials were given, namely the reference materials for brass (B-5-7-25), and tin bronze (E 3-5-58). Sample objects, randomly chosen by the museum staff, were tested three times on three different spots to test the consistency in weight percentages of the elements. The results of these test scannings and corresponding CRM values, along with the error margins are as follows:

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[19] For further information please refer to the web-site of the institute at http://irmm.jrc.ec.europa.eu (retrieved on July 20, 2011 at 20:30 GMT +2).

[20] Quaternary bronze, Brass, Arsenic copper, Lead bronze, and Tin bronze.

Table 1 - Results of the Brass CRM (BCR-691, B-5-7-25) for the calibrated P-XRF device

BRASS CRM							
	%				CRM BCR-691 (B-5-7-25)		
Element	**1st**	**2nd**	**3rd**	±	**Element**	**Cert.value**	**%**
Cu	81.01	81.01	81.06				
Zn	15.06	15.1	15	**0.3**	**Zn**	148	14.8
Sn	2.07	2.05	2.03	**0.03**	**Sn**	20.6	2.06
Pb	0.56	0.52	0.59	**0.2**	**Pb**	79	0.79
Fe	0.51	0.5	0.51				
Mn	0.35	0.36	0.36				
Ni	0.22	0.22	0.23				
Pt	0.19	0.19	0.19				
Mo	0.033	0.033	0.035				

Table 2 - Results of the Tin Bronze CRM (BCR-691, E-3-5-58) for the calibrated P-XRF device

TIN BRONZE CRM							
	%				CRM BCR-691 (E-3-5-58)		
Element	**1st**	**2nd**	**3rd**	±	**Element**	**Cert.value**	**%**
Cu	90.43	90.44	90.43				
Zn	0.14	0.14	0.12	**0.04**	**Zn**	1.57	0.157
Sn	7.1	7.08	7.1	**0.1**	**Sn**	70	7
Pb	0.32	0.31	0.31	**0.12**	**Pb**	2.04	0.204
As	0.2	0.23	0.22	**0.03**	**As**	1.94	0.194
Sb	0.71	0.7	0.71				
Ni	0.5	0.49	0.49				
Pb	0.32	0.31	0.31				
Fe	0.31	0.31	0.31				
Mn	0.29	0.3	0.3				

Taking both tests on certified reference materials into account, it is apparent that the margin of error is < 0.1% in almost all cases. The biggest margin is on Sn ratio at the tin bronze CRM, where an error hits 0.1% at the peak of slip. These results are adequately safe and sufficient to start the XRF tests, knowing that the difference with the actual values will be ± % 0.1.

2.4 MICRO-SANDBLASTING DEVICE

The micro-sandblasting device that has been used in this study, was assembled from specially crafted singular parts by the technical staff of the Museum of the Anatolian Civilizations, in scope of a joint collaboration with the Römisch-Germanische Zentralmuseum Mainz, Research Institute for Pre-Protohistory. Therefore it has no brand or model name.

The micro-sandblasting device was used to clean the Zn contamination off the surface of the objects, whenever a suspicious Zn-peak occured. As a basic micro-sanding material, oxidized aluminium was used. Sanding technique was applied with 1 to 6 bar operating pressure to the object's surface, where the aluminium sanding acted as the cleaning agent of the artificial contamination on the objects.

The technique was clearly successful for this study. It, at least, reduced the Zn contamination on all objects, without any exception. However, to zeroize the entire contamination, usage of a simple formic acid was also needed.

The device consists of four parts, namely a dental sanding cabine, a sanding tank, a compressor, and a dust absorbing unit. The technical specifications are as follows:

<u>Voltage:</u> 230 V, 50/60 Hz

<u>Operating pressure:</u> 1 - 6 bar (14.5 - 87 psi)

<u>Connection pressure:</u> 6 - 10 bars (87 - 145 psi)

2.5 METHOD OF THE STUDY

Following the failure of the first XRF study on Kalınkaya-Toptaştepe metal objects in 2006, a comprehensive research was carried out, targeting the possible reasons of the setback due to the enigmatic, yet notorious Zn ratios on most of the objects[21]. Since the objects are dated back to EBA period, or roughly the 3rd millennium BCE, a consicous, anthropogenic addition of Zn in the composition of metals is out of question. The earliest appearance of Zn is recorded in modern India from a late 1st millennium BCE context as a metal known as "rasa", burned to produce an eye salve, which is about two millennia later than the metal objects in Kalınkaya (Craddock, 1990; 1995). Zn occurs in Anatolia in context of Urartian metalwork in the late 1st millennium BCE (Pernicka, 1995), and appears in Europe as late as the 17th century CE (Henderson, 2000). Since all these chronological and spatial alternatives could be excluded, the use of Zn powder in an electrochemical reduction method, which would be an efficient way to remove the patina off the surface, was suggested as a reasonable alternative. The presumed contamination applied to most objects with blank unpatinated surfaces. A thorough but non-destructive method of removal of this Zn contamination was then the first priority of the study. Only then, could the genuine results of the original metal composition of Kalınkaya-Toptaştepe objects (see fig. 13) be revealed.

[21] Please refer to the catalogue on Chapter 4, for the entire results mentioned.

Fig. 13 - Kalınkaya-Toptaştepe EBA metal objects that have been analyzed.

Original photograph taken during the thesis' laboratory study.

Solving the main problem that forced the first XRF studies to be halted in 2006, the idea of removing the Zn contamination off the surface of the objects came up with the help of the specially handcrafted micro sand-blasting device described above, installed at the Restoration and Conservation Laboratory of the Museum of the Anatolian Civilizations (see fig. 14).

Fig. 14 - Mechanical cleaning with micro sand-blasting device.

Original photograph taken during the thesis' laboratory study.

Prior to this specific surface treatment, XRF tests on the objects were first carried out without applying any cleaning/contamination removing measures. The results were almost entirely same as those obtained in 2006, with the same amounts of chemical compounds showing up[22], including the notorious Zn ratios. So, the mechanical cleaning procedure was applied on the objects one-by-one, with XRF tests scannings after each attempt. Depending on the size of the object, 2 to 5 scannings were carried out to get a reliable statistical average of one item's alloy values. For pins, generally two measurements (head and shaft) were considered to be sufficient, excluding the

[22] With the exception of As, which eventually overlapped with the Pb peak in 2006 due to a less fine-tuned database in 2006, and the missing software values for As. New results obtained with recalibrated equipment and newly installed software confirmed the presence of As, as an alloying agent or a natural contamination of the copper ore, to be categorized as Arsenic Bronze (Cu-As). For the detailed results, please see the catalogue on Chapter 4.

possibility of a composite object where pinhead and shaft were cast seperately. Larger objects like daggers were measured up to 5 times, since the expected inhomogenous distribution of alloying substances within the object, which is typical for handmade objects, might give a wrong impression about the actual percentages of alloying agents. One has to be aware of the fact that our non-destructive handheld XRF device gives only surface, thus semi-quantitative values, since the X-Rays penetrate solid surfaces for only about 3 microns. For that reason it was taken care not to scan heavily patinated spots, since the results obtained there would only give the results of the oxidized layer, not the actual metal composition. This issue did not occur for most of the objects retrieved from the 1971 campaign, since any trace of patina was then chemically removed, however replacing it with a Zn contamination. For the partly heavily corroded metal items from the short 1973 season this turned out to be a slight obstruction to get trustworthy values, however it was still possible to pin down single spots with a very thin, or no corrosion layer at all to guarantee results that stand scrutiny.

