ÜMIT GÜDER · TURAN TAKAOĞLU · ABDULKADIR ÖZDEMIR

MIDDLE CHALCOLITHIC COPPER TOOLS FROM GÜLPINAR IN NORTH-WESTERN ANATOLIA – AN ARCHAEOMETRIC APPROACH

A small group of copper tools of the 5th millennium BC recently identified at the prehistoric settlement of Gülpınar in the coastal Troad complements our general knowledge of the early metal use both in western Anatolia and the Aegean world (**figs 1-2**). Although archaeological evidence demonstrates that copper was first used in Anatolia as early as the Neolithic period (Schoop 1995, 141; Pernicka 2006, 349), the information about the history of copper in the western Anatolian littoral and the Aegean is extremely limited. An assessment of the archaeological evidence regarding the use of metal in pre-Bronze-Age sequences of Aegean history has demonstrated that the tools made of copper were already in use both on the Aegean islands and in northern Greece and Thrace as early as the first part of the 5th millennium BC (Zachos 2007). The evidence for the use of copper in the western Anatolian littoral is, however, relatively patchy. The use of copper has been recognized only at sites such as Kumtepe A in the Troad (Gabriel 2006, 356), Liman Tepe

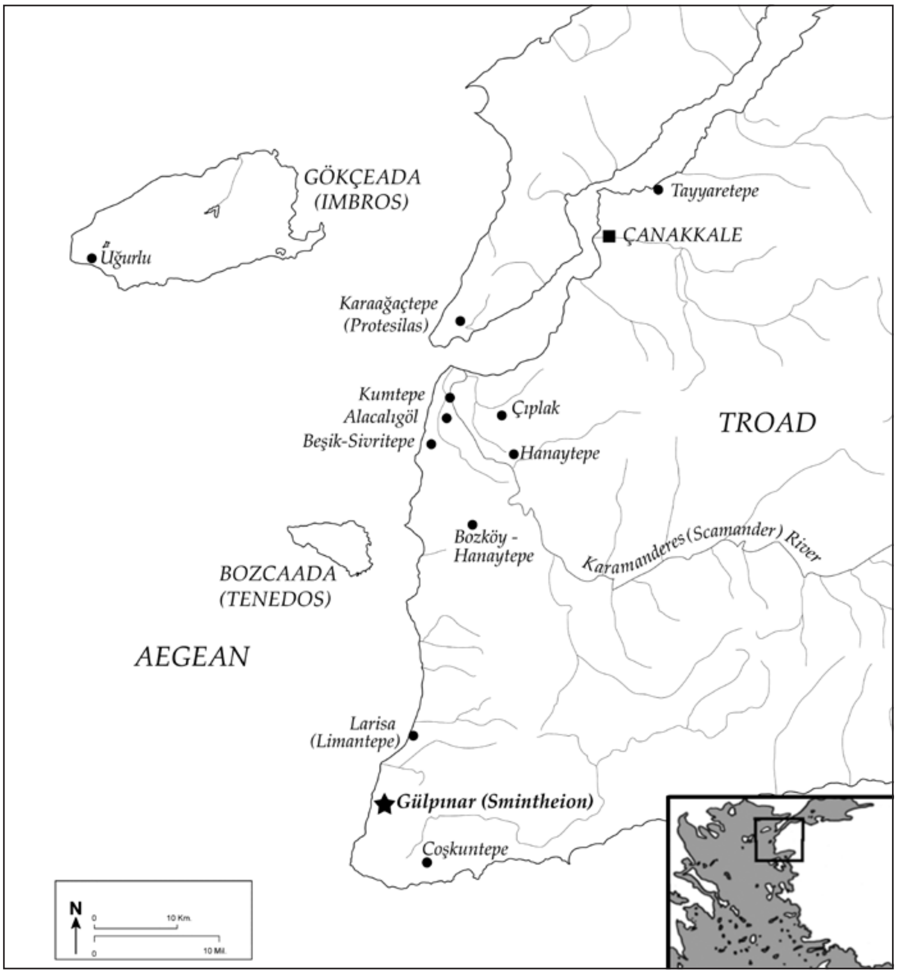


Fig. 1 Map showing Gülpınar (Çanakkale/TR) and other main settlements with pre-Trojan sequences in the Troad. – (Map Gülpınar [Smintheion] Excavations Project).