It was clearly seen that the Zn ratios were decreasing continuously, while the genuine compounds, such as Cu, Sn, As; or impurities like Pb and Fe were increasing proportionally. No single object with a confirmed Zn value in the spectrometrical test was an exception in this case, the obvious surface contamination was reduced and in most cases set to zero. Although they have mostly been zeroized, in some cases, the Zn layer could only be reduced, with the former Zn ratio being distributed among other genuine compounds exactly proportionally, without any exception.

In case of the Zn value not being reset to zero by micro-sandblasting technique, a simple and surface-deep formic acid had been applied to clean off the surface (and sub-surface, since the Zn contamination effects also slighly deeper layers, e.g. surface cracks) for XRF testing. Then, again with no exception at all, the Zn contamination on all related objects had been wiped-off and the genuine results of the original chemical compositions of the Kalınkaya-Toptaştepe objects could be finally attested. Double-checks were made, with cleaning a small section and testing that section (e.g. the tip of an object), combined with another test on an uncleaned section (e.g. the body of an object). The result was that the cleaned-off part presents the genuine results with no Zn, whereas the non-cleaned parts still have the same amount of Zn contamination on. Thus, it has clearly been proved that the existence of Zn on any object is definitely not a part of any genuine composition or alloying tradition, but definitely the result of the electrochemical reduction method applied in the 1970s campaign (Geniş & Zimmermann, 2011).

A total of 45 metal objects[23], that was available either on the museum's depot, and on permanent display cases at the museums exhibition hall, have been analyzed with the same method. First, their XRF analyzes were made without any cleaning, furthermore the above sketched mechanical cleaning method had been applied using micro-sandblasting technique. Finally, if the sandblasting application did not suffice, a simple formic acid cleaning measure was found to be feasable, always bearing in mind to not irreversibly alter the objects material or do any harm to these items with high archaeological and historical value. Conclusively, the entire Zn contamination was successfully removed from all objects, and the former contaminated ratio of Zn was distributed almost equally among the compounds of its ancient, original material matrix.

[23] Objects with the inventory numbers of KK 62-73, KK 67-73, KK 75-73 could not be tested, since they were not available within the objects collection that was brought in to the laboratory for testing.

CHAPTER 3:
RESULTS AND DISCUSSION

3.1 RESULTS

Genuine chemical compositions of the EBA metal items from Kalınkaya-Toptaştepe, from the 3rd millennium BCE context, have been acquired as follows:

Table 3 - Complete semi-quantitative results of the genuine chemical compositions of Kalınkaya-Toptaştepe metal items from the EBA context. Original thesis study.

OBJECT	Cu	Sn	As	Pb	Fe	Ni
KK 19-71 (Standart)	97.2%	0.00%	2.35%	0.23%	0.00%	0.00%
KK 37-71 (Pin)	97.51%	0.00%	1.22%	0.84%	0.14%	0.00%
KK 48-71 (Bracelet)	89.4%	10.2%	0.32%	0.11%	0.00%	0.00%
KK 56-71 (Macehead)	93.58%	0.00%	4.88%	1.43%	0.00%	0.00%
KK 57-71 (Dagger)	97.2%	0.00%	2.71%	0.11%	0.00%	0.00%
KK 70-71 (Sheet)	97.26%	0.00%	2.35%	0.35%	0.00%	0.00%
KK 71-71 (Dagger)	93.3%	0.76%	1.55%	0.30%	0.81%	3.2%
KK 73-71 (Pin)	98.36%	0.00%	1.3%	0.23%	0.11%	0.00%
KK 77-71 (Bracelet)	91.2%	8.69%	0.14%	0.00%	0.00%	0.00%
KK 78-71 (Pin)	92.3%	7.22%	0.81%	0.13%	0.52%	0.00%
KK 82-71 (Awl)	97.63%	2.25%	0.00%	0.12%	0.00%	0.00%
KK 84-71 (Pin)	82.6%	10.7%	0.00%	3.76%	3.02%	0.00%
KK 87-71 (Dagger)	96.69%	0.00%	3.06%	0.14%	0.1%	0.00%
KK 96-71 (Bracelet)	99.78%	0.00%	0.00%	0.19%	0.00%	0.00%
KK 97-71 (Bracelet)	97.98%	0.00%	0.82%	0.36%	0.14%	0.00%

OBJECT	Cu	Sn	As	Pb	Fe	Ni
KK 100-71 (Statuette)	96.01%	0.00%	3.89%	0.10%	0.00%	0.00%
KK 101-71 (Bracelet)	91.8%	8.23%	0.00%	0.00%	0.00%	0.00%
KK 103-71 (Bracelet)	96.2%	0.00%	3.83%	0.00%	0.00%	0.00%
KK 104-71 (Bracelet)	87.1%	12.3%	0.57%	0.13%	0.00%	0.00%
KK 105-71 (Pin)	87.54%	12.08%	0.00%	0.17%	0.00%	0.00%
KK 106-71 (Pin)	91.2%	7.93%	0.34%	0.57%	0.00%	0.00%
KK 107-71 (Pin)	87.74%	11.26%	0.61%	0.22%	0.19%	0.00%
KK 109-71 (Pin)	90.09%	8.34%	0.89%	0.48%	0.15%	0.00%
KK 111-71 (Pin)	93.24%	2.79%	0.89%	0.48%	0.15%	0.00%
KK 112-71 (Pin)	89%	9.77%	1.94%	0.23%	0.00%	0.00%
KK 114-71 (Bracelet)	99.20%	0.00%	0.2%	0.2%	0.00%	0.00%
KK 115-71 (Dagger)	91%	7.58%	1.32%	0.23%	0.00%	0.00%
KK 116-71 (Pin)	88.8%	0.00%	9.62%	0.21%	0.35%	0.00%
KK 117-71 (Bracelet)	85.43%	0.00%	14.34%	0.07%	0.00%	0.24%
KK 121-71 (Bracelet)	93.32%	0.00%	6.45%	0.19%	0.00%	0.00%
KK 122-71 (Bracelet)	90.9%	9.02%	0.00%	0.09%	0.00%	0.00%
KK 123-71 (Bracelet)	93.5%	0.00%	4.88%	1.43%	0.00%	0.00%
KK 124-71 (Bracelet)	93.1%	0.00%	6.84%	0.00%	0.00%	0.00%
KK 125-71 (Bracelet)	99.7%	0.00%	0.14%	0.16%	0.1%	0.00%
KK 126-71 (Pin)	97.45%	0.00%	2.31%	0.16%	0.00%	0.00%
KK 147-71 (Pin)	96.17%	0.00%	3.4%	0.25%	0.00%	0.00%
KK 33-1-72 (Statuette)	90.1%	7.69%	0.00%	1.27%	0.93%	0.00%
KK 12-73 (Hammer)	95.05%	0.00%	4.8%	0.00%	0.15%	0.00%
KK 22-73 (Pin)	96.17%	0.00%	3.35%	0.00%	0.41%	0.00%
KK 49-73 (Pin)	96.6%	0.00%	0.83%	0.24%	2.83%	0.00%

OBJECT	Cu	Sn	As	Pb	Fe	Ni
KK 60-73 (Pin)	98.5%	0.00%	0.99%	0.28%	0.00%	0.00%
KK 61-73 (Ring)	96.9%	0.00%	1.92%	0.00%	1.19%	0.00%
KK 63-73 (Bracelet)	91.4%	0.00%	8.6%	0.00%	0.00%	0.00%
KK 64-73 (Bracelet)	98.2%	0.00%	1.02%	0.00%	0.74%	0.00%
KK 65-73 (Pin)	98%	1.76%	0.11%	0.00%	0.11%	0.00%

Every single object was at least double-checked, acquiring several measurements from different parts of the objects. The results complemented one another. That said, whenever objects revealed intriguing results, such as a very high As amount (14.34%) seen in KK-117-71, multiple XRF tests on various surface spots of such objects were carried out. The results were very close to each other, if not the same. Moreover, the device mode was eventually set to "express alloy" from "analytical analyisis" mode for different measurements. Results complemented each other again. Therefore, it is safe to say that the results acquired in this study[24], are firm, solid, and genuine results of the objects, providing a reliable figure of their gross elemental composition.

In another exceptional case, a very-finely worked bull statuette (KK 33-1-72) on permanent display at the museum, the eyes, appearently applied in a silverish-whitish color were specifically tested as well. This statuette, easily distinguishable from its crude counterpart (KK 100-71) and the mainly simple, utilitarian items of the EBA necropolis of Kalınkaya, is a surprisingly fine example of high-skilled craftsmanship, and part of the cattle symbolism phenomenon observed at several EBA Central

[24] Final numbers given in this thesis are taken as exact average values of multiple tests on various spots. However, the differences on various spots of the same object were very little and almost entirely inconsiderable.

Anatolian communities (Zimmermann & Geniş, 2011). The result confirmed that the eyes of this bull statuette were coated with a thin layer of pure Ag.

To fulfill a study on revealing the ancient technology of the materials, a microscopic investigation was also considered essential. This study was mainly been carried out by the supervisor of this study, Prof. Dr. Ali Kalkanlı, using the optical microscope of the Museum of the Anatolian Civilizations.

In course of this microscopical analysis, it has been confirmed that all objects were finely casted. The dendrites clearly seen on the surface of the artificially cleaned objects are most probably the results of acid inclusion during the electrochemical method applied in the 1970s (Geniş & Zimmermann, 2011). No single object was made by cold-hammering, rather, all of them were cast; however in case of the daggers[25] additional modification by hammering and the visible traces of re-shapening the edges with a hone are seen.

3.2. DISCUSSION AND CONCLUDING REMARKS

The small group of metal funeral gifts analyzed for this study represents a good example for EBA Central Anatolian metalwork performed in a small rural settlement. The, by far, largest group of items consist of simple jewelry items like plain and simply decorated bracelets and pins, used as decorative dress fasteners, that were most probably personal belongings of the deceased, and not specially manufactured by the bereaved for the funeral ceremony. These are accompanied by a few tools and weapons, and could all be produced by a local metal smith due to their modest stylistic and technological range.

Exceptional are 2 bull statuettes, however both profoundly different in style and working expertise. The crude statuette (KK 100-71) appears to be a grotesque failure,

[25] KK 57-71, KK 71-71, KK 81-71, KK 115-71.

desperately trying to copy the "masterfully accomplished" (Starr, 1991) large zoomorphic statuettes from neighbouring Alacahöyük. Casting pipes were not removed, and the whole object appears to be unfinished, or abandoned by the not sufficiently skilled metalworker (Zimmermann, 2006b). Its counterpart, KK 33-1-72, confiscated by local police force from the looters, is, although rather small in size, worked in the tradition of the technologically much more advanced bull figurines of Alacahöyük. The suspicion arises that this statuette (which could unfortunately not be investigated more thoroughly for being on permanent display) was either produced by a experienced master-worker at neighbouring Alacahöyük or –as an unlikely but still reasonable possibility- looted from a grave in the immediate vicinity of the Alacahöyük's royal tombs. The crude statuette, in contrast, might then be rather understood as the work of an apprentice, labouring at Kalınkaya.

What else divides both figurines further (and probably supports the former hypothesis of their production place) is their chemical composition as well. The crude bull statuette (KK 100-71) is made of Arsenic-rich Cu, with the As amount of 3.89% with no Sn peak seen in the spectrometric test; the far better accomplished figurine (KK 33-1-72) is Tin Bronze (Cu-Sn) with a fairly high Sn content of 7.69%.

What brings us to the nutshell of this study, namely the chemical composition of the metal items in its implications for local metalworking activities in EBA Central Anatolia.

Two major material groups transpire from the 45 items analyzed: Cu-As alloys and Cu-Sn alloys, both of them almost evenly distributed within the assemblage of our Kalınkaya metal objects. Unalloyed Cu items[26] (which nevertheless contain traces of other metals as natural, unintentional contaminants) are the minority. Within these groups, some noteworthy deviations should be discussed here: Arsenic-rich copper might be the result of processing polymetallic ores, since As as an alloying agent is

[26] KK 96-71, KK 114-71, KK 125-71.

highly toxic, especially when smelted. However it cannot be excluded that Arsenopyrite was consciously added to the Cu, not being aware of the fatal illnesses a frequent exposure to such a substance can cause (Pernicka, 1995). High As content might be the result of an As enriching of the object's surface during the cooling down of an item, and not necessarily mean the adding of a high amount of As.

This phenomenon of a unexpectedly high content of an alloying agent has to be evaluated differently for bronze. Here, amounts that go beyond 7 weight percentage, or even further beyond 10 weight percentage, do not improve the technical quality of the bronze (Pernicka, 1995). Since Sn was a rare and much sought alloying agent, it seems unlikely that even less skilled metalsmiths spoiled such a valuable substance without a proper reason. The answer lies probably not in the technical qualities of the finished product like strength and durability, but the object's final color, as already suggested for EBA metal items from neighboring sites (Zimmermann, 2007c; Zimmermann & Yıldırım, 2008). Here, with an ever-increasing amount of tin, the object's color is steered towards an ever-intensified silverish sheen, which makes perfects sense for giving, e.g. jewellery items, a different hue according the predominant fashion of that particular period.

Pb occurs in rather tiny amounts with can be explained with natural contaminants of the copper ore; if the amount goes beyond 1%, as attested at some items[27], recycling of Pb-rich scrap metal could be a possible explanation, for a regular adding of Pb to drop the smelting temperature was not performed on a regular basis at that time (Pernicka, 1995).

The presence of Ni in two objects[28], however, is possibly related to the processing of Cu ores from ultrabasic, ophiolithic rocks, known for example from the Taurus

[27] KK 56-71, KK 84-71, KK 123-71, KK 33-1-72.

[28] KK 71-71, KK 117-71.

mountain ridge (Hauptmann & Palmieri, 2000). Once again, recycling of scrap metal produced from an ophiolithic rock source is a reasonable hypothesis.

One major observation, to combine archaeological with archaeometrical issues, is the obvious secure supply of a small rural hamlet like Kalınkaya with precious Sn in the advanced 3rd millennium BCE[29]. This is indeed important to mention, since some regions, especially the Black Sea coast, seemed to have been cut off from Sn supply, or were, for reasons yet unknown, not utilizing Sn until the 2nd millennium BCE (Bilgi, 1984; 1990; Zimmermann & İpek, 2010).

By way of conclusion, the so-called "Zn affair", and its resolution, should serve as both a warning sign and an opportunity for future research. Since this procedure was probably much in fashion a few decades ago, there is definitely a high probability that more electrochemically cleaned and contaminated objects are waiting in numerous museum depots of Turkey. So any pre-Iron Age metal objects which eventually reveal a high Zn content during spectrographic surface analysis should not automatically be considered as early brass, but clearly as the result of an ill-advised cleaning application.

This study has reached its goal, and found answers to its questions; however, it has triggered a new set of questions and further needs for research. As mentioned in the text; lead isotope analysis to found out the actual source(s) of Kalınkaya's copper-based metal items, and further archaeological expeditions in Kalınkaya are needed to be launched to draw a broader picture of the ancient lifesyle and technology of the site. This study reveals the metallurgical activities and technology of Kalınkaya in the 3rd millennium BCE, however many other objects found in similar parts, and small hamlets of the EBA Central Anatolia, not yet been scientifically investigated. Launching archaeometrical analysis on these items and sites as well, will strongly contribute to understanding the technology of the EBA Central Anatolia.