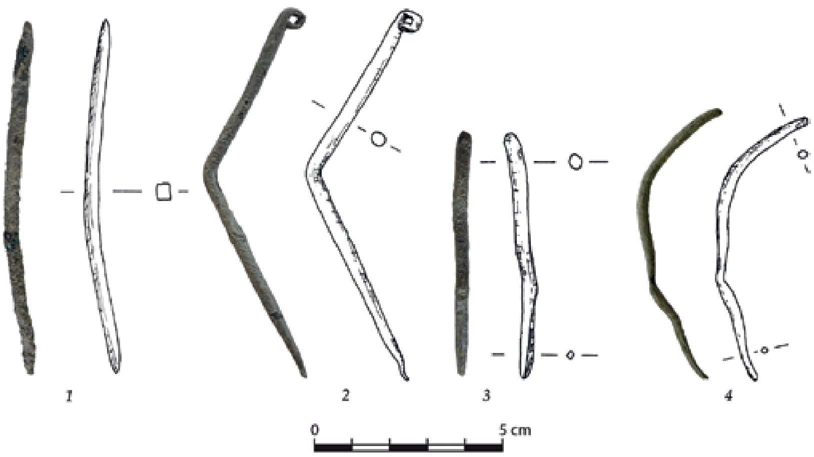


Fig. 2 Four copper tools from the phase IIIa settlement at Gülpınar: **1** awl. – **2** roll-headed pin. – **3** awl. – **4** pin with missing parts. – (Photos and drawings Gülpınar [Smintheion] Excavations Project). – Scale 1:2.

and Kulaksızlar in central western Anatolia (Tuncel / Şahoğlu 2018, 524-525; Takaoğlu in print, fig. 14), and the site of Uğurlu on the island of Gökçeada (Imbros) (pers. comm. B. Erdoğu). The analysis of the Gülpınar copper tools presented here aims to throw new light on the aspects of metallurgy that prevailed in the 5th millennium BC in the western Anatolian littoral concerning manufacturing techniques and acquisition of raw materials.

THE SITE

The Chalcolithic site of Gülpınar is situated on the south-western corner of the modern Biga Peninsula (Ancient Troad) in northwest Turkey (Takaoğlu / Özdemir 2018). The site was identified beneath the remains of the Greek and Roman Sanctuary of Apollo Smintheus (Smintheion). The sanctuary was renowned in the Hellenistic period with the Temple of Apollo Smintheus dating to the 2nd century BC, with friezes and reliefs that depict scenes related to the legendary Trojan War as described in the *Iliad* (I, 37. 390. 431) of Homer (Özgünel 2003). Because a horizontal stratification exists at Gülpınar, the distribution of prehistoric cultural layers has been recovered over a large area of approximately 1.2 ha during the excavations, enabling us to document all phases of occupation in every section of the settlement. The remains of the prehistoric settlement generally appear at varying depths of 50 cm to 220 cm from the ground surface at Gülpınar. As far as the areas excavated are concerned, the earliest cultural layer identified at Gülpınar is phase I, which was occupied sometime during the Late Neolithic period around 6000 BC. After an interval, the following phase II settlement belongs to the Early Chalcolithic period, which is dated to ca. 5300-4900/4800 BC at the site according to ^{14}C dating. The phase III settlement ascribed to the Middle Chalcolithic period was built directly above the architectural remains of the phase II settlement. The phase III settlement, which is divided into two sub-phases, was inhabited between 4900/4800-4450/4300 BC. The four copper objects discussed in this paper were found in architectural layers representing the first phase of the Middle Chalcolithic period, which is phase IIIa (**tab. 1**).

MATERIALS AND THEIR CONTEXT

The copper tools from phase IIIa at Gülpınar were recovered together with other items of the Middle Chalcolithic period (**fig. 2**). The first copper tool (1) was found in Room 39 of Structure L in Sector 2 (**fig. 3**),

<table>
<tr><th>Period</th><th>Sub-Period</th><th>Cal. BC</th><th>Gül-pınar</th><th>Kum-tepe A</th><th>Beşik Sivri-tepe</th><th>Uğurlu</th><th>Ulucak</th><th>Yeşilova</th><th>Yassı-tepe Höyük</th><th>Liman Tepe</th><th>Kulak-sızlar</th></tr>
<tr><td rowspan="8">Early Chalcolithic</td><td rowspan="3">1</td><td>5600</td><td rowspan="3"></td><td rowspan="7"></td><td rowspan="8"></td><td></td><td rowspan="3">III</td><td rowspan="13"></td><td rowspan="4"></td><td rowspan="10"></td><td rowspan="11"></td></tr>
<tr><td>5500</td><td rowspan="7">III</td></tr>
<tr><td>5400</td></tr>
<tr><td rowspan="5">2</td><td>5300</td><td rowspan="5">II</td><td rowspan="12"></td></tr>
<tr><td>5200</td><td rowspan="4">IV</td></tr>
<tr><td>5100</td></tr>
<tr><td>5000</td></tr>
<tr><td>4900</td><td rowspan="5"></td></tr>
<tr><td rowspan="7">Middle Chalcolithic</td><td rowspan="3">1</td><td>4800</td><td rowspan="6">III</td><td rowspan="7"></td><td rowspan="6">II</td><td rowspan="7"></td></tr>
<tr><td>4700</td></tr>
<tr><td>4600</td><td rowspan="5">VII</td></tr>
<tr><td rowspan="4">2</td><td>4500</td><td rowspan="4"></td></tr>
<tr><td>4400</td><td rowspan="3"></td></tr>
<tr><td>4300</td><td rowspan="2">III</td></tr>
<tr><td>4200</td><td></td><td></td></tr>
</table>