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[29] For a detailed account on the subject, refer to Muhly, 1993.

CHAPTER 4 :
COMPLETE ILLUSTRATED AND DESCRIPTIVE LIST OF OBJECTS[30]

PINS

1) Pin with pyramidal head, Inv. No. 37-71

Fig. 15 - Pin with pyramidal head, Inv. No. 37-71

Pin with pyramidal head; shallow indentation at top of shaft. tip broken off; most of patina electrochemically removed .

Weight: 3.1 g.

Findspot: Outside square b/3

2010 XRF Results: Cu (97.5%), As (1.22%), Pb (0.84%), Fe (0.14%)

2006 XRF Results: Cu (95.3%), Zn (3.88%), Pb (0.85%)

[30] The names of the objects and the categorization of the list is mainly based on the "Catalogue of Finds", taken from Zimmermann, 2006a. All photos were taken in the Museum of Anatolian Civilizations, with the permission of the Ministry of Culture and Tourism. All drawings were made by Ben Claasz Coockson from Bilkent University, Department of Archaeology, and are being published for the first time as a complete list.

2) Pin with spherical head, Inv. No. 73-71

Fig. 16 - Pin with spherical head, Inv. No. 73-71

Pin with spherical head; sharp rib at top of shaft; tip broken off.

<u>Weight:</u> 4.3 g.

<u>Findspot:</u> Outside square b/3

<u>2010 XRF Results:</u> Cu (98.36%), As (1.3%), Pb (0.23%), Fe (0.11%)

<u>2006 XRF Results:</u> Cu (95.7%), Zn (3.65%), Pb (0.29%), Fe (0.17%)

3) Club-headed pin, Inv. No. 78-71

Fig. 17 - Club-headed pin, Inv. No. 78-71

Club-headed pin; semi-spherical top.

<u>Weight:</u> 2.4 g.

<u>Findspot:</u> Outside square b/3

<u>2010 XRF Results:</u> Cu (92.3%), As (0.81%), Sn (7.22%), Pb (0.13%), Fe (0.52%)

<u>2006 XRF Results:</u> Cu (90.6%), Zn (3.46%), Fe (0.42%), Pb (0.33%)

4) Pin with spherical head, Inv. No. 84-71

Fig. 18 - Pin with spherical head, Inv. No. 84-71

Pin with spherical head; lower section broken off.

<u>Weight:</u> 7.6 g.

<u>Findspot:</u> Burial M-02-71

<u>2010 XRF Results:</u> Cu (82.6%), Sn (10.7%), Pb (3.76%), Fe (3.02%)

<u>2006 XRF Results:</u> Cu (84.7%), Pb (3.3%), Fe (2.46%)

5) Fragment of of pin with spherical head, Inv. No. 105-71

Fig. 19 - Fragment of pin with spherical head, Inv. No. 105-71

Pin with crude, unevenly cast spherical head; shaft broken off.

<u>Weight:</u> 12.9 g.

<u>Findspot:</u> Burial M-01-71

<u>2010 XRF Results:</u> Cu (87.4%), Sn (12.3%), Pb (0.17%)

<u>2006 XRF Results:</u> Cu (85.25%), Sn (11.04%), Zn (3.08%), Pb (0.27%)

6) Pin with spherical head, Inv. No. 106-71

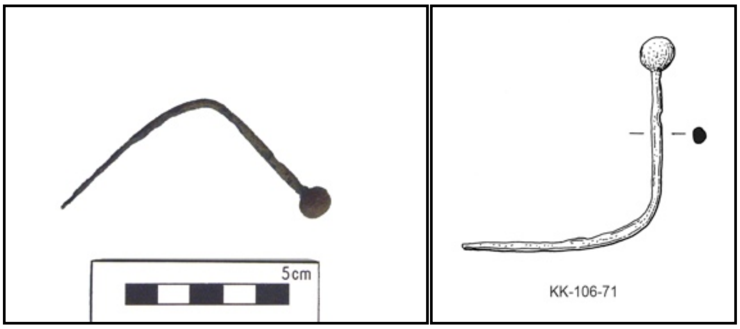

Fig. 20 - Pin with spherical head, Inv. No. 106-71

Pin with spherical head; bent shaft.

Weight: 9.4 g.

Findspot: Burial M-01-71

2010 XRF Results: Cu (91.2%), As (0.34%), Sn (7.93%), Pb (0.57%)

2006 XRF Results: Cu (82.4%), Sn (12.5%), Zn (6.41%), Pb (0.19%)

7) Pin with spherical head, Inv. No. 107-71

Fig. 21 - Pin with spherical head, Inv. No. 107-71

Pin with spherical head; two thin ribs at top of shaft, lower shaft section bent; tip broken off.

Weight: 9.2 g.

Findspot: Burial M-02-71

2010 XRF Results: Cu (87.7%), As (0.61%), Sn (11.26%), Pb (0.22%), Fe (0.19%)

2006 XRF Results: Cu (85.4%), Sn (11.5%), Zn (2.74%), Pb (0.23%), Fe (0.18%)

8) Macehead, or wart-headed pin, Inv. No. 109-71

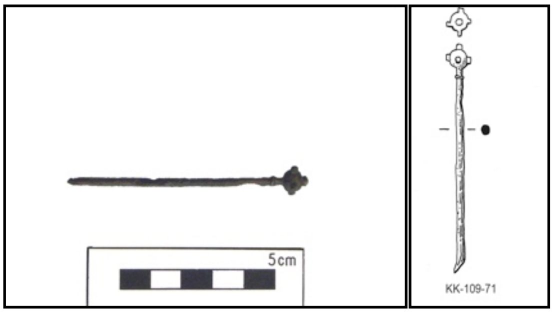

Fig. 22 - Macehead, or wart-headed pin, Inv. No. 109-71

Globular-headed pin; head with five protruding cylindrical knobs; thin rib around upper shaft; bent at lower end.

<u>Weight:</u> 5.6 g.

<u>Findspot:</u> Burial M-01-71

<u>2010 XRF Results:</u> Cu (91.6%), As (0.49%), Sn (7.22%),Pb (0.32%), Fe (0.19%)

<u>2006 XRF Results:</u> Not available.

9) Pin with spherical head, Inv. No. 111-71

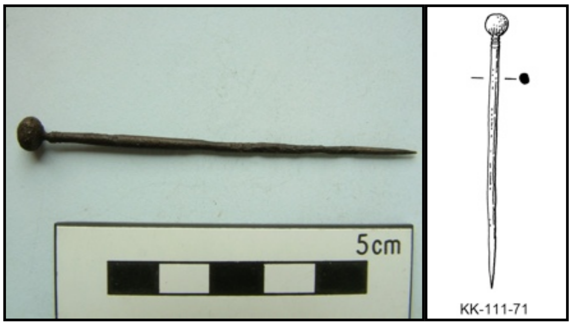

Fig. 23 - Pin with spherical head, Inv. No. 111-71

Pin with small spherical head; three thin ribs at top of shaft.

<u>Weight:</u> 2.8 g.

<u>Findspot:</u> Burial M-08-71

<u>2010 XRF Results:</u> Cu (93.2%), As (1.94%), Sn (2.79%), Pb (0.69%), Fe (1.18%)

<u>2006 XRF Results:</u> Cu (93.3%), Zn (2.87%), Sn (2.4%), Fe (1.14%), Pb (1.03%)

10) Thistle-headed pin, Inv. No. 112-71

Fig. 24 - Thistle-headed pin, Inv. No. 112-71

Pin with vase- or thistle-shaped head; decorated with series of wavy-line incisions; sharp rib around upper shaft section; shaft bent, tip broken off.

Weight: 6.1 g.

Findspot: Burial M-08-71

2010 XRF Results: Cu (89%), As (1.32%), Sn (7.58%), Pb (0.23%)

2006 XRF Results: Cu (90.7%), Sn (9.02%), Pb (0.23%)

11) Pin with spherical head, Inv. No. 116-71

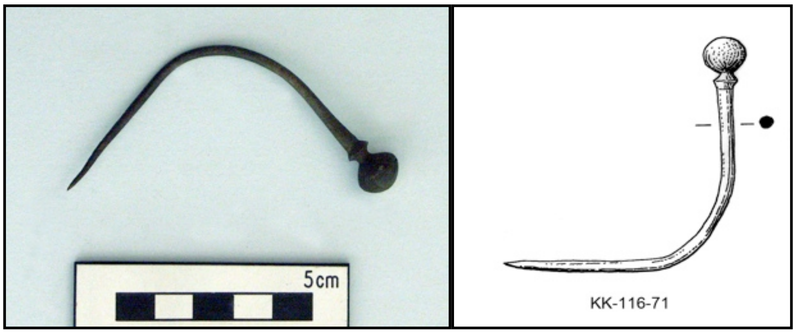

Fig. 25 - Pin with spherical head, Inv. No. 116-71

Pin with spherical head; sharp rib at top; shaft bent.

Weight: 9.9 g.

Findspot: Outside square b/3

2010 XRF Results: Cu (88.8%), As (9.62%), Pb (0.21%), Fe (0.35%)

2006 XRF Results: Cu (97.4%), Zn (2.19%), Pb (0.35%), Fe (0.24%)

12) Pin with spherical head, Inv. No. 126-71

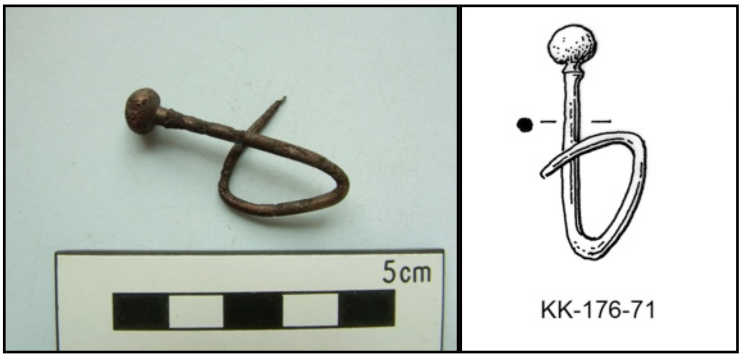

Fig. 26 - Pin with spherical head, Inv. No. 126-71

Pin with spherical head; rib around upper section; shaft flexed.

Weight: 4.1 g.

Findspot: Outside square b/4

2010 XRF Results: Cu (97.4%), As (2.31%), Pb (0.16%)

2006 XRF Results: Cu (98.2%), Zn (1.74%), Pb (0.22%)

13) Pin with spherical head, Inv. No. 147-71

Fig. 27 - Pin with spherical head, Inv. No. 147-71

Pin with spherical head; sharp rib around upper shaft; shaft bent.

Weight: 5.4 g.

Findspot: Outside square b/4

2010 XRF Results: Cu (96.1%), As (3.4%), Pb (0.25%)

2006 XRF Results: Cu (98.1%), Zn (1.49%), Pb (0.37%), Fe (0.15%)

14) Long pin, Inv. No. 22-73

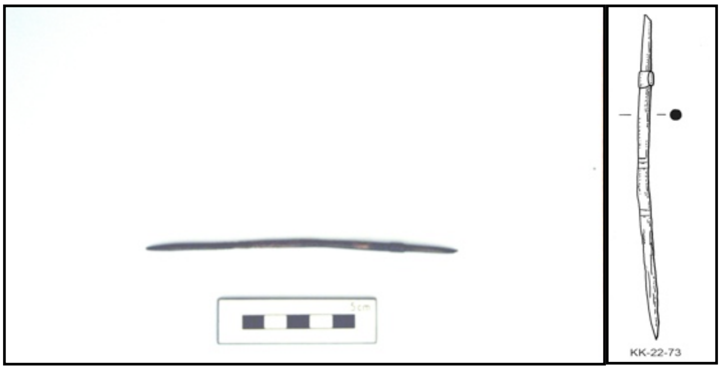

Fig. 28 - Long pin, Inv. No. 22-73

Pin with thin bronze sheet wrapped around shaft in the upper third section; five shallow incisions.

<u>Weight:</u> 10.5 g.

<u>Findspot:</u> Burial M-15-73

<u>2010 XRF Results:</u> Cu (96.1%), As (3.35%), Fe (0.41%)

<u>2006 XRF Results:</u> Not available.

15) Pin with spherical head, Inv. No. 49-73

Fig. 29 - Pin with spherical head, Inv. No. 49-73

Pin with small spherical head; three thin ribs at top of shaft; shaft bent.

<u>Weight:</u> 3.5 g.

<u>Findspot:</u> Burial M-13-73

<u>2010 XRF Results:</u> Cu (96.6%), As (0.83%), Pb (0.24%), Fe (2.83%)

<u>2006 XRF Results:</u> Not available

16) Long club-headed pin, Inv. No. 60-73

Fig. 30 - Long club-headed pin, Inv. No. 60-73

Pin with slim club-like head.

Weight: 10.7 g.

Findspot: Burial M-02-73

2010 XRF Results: Cu (98.5%), As (0.99%), Fe (0.28%)

2006 XRF Results: Not available.

17) Pin with pyramidal head, Inv. No. 62-73

Fig. 31 - Pin with pyramidal head, Inv. No. 62-73

Pin with pyramidal head.

Weight: 2.9 g.

Findspot: Burial M-07-73

2010 XRF Results: Not available.

2006 XRF Results: Not available.

18) Club-headed pin, Inv. No. 65-73

Fig. 32 - Club-headed pin, Inv. No. 65-73

Pin with slightly swollen tip and swollen middle section; object heavily corroded with thick layer of green patina.

<u>Weight:</u> 12.6 g.

<u>Findspot:</u> Burial M-20-73

<u>2010 XRF Results:</u> Cu (98%), As (0.11%), Sn (1.76%)

<u>2006 XRF Results:</u> Cu (95.9%), Sn (3.98%), Fe (0.53%)

19) Club-headed pin, Inv. No. 75-73

Fig. 33 - Club-headed pin, Inv. No. 75-73

Pin with flaring club-head.

<u>Weight:</u> 4.2 g.

<u>Findspot:</u> Burial M-14-73

<u>2010 XRF Results:</u> Not available.

<u>2006 XRF Results:</u> Not available.

RINGS

20) Small ring, Inv. No. 61-73

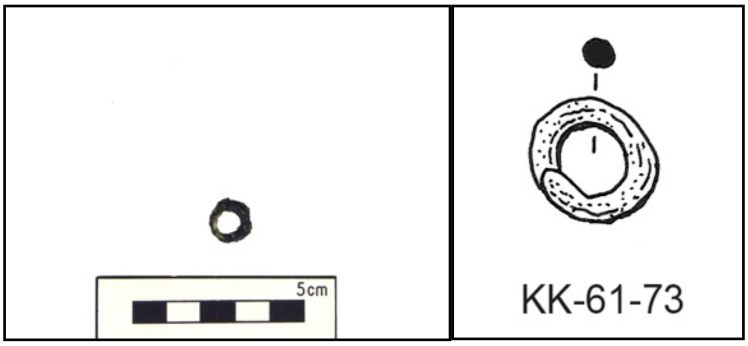

Fig. 34 - Small ring, Inv. No. 61-73

Adjustable ring with overlapping ends; thick green patina preserved.