Tab. 1 A tentative chronological chart of the western Anatolian littoral during the Early and Middle Chalcolithic periods based on ^{14}C dates from the excavated sites.

at the same level as a stone-paved bench and grinding stones stored on it in the south corner of the room (Özdemir 2017, 216). This copper object is an awl made of hammered wire, rectangular in section. It is 9.3 cm long and both ends of the rectangular shaft taper to a blunt point. Examples comparable to this type of awl from phase III at Gülpınar have also been encountered at the 5th millennium BC sites of Kulaksızlar in central western Anatolia (Takaoğlu in print, fig. 14a) and phase II at Uğurlu on the island of Gökçeada (Imbros) (pers. comm. B. Erdoğu). This type of awl is also known from the sites of northern Greece and Thrace, such as Sitagroi, Dikilitash, Dimitra and Paradeisos (Renfrew/Slater 2003, 302; Seferiades 1992, 115; Grammenos 1997, 270; Hellström 1987, 85-86; Zachos 2007, figs 11.2 and 11.3), as well as the Cycladic sites of the Zas Cave and Ftelia on Mykonos (Zachos 2007, fig. 11.4; Maxwell et al. 2018, 160 fig. 2). They are also known from sites as far as the Amuq Plain to Iran (Schoop, 1995, 113. 119. 122. 128-130. 135).

The second copper tool (2), a roll-headed pin, was found in the food preparation area 7 in the northwest of Sector 1 (**fig. 3**). This food preparation area was identified in the northwest of a buttressed wall running in a northeast-southwest direction (Özdemir 2017, 223). This space was a common workshop area where different activities took place. The pin (2) was found together with bone tools in a locus associated with mat-making activities. It is 10.8 cm in length. This complete tool with a circular cross-section was made of hammered wire. One end of the circular shaft was bent back on itself to form the eye or a loop, while the other end of the shaft tapers to a point. It is difficult to estimate if the shaft was intentionally bent in the middle during the manufacturing stage. No comparable pins have been recorded from the sites of north-western Anatolia in this period, although stylistically comparable tools have been found from the Early Bronze Age in the region. The closest parallels to this type of pin with a looped head come from the Middle Chalcolithic level XVI at Mersin Yümüktepe in Cilicia, dating to around 5300 BC (Garstang 1953, fig. 85; Schoop 1995, 116-118). Comparable roll-headed pins are also known from Ftelia on Mykonos and Sitagroi III in Macedonia (Maxwell et al. 2018, 148; Renfrew/Slater 1986, pl. 8.2f; McGeehan-Liritzis 1996, 87 no. 485).

Fig. 3 Plan of the Gülpınar prehistoric phases and the locations of the copper tools (★). – (Map Gülpınar [Smintheion] Excavations Project).

The third copper tool (3) was recovered together with other finds in the grid section G13 during the excavations in Sector 3 north of Sector 1, in order to determine the extent of the prehistoric settlement of Gülpınar (**fig. 3**). This tool resembles an awl. Measuring 6.4 cm in length, it was made of hammered wire roughly circular in section. One end of it tapers to a point where the cross-section turns to a rectangular shape. The other, rounded end preserves the circular cross-section of the shaft.

The fourth copper tool (4) was found together with other items used for different purposes in Structure C Room 14 in Sector 1 (**fig. 3**). Measuring 8.7 cm in length, it is similar to object 2, except for having the loop at one end. It is slightly bent at a point close to the middle. One end of the shaft was tapered, while the other bears traces of having been broken. This end could originally have had a loop.

ANALYTICAL PROCEDURES AND RESULTS

The first step of the archaeometric analyses of these four copper tools from Gülpınar was to examine their surfaces macroscopically. By doing this, it was hoped to determine the oxide colours and thereby gain information about the items' corrosion layers. The chemical contents on the surfaces of objects 2, 3 and 4 were measured with the Spectro X-Sort Combi portable XRF (X-Ray Fluorescence) instrument. Analyses were performed from different parts of each object by using the »light elements« mode (50 kV voltage, 0.016 mA current, average 12 seconds measurement time) of the instrument. The number of measurements varied according to the forms of the analyzed objects. Thus, eight analyses were performed on object 2, four measurements on object 3 and five measurements on object 4. (Object 1 was unfortunately not subjected to any archaeometric analysis due to problems derived from access to this specimen, which is kept in the depot of the Çanakkale Archaeology Museum.)