Weight: 0.9 g.

Findspot: Burial M-06-73

2010 XRF Results: Cu (96.9%), As (1.92%), Fe (1.19%)

2006 XRF Results: Not available.

21) Small golden ring, Inv. No. 67-73

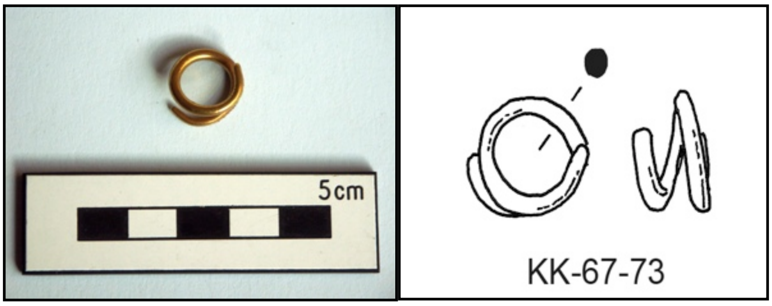

Fig. 35 - Small golden ring, Inv. No. 67-73

Looped ring with rounded ends; traces of oxidated bronze on golden surface.

Weight: 3.6 g.

Findspot: Burial M-20-73

2010 XRF Results: Not available.

2006 XRF Results: Not available.

BRACELETS

22) Bracelet, Inv. No. 48-71

Fig. 36 - Bracelet, Inv. No. 48-71

Bracelet; broken parts crudely fixed with glue; decorated with three groups of crude notches/incisions.

Weight: 15.6 g.

Findspot: Outside square b/3

2010 XRF Results: Cu (89.4%), As (0.32%), Sn (10.2%), Pb (0.11%)

2006 XRF Results: Cu (89.3%), Sn (10.5%), Pb (0.15%)

23) Fragmented bracelet, Inv. No. 77-71

Fig. 37 - Fragmented bracelet, Inv. No. 77-71

Bracelet; one quarter missing; surface damaged, where faint traces of notch patterns.

Weight: 10.1 g.

Findspot: Outside square b/3

2010 XRF Results: Cu (91.2%), As (0.14%), Sn (8.69%)

2006 XRF Results: Cu (90.1%), Sn (9.77%)

24) Bracelet, Inv. No. 96-71

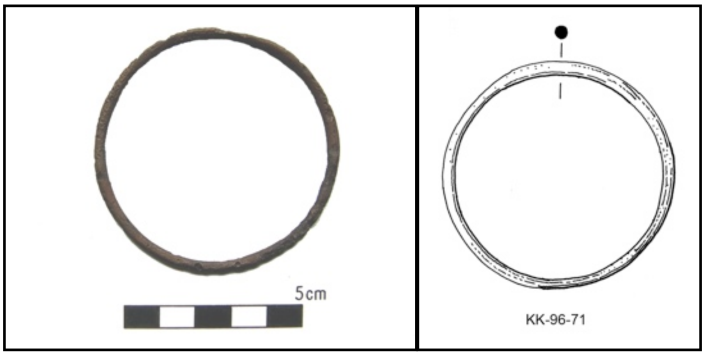

Fig. 38 - Bracelet, Inv. No. 96-71

Bracelet; undecorated.

Weight: 9.8 g.

Findspot: Outside square b/3

2010 XRF Results: Cu (99.7%), Pb (0.19%)

2006 XRF Results: Cu (98.1%), Zn (1.54%), Pb (0.34%), Fe (0.14%)

25) Small bracelet, Inv. No. 97-71

Fig. 39 - Small bracelet, Inv. No. 97-71

Adjustable bracelet with double-looped pointed ends; undecorated.

Weight: 6.7 g.

Findspot: Outside square b/4

2010 XRF Results: Cu (97.9%), As (0.82%), Pb (0.36%), Fe (0.14%)

2006 XRF Results: Cu (98.5%), Pb (0.49%), Fe (0.11%)

26) Bracelet, Inv. No. 101-71

Fig. 40 - Bracelet, Inv. No. 101-71

Bracelet with ends bent together; decorated with six groups of crude notches.

Weight: 11.9 g.

Findspot: Burial M-02-71

2010 XRF Results: Cu (91.8%), Sn (8.23%)

2006 XRF Results: Cu (90.6%), Sn (9.3%)

27) Bracelet, Inv. No. 103-71

Fig. 41 - Bracelet, Inv. No. 103-71

Bracelet with ends bent together; undecorated.

Weight: 9.1 g.

Findspot: Burial M-01-71

2010 XRF Results: Cu (96.2%), As (3.83%)

2006 XRF Results: Cu (97.9%), Zn (1.68%), Pb (0.33%)

28) Bracelet, Inv. No. 104-71

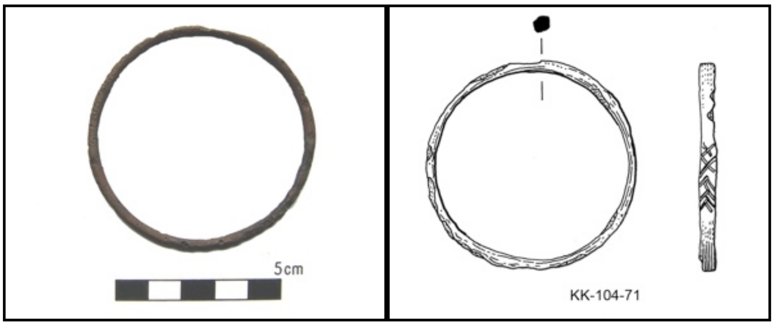

Fig. 42 - Bracelet, Inv. No. 104-71

Bracelet; decorated with group of herringbone incisions.

Weight: 16.4 g.

Findspot: Burial M-01-71

2010 XRF Results: Cu (87.1%), As (0.57%), Sn (12.3%), Pb (0.13%)

2006 XRF Results: Cu (86.1%), Sn (10.9%), Zn (2.48%), Pb (0.45%)

29) Bracelet, Inv. No. 114-71

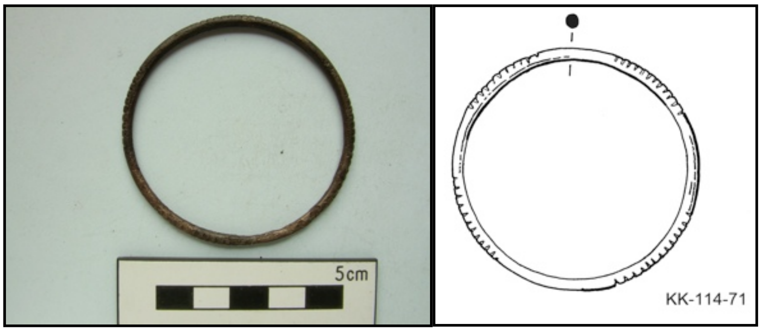

Fig. 43 - Bracelet, Inv. No. 114-71

Bracelet; decorated with four groups of fine parallel notches.

Weight: 10.2 g.

Findspot: Burial M-02-71

2010 XRF Results: Cu (99.2%), As (0.2%), Pb (0.2%)

2006 XRF Results: Cu (98.1%), Zn (1.32%), Pb (0.51%)

30) Small bracelet, Inv. No. 117-71

Fig. 44 - Small bracelet, Inv. No. 117-71

Adjustable bracelet with overlapping pointed ends; undecorated; only jewel that includes Ni within its chemical composition.

Weight: 7.2 g.

Findspot: Outside square b/3

2010 XRF Results: Cu (85.4%), As (14.3%), Ni (0.24%), Pb (0.07%)

2006 XRF Results: Cu (96.8%), Zn (2.72%), Ni (0.26%), Pb (0.21%), Fe (0.1%)

31) Bracelet, Inv. No. 121-71

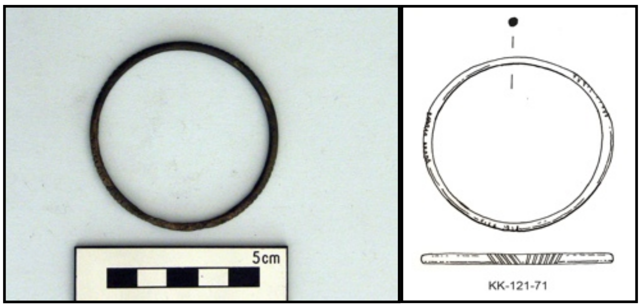

Fig. 45 - Bracelet, Inv. No. 121-71

Bracelet; decorated with three groups of fine diagonal incisions.

Weight: 10.5 g.

Findspot: Burial M-02-71

2010 XRF Results: Cu (93.3%), As (6.45%), Pb (0.19%)

2006 XRF Results: Cu (98.5%), Zn (1.08%), Pb (0.39%)

32) Bracelet, Inv. No. 122-71

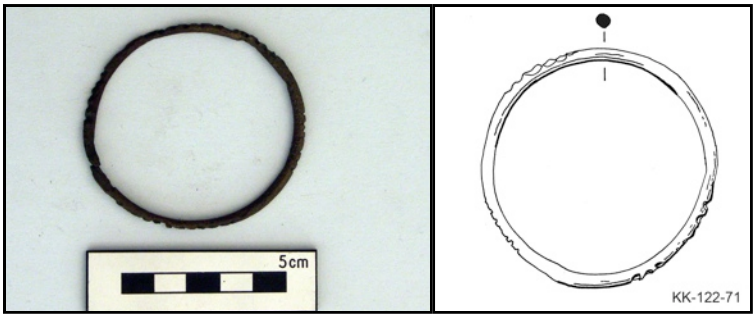

Fig. 46 - Bracelet, Inv. No. 122-71

Bracelet; decorated with three groups of crude notches.

Weight: 12.8 g.

Findspot: Burial M-02-71

2010 XRF Results: Cu (90.9%), Sn (9.02%), Pb (0.09%)

2006 XRF Results: Cu (87.3%), Sn (9%), Zn (3.25%), Pb (0.47%)

33) Bracelet, Inv. No. 123-71

Fig. 47 - Bracelet, Inv. No. 123-71

Adjustable bracelet with conical ends; undecorated.

Weight: 18.8 g.

Findspot: Outside square b/4

2010 XRF Results: Cu (93.5%), As (6.39%)

2006 XRF Results: Cu (96.5%), Zn (3.8%), Pb (0.36%)

34) Bracelet, Inv. No. 124-71

Fig. 48 - Bracelet, Inv. No. 124-71

Adjustable open bracelet with conical ends; undecorated.

Weight: 7.2 g.

Findspot: Outside square b/4

2010 XRF Results: Cu (93.1%), As (6.84%)

2006 XRF Results: Cu (99.9%), Pb (0.19%)

35) Bracelet, Inv. No. 125-71

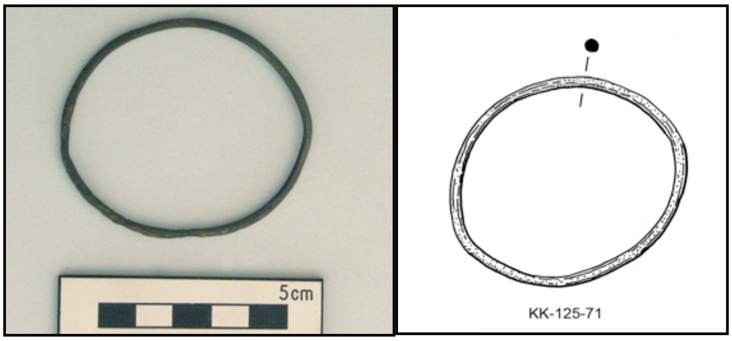

Fig. 49 - Bracelet, Inv. No. 125-71

Bracelet, undecorated.

Weight: 8.3 g.

Findspot: Burial M-16-71

2010 XRF Results: Cu (99.7%), As (0.14%), Pb (0.16%), Fe (0.1%)

2006 XRF Results: Cu (98.9%), Zn (0.77%), Pb (0.28%), Fe (0.13%)

36) Bracelet, Inv. No. 63-73

Fig. 50 - Bracelet, Inv. No. 63-73

Adjustable bracelet with overlapping pointed ends; undecorated.

Weight: 15 g.

Findspot: Burial M-20-73

2010 XRF Results: Cu (91.4%), As (8.6%)

2006 XRF Results: Cu (99.6%)

37) Bracelet, Inv. No. 64-73

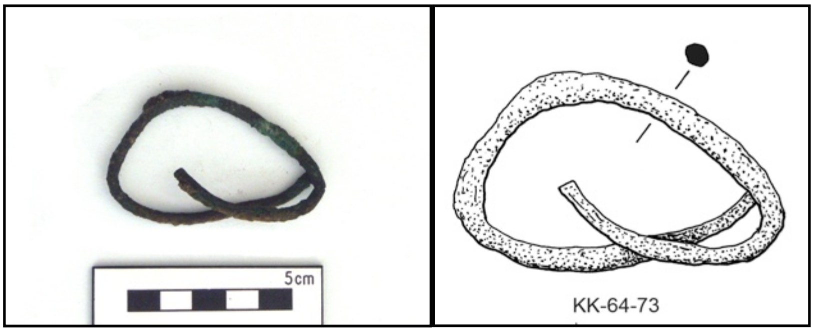

Fig. 51 - Bracelet, Inv. No. 64-73

Adjustable, bent bracelet with flat cut ends; undecorated.

Weight: 14.2 g.

Findspot: Burial M-20-73

2010 XRF Results: Cu (98.2%), As (1.02%), Fe (0.74%)

2006 XRF Results: Cu (99.6%), Fe (0.37%)

TOOLS

38) Crude shafthole sheet, Inv. No. 70-71

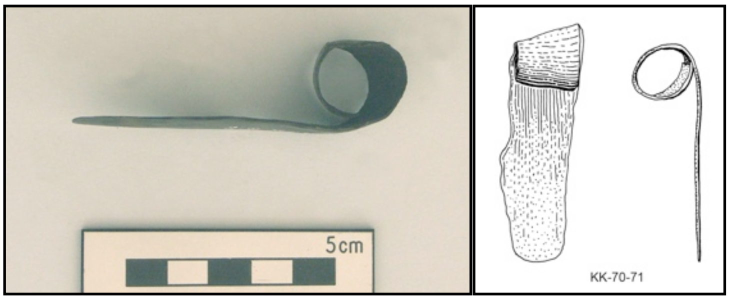

Fig. 52 - Crude shafthole sheet, Inv. No. 70-71

Thick sheet of copper-based metal; cylindrically bent at one end to form shafthole.

Weight: 24.2 g.