The analyzed finds were cut using a water-cooled diamond disc from the non-pointed ends of 3 and 4 for metallography and electron microscopy examination. These samples, which were moulded with epoxy using a vacuum impregnation system, were then ground on rotary discs with 320, 600 and 1200 grit silicon carbide grinding papers. Polishing was carried out using 3 and 1 micron diamond suspension, and final polishing was carried out with 0.3 micron alumina powder. As a final step, etching was carried out using an etchant with iron (III) chloride and hydrochloric acid content. Microstructure photographs of samples before and after etching were recorded digitally by a Nikon E-Pol 200 light microscope.

A JEOL SEM-7100-EDS scanning electron microscope was also used for the imaging of microstructures which could not be identified by light microscope examination alone. General image scanning of the etched structures was carried out with a secondary electron detector and chemical analyses were conducted with EDS (Energy-Dispersive X-Ray Spectrometer) equipment. EDS measurements were performed on the metallic bodies and inclusions of different morphology and colour to get information about their origins. To allow for meaningful evaluations to be made from the chemical analysis results, a total of 17 analyses from metallic bodies and 33 from intermetallic phases were performed.

In addition, micro-hardness measurements were conducted using the Vickers method on an HV-1000Z model hardness tester of Pace Technologies. The hardness was tested by selecting points in the metallic body ranging from the centre to the surface of the cross-section using 200 grams weight (HV0.2). Care was taken to ensure that the measurement points did not coincide with corroded regions or inclusions.

Morphological Observations

The first of the four copper tools (1) is of varying thickness and has a rectangular cross-section. It is noticeable that the cross-section increasingly resembles the round form towards the ends. The other objects have a round cross-section of uniform thickness, except for object 4, tapering to one end. Close to the middle section of object 4, there is a tapered region that forms a neck due to corrosion. The lengths of the exa-

No. 2	Mg	Al	Si	P	Ti	Fe	Cu	As	Sn
Min	0	3.6	23.1	0	0.2	2.8	12.5	0	0
Max	11.9	58.9	42.5	0.2	0.6	6.9	54.7	0.0	0.09
Mean	1.9	35.1	31.2	0.1	0.3	4.2	27.2	0.0	0.01
No. 3	Mg	Al	Si	P	Ti	Fe	Cu	As	Sn
Min	0	0	36.4	0	0.4	4.3	44.5	0	0
Max	0	6.4	42.4	0.3	0.6	7.4	55.8	0.04	0.61
Mean	0	3.5	39.9	0.1	0.5	6.0	49.4	0.03	0.44
No. 4	Mg	Al	Si	P	Ti	Fe	Cu	As	Sn
Min	0	0	19.6	0	0.1	2.3	10.3	0	0
Max	0.7	66	40.9	0.2	0.8	9.7	76.0	0.05	0.90
Mean	0.1	15.0	28.4	0.1	0.4	5.3	50.2	0.02	0.41

Tab. 2 The results of the XRF analyses (the mean values were normalized to 100 %).

mined finds vary between 6 cm and 11 cm. The longest of them (2) ends in a taper, while the other end is turned into a roll-headed form.

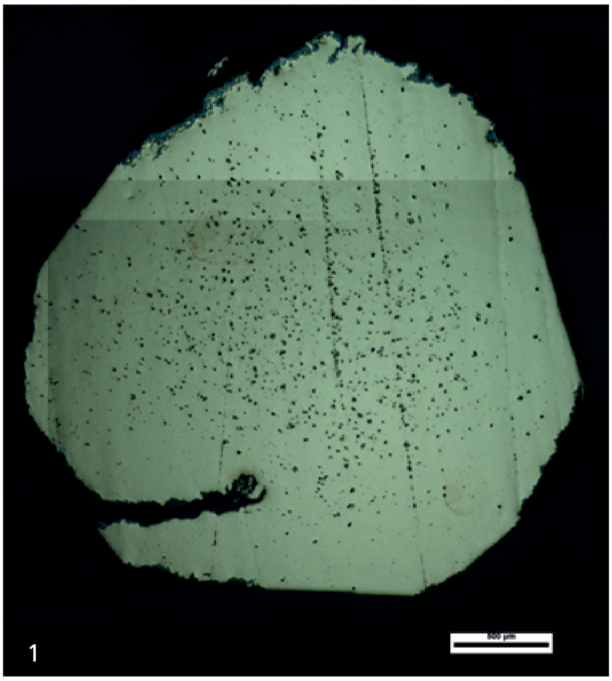
The copper tools under examination were recovered with a silvery gray matt surface. Green-turquoise copper oxidation products were detected as spots on object 1. It is reported that impurity elements such as antimony and arsenic in early copper objects can form such layers on the surface because of surface segregation (Wertime 1973, 877). It is observed that there is a black corrosion layer of a different character in parts where the gray-coloured layer is absent.

Surface Analysis with Portable XRF

Table 2 shows the results of the analyses performed with the portable XRF device on objects 2, 3 and 4. Considering the lowest and highest concentrations of the elements detected on the surface of the tools, there are substantial differences between the values. A heterogeneous situation indicates that the surfaces of the tools were covered with a patina layer consisting of a mixture of copper oxide, copper salts and the soil materials originating from the site. When the results were evaluated, no enrichment of arsenic, which would have formed a metallic gray colour by surface segregation, was detected. Instead, a high proportion of aluminium was encountered in metallic gray layers. The source of this aluminium might be the fusion of the soil with the corrosion layer. It is thought that the amount of copper increased in the sections where the gray layer is absent and the black colour is visible. When the colour and content are evaluated, it is concluded that this region is composed of a tenorite-copper oxide (CuO) layer. Both the patina and tenorite layers were found to have 3 % to 9 % iron content.

Optical Microscope Examination

The physical properties of the sections could also be determined from a metallographic examination of samples prepared from objects 3 and 4. In the photographs taken with a light microscope, the polygonal cross-section of object 3 was measured as having the largest width of 3 mm and the smallest width of 2.8 mm (**fig. 4, 1**). The cross-section of object 3 clearly shows the straight edges formed during hammering. A kind of folding line, that looks like a crack intruding from the surface, was formed by the hammering of two



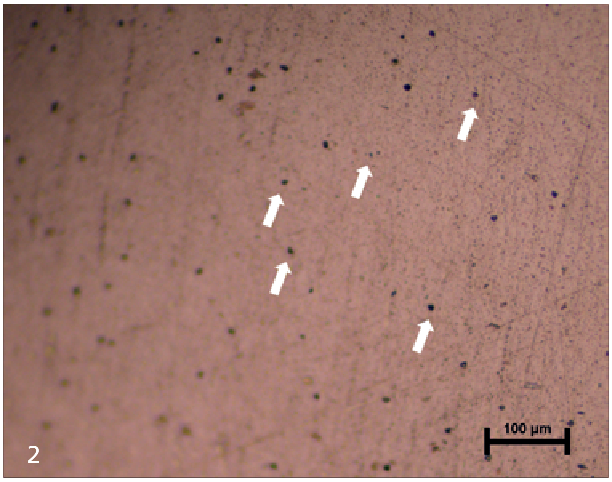


Fig. 4 Optical microscope examination. – **1** coarse spherical voids in the cross-section of object 3. – **2** black and light gray intermetallic phases at the unetched sample from object 4. – (Photos Ü. Güder).

sides of a rod to obtain a round section. The original rod might have been a cast-blank with a rectangular cross-section (Thornton/Lamberg-Karlovsky 2004, 50). On the other hand, the cross-section of object 4 has an elliptical appearance with edge lengths of 1.6 mm and 2 mm. A corrosion layer surrounding the metal body was observed in various thicknesses in both samples. This layer is thicker in object 4 when compared to object 3. Finally, it was detected in the non-etched sample that the intermetallic inclusions found in the metal vary in both colour and size (**fig. 4, 2**).

After the etching process, a light microscopy examination revealed similar microstructures of copper phases, notably around the centre of the samples. The microstructures have been identified as uniform grain structures and twinning was observed within these grains. In the microscope image of the microstructure of object 4, it was observed that the grain sizes are larger than in the previous object. Moreover, the number of observed intermetallic phases is less than in object 3 (**fig. 5, 1-2**).

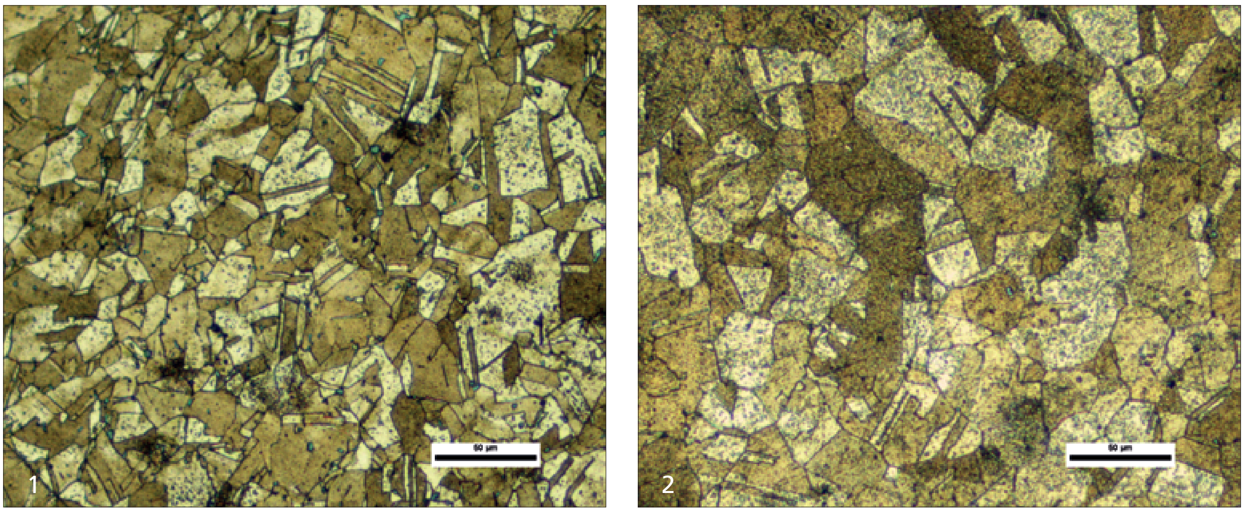


Fig. 5 Optical microscope examination. – **1** twins in copper grains and grayish-blue intermetallic phases in the microstructure of object 3. – **2** bigger grain size in the microstructure of object 4. – (Photos Ü. Güder).

No. 3	Cu	As	Pb	Fe	Sb	Co	Ag	Sn
Min	97.7	0.5	0.3	-	-	-	-	-
Max	98.9	1.3	0.9	0.1	0.20	-	0.1	0.20
Mean	98.2	1.0	0.5	0.1	0.07	-	0.05	0.08
No. 4	Cu	As	Pb	Fe	Sb	Co	Ag	Sn
Min	97.7	0.5	0.2	0.1	-	-	-	-
Max	99.0	1.1	0.8	0.3	0.20	0.10	0.20	0.20
Mean	98.4	0.9	0.3	0.2	0.09	0.02	0.06	0.03

Tab. 3 The results of the EDS analysis on the metal regions and their mean values (9 points were analyzed on object 3 and 8 points on object 4).

Electron Microscopy and EDS Examination

Strain lines were observed in photographs taken from the metal portion of object 4 and examined under a scanning electron microscope (fig. 6). However, these lines are concentrated only in certain regions and only a few of them were detected. Strain lines are formed by shaping annealed copper in a cold state. It is normal to see some of them in cases where annealing is inadequate. The small number of strain lines in the studied sample is important, since it demonstrates that the heating-forging cycles were repeated multiple times. In addition to strain lines, during electron microscopy examination, the annealing twins which were first detected in the light microscope were more clearly observed.

In the EDS measurements performed on the metallic body to determine the chemical content, approximately 1 % arsenic was detected in both samples. Considering the other metal content, the mean antimony is below detection limits. Lead values are 0.5 % and 0.3 %, and iron values are 0.1 % and 0.2 %, respectively (tab. 3).

In the EDS analysis targeting the inclusions visible inside the copper grains, three different groups were identified (tab. 4). In the darkest coloured and largest group, the chemical composition shows a distribution remarkably close to the main metal body. These inclusions are oxidation products of the metal composition which developed in the gas pores formed during casting. Such pores were also observed in the samples

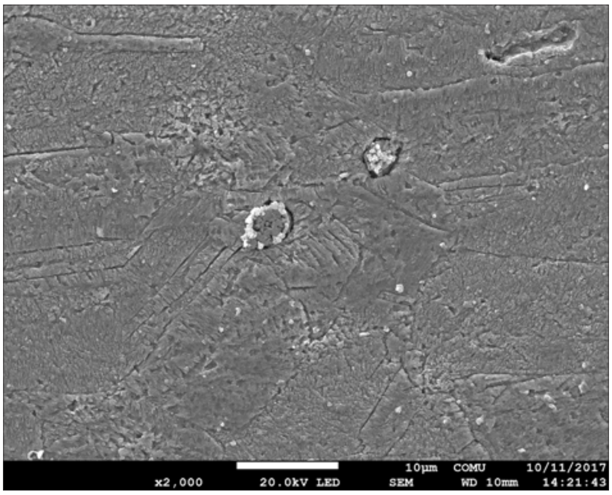


Fig. 6 Formation of annealing twins and strain lines in the microstructure of object 4. – (Photo Ü. Güder).

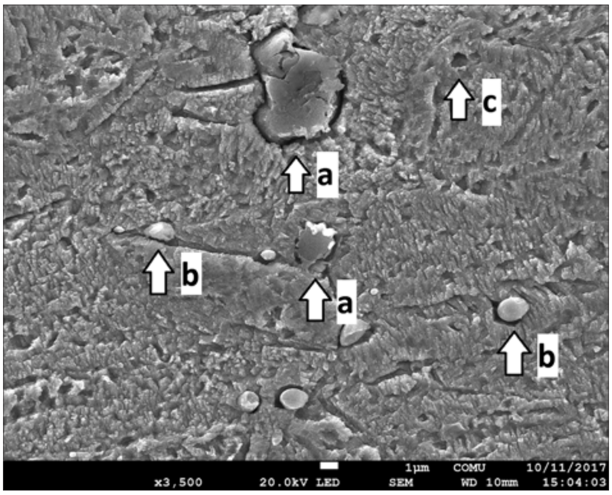


Fig. 7 Image created by the SEM instrument of iron-rich intermetallic phases (**a**), sulphide-rich inclusions (**b**) and one void formed by extracted sulphide inclusions during the sample preparation (**c**). – (Photo Ü. Güder).

Inclusions.1										
No. 3 (5 Targets)	Cu	As	Pb	Fe	Sb	Co	Ag	Sn	Ni	S
Min	90.9	0.8	-	-	-	-	-	-	-	-
Max	98.6	1.1	1.5	5.9	0.1	0.1	0.1	0.1	-	0.1
Mean	96.9	0.97	0.75	1.26	0.02	0.02	0.02	0.04	-	0.02
No. 4 (3 Targets)	Cu	As	Pb	Fe	Sb	Co	Ag	Sn	Ni	S
Min	96.9	0.8	0.9	0.2	-	-	-	-	-	-
Max	97.5	1.2	1.9	0.3	0.1	-	0.1	0.1	-	-
Mean	97.09	0.97	1.5	0.23	0.07	-	0.07	0.07	-	-
Inclusions.2										
No. 3 (5 Targets)	Cu	As	Pb	Fe	Sb	Co	Ag	Sn	Ni	S
Min	10	-	0.4	47	-	0.8	-	-	-	0.1
Max	35.3	0.6	4.2	86.8	0.1	10.1	-	0.1	0.5	4.4
Mean	21.24	0.2	2.02	69.63	0.04	4.67	-	0.04	0.32	1.84
No. 4 (5 Targets)	Cu	As	Pb	Fe	Sb	Co	Ag	Sn	Ni	S
Min	14.5	-	-	48.4	-	-	-	-	-	-
Max	48.3	0.5	3.9	85.5	0.1	-	-	0.2	0.3	2.9
Mean	27.34	0.16	2.04	69.6	0.02	-	-	0.04	0.14	0.66
Inclusions.3										
No. 3 (11 Targets)	Cu	As	Pb	Fe	Sb	Co	Ag	Sn	Ni	S
Min	57.8	-	4.4	-	-	-	-	-	-	7.4
Max	84.5	0.3	7.8	28	0.1	1.3	0.2	-	0.1	16.3
Mean	76.09	0.09	5.86	4.83	0.03	0.18	0.08	-	0.01	12.83
No. 4 (4 Targets)	Cu	As	Pb	Fe	Sb	Co	Ag	Sn	Ni	S
Min	71	-	4.6	1.9	-	-	-	-	-	12.6
Max	80.5	-	6	4.6	-	0.1	0.4	-	0.1	17.3
Mean	77.05	-	5.0	3.16	-	0.02	0.2	-	0.02	14.55

Tab. 4 The results of the EDS analysis on the intermetallic phases (the mean values were normalized to 100 %).

before etching. In the second group, iron-rich (48.4-85.5 %) structures, mostly angular, were observed in a smaller number than the other inclusions. In the third group, round or elongated structures containing remarkable levels of sulphur (12.6-17.3 %) are included. In some of the iron-rich intermetallic phases, cobalt was found in quantities of up to 10 %.

In the images obtained by electron microscopy examination of the inclusions, it is understood from the remaining compatible spaces that some of the inclusions in the third group were separated from the surface during the sample preparation process. It is also suggested that the angular structures found among the iron-rich remains are unreacted fragments of the ore formed during the smelting phase (**fig. 7**).

In the SEM examination, it was observed that iron-rich intermetallic phases were concentrated in the centre, whereas those containing sulphur were concentrated in the areas close to the surface. In addition, grain size measurements clearly show that in object 3 grains near the outer wall shrank to 3.9 microns in diameter (ultra-small by ASTM standards) and deformed (**fig. 8**). In the inner regions, grain sizes are up to 27 microns (small according to ASTM standards). The grain sizes of the copper phases in object 4 have a more homogeneous appearance and were observed to be small and medium-sized according to ASTM standards.

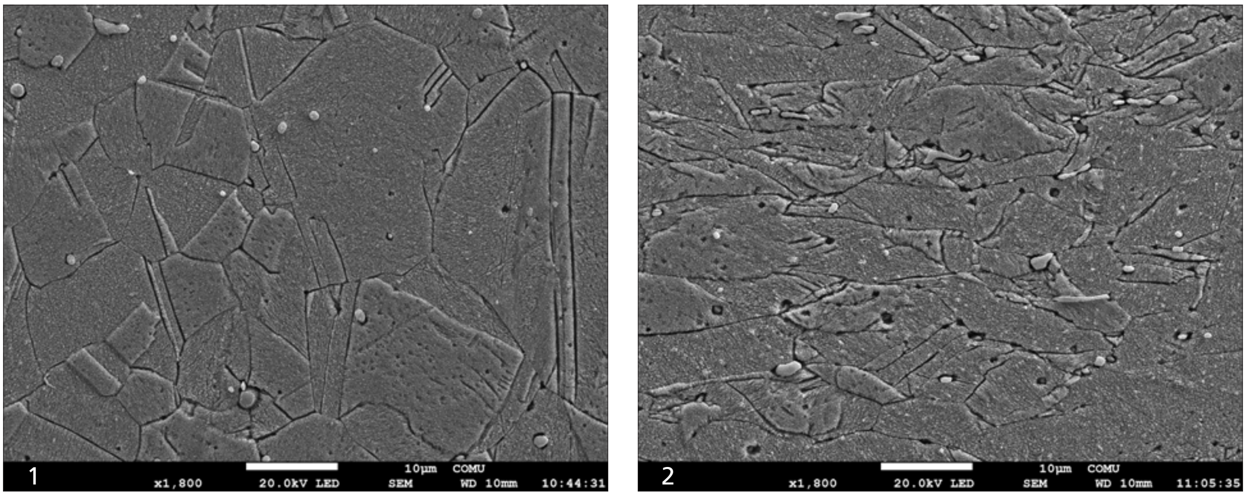


Fig. 8 SEM examination: **1** uniform small copper grains in the core section of the sample from object 3. – **2** deformed (due to cold working) ultra-small grains in the same sample. – (Photos Ü. Güder).

Micro-Hardness Testing

The hardness measurement results of points selected on samples starting from the centre and moving towards the surface are shown in figure 9. According to these results, there is a difference of approximately 14 HV between the centre and the surface region of object 3. In object 4, which has a homogeneous internal structure, this difference is only 2 HV. Furthermore, it is noteworthy that the hardness of object 3 is more than twice that of object 4.

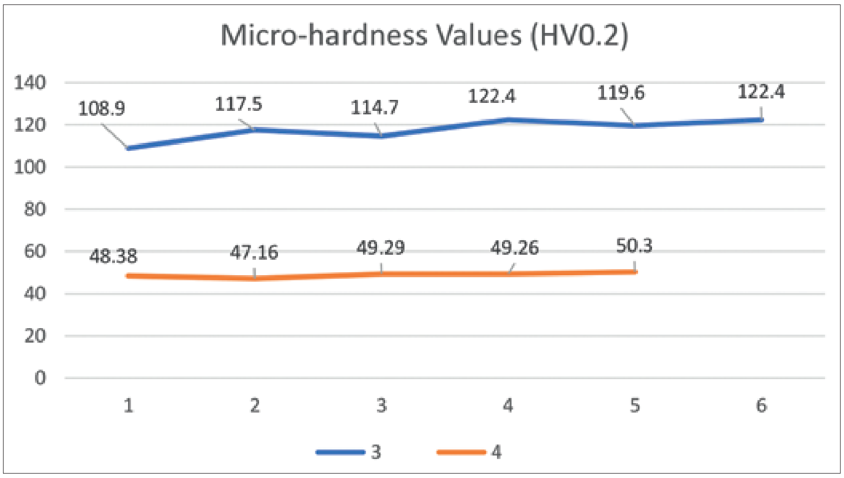
DISCUSSION

Macroscopic investigations and portable XRF analysis of copper tools from Gülpınar provided sufficient evidence to allow a preliminary determination to be made that these objects were produced from similar materials. Analyses for detailed material characterizations were performed on samples taken from two copper tools (3 and 4) selected from the four objects. As a result of analyses, the production method of the tools, the casting of arsenical copper, as well as cold forging and annealing techniques were all identified. A detailed description of the results is presented below.

Production Material

Due to their attractive colours, copper oxides, such as malachite, were used in the production of jewels in the Neolithic period in Anatolia much earlier than the use of native copper (Yalçın 2008, 17-18). As the archaeometric analyses conducted on the earliest copper tools recovered in Mersin Yümüktepe indicate, the smelting of copper