Findspot: Outside square b/4

2010 XRF Results: Cu (97.2%), As (2.35%), Pb (0.35%)

2006 XRF Results: Cu (98.9%), Zn (0.69%), Pb (0.31%), Fe (0.1%)

39) Awl, Truncator, or Tweezer, Inv. No. 82-71

Fig. 53 - Awl, truncator, or tweezer, Inv. No. 82-71

Object with square cross-section; whether an awl, a truncator, or a tweezer; surface cracked and damaged.

Weight: 2.9 g.

Findspot: Outside square b/3

2010 XRF Results: Cu (97.6%), Sn (2.25%), Pb (0.12%)

2006 XRF Results: Cu (98.1%), Zn (1.64%), Pb (0.19%), Fe (0.15%)

40) Hook-butted axe-hammer, Inv. No. 12-73

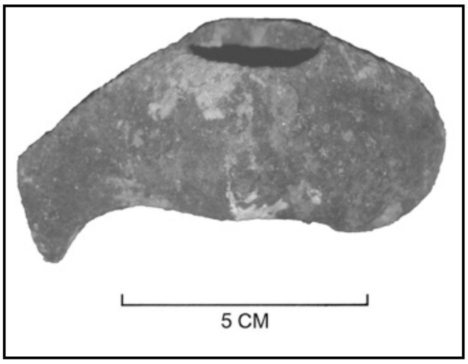

Fig. 54 - Hook-butted axe-hammer, Inv. No. 12-73

Squat body, flat blunt hammerhead; butt with broad leaflet-shaped hook; traces of organic wrapping on patina; wooden splinters in shatfhole.

Weight: Not available.

Findspot: Burial M-01-73

2010 XRF Results: Cu (95%), As (4.8%), Fe (0.15%)

2006 XRF Results: Not available.

WEAPONS

41) Tanged dagger, Inv. No. 57-71

Fig. 55 - Tanged dagger, Inv. No. 57-71

Dagger with triangular blade; bevelled edges, shoulders with hafting traces; trapezoid tongue with one central rivet hole, half of a second rivet hole at edge of broken-off tongue.

Weight: 46.3 g.

Findspot: Outside square b/4

2010 XRF Results: Cu (97.2%), As (2.71%), Pb (0.11%)

2006 XRF Results: Cu (97.5%), Zn (2.15%), Pb (0.31%)

42) Tanged dagger, Inv. No. 71-71

Fig. 56 - Tanged dagger, Inv. No. 71-71

Dagger with triangular resharpened blade; rectangular tongue with one central rivet hole. Shallow broad midrib, the edges badly worn. This object has the highest Ni ratio.

Weight: 24,5 g.

Findspot: Unknown; looted.

2010 XRF Results: Cu (93.3%), As (1.55%), Sn (0.76%), Ni (3.2%), Pb (0.35%)

2006 XRF Results: Cu (96.1%), Zn (2.58%), Pb (0.42%)

43) Tanged dagger, Inv. No. 87-71

Fig. 57 - Tanged dagger, Inv. No. 87-71

Heavily corroded, rhombic dagger with badly worn bevelled edges. The partly broken-off rectangular tongue.

<u>Weight:</u> 19.2 g.

<u>Findspot:</u> Burial M-08-71

<u>2010 XRF Results:</u> Cu (96.6%), As (3.06%), Pb (0.14%), Fe (0.1%)

<u>2006 XRF Results:</u> Cu (98.3%), Zn (1.47%), Pb (0.17%), Fe (0.09%)

44) Tanged dagger, Inv. No. 115-71

Fig. 58 - Tanged dagger, Inv. No. 115-71

Badly worn dagger with slim triangular blade; shallow triangular midrib; rectangular tongue with single rivethole; severly damaged due to earlier electrochemical treatment.

<u>Weight:</u> 13.6 g.

<u>Findspot:</u> Burial M-08-71

<u>2010 XRF Results:</u> Cu (91%), As (1.32%), Sn (7.58%), Pb (0.12%)

<u>2006 XRF Results:</u> Cu (91.1%), Sn (8.56%), Pb (0.28%)

45) Spherical macehead, Inv. No. 56-71

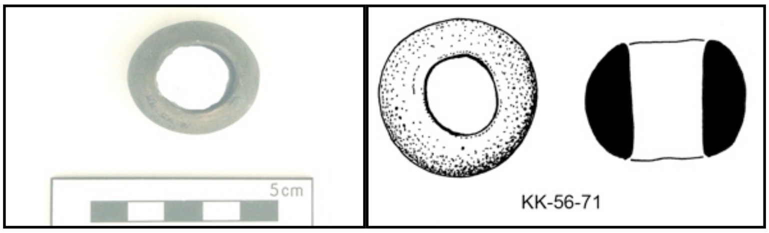

Fig. 59 - Spherical macehead, Inv. No. 56-71

Massive spherical macehead, undecorated.

Weight: 75.3 g.

Findspot: Outside square b/4

2010 XRF Results: Cu (93.5%), As (4.88%), Pb (1.43%)

2006 XRF Results: Cu (95.3%), Zn (1.58%), Pb (3.08%)

STATUETTES AND CEREMONIAL STANDARD

46) Crude bull statuette, Inv. No. 100-71

Fig. 60 - Crude bull statuette, Inv. No. 100-71

Bull statuette with crudely indicated horns, mouth and tail; hind legs bent. surface uneven; crudely made and careless finish, many casting pipes not removed.

Weight: 282.8 g.

Findspot: Burial M-C-71

2010 XRF Results: Cu (96%), As (3.89%), Fe (0.1%)

2006 XRF Results: Not available.

47) Bull statuette, Inv. No. 33-1-72

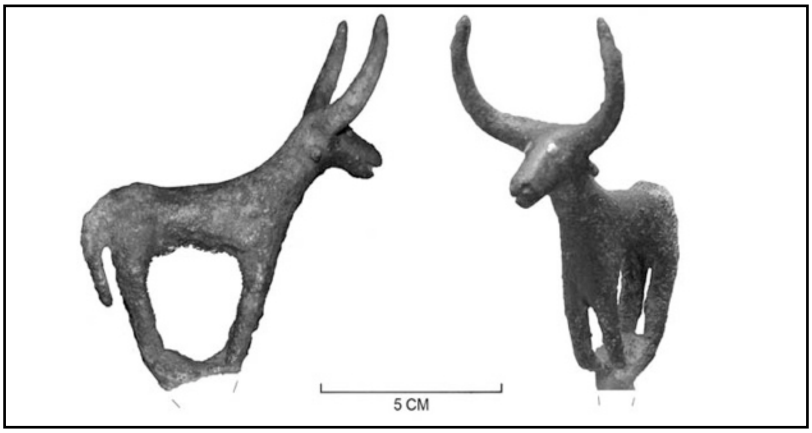

Fig. 61 - Bull statuette, Inv. No. 33-1-71

Fine worked bull statuette; head, horns, nostrils and tail indicated; eyes indicated with pure silver (100% Ag) coat on metal surface.

Weight: Not available.

Findspot: Unknown; looted.

2010 XRF Results: Cu (90.1%), Sn (7.69%), Pb (1.27%), Fe (0.93%)

2006 XRF Results: Not available.

48) Ceremonial standard, Inv. No. 19-71

Fig. 62 - Ceremonial standard

Crudely worked, flat and slightly bent ceremonial standard; framed with three rectangular/semi-spherical projections; inner part has an abstract lattice motive, or an abstract depiction of a horned animal.

Weight: Not available.

Findspot: Unknown; looted.

2010 XRF Results: Cu (97.2%), As (2.35%), Pb (0.23%)

2006 XRF Results: Not available.

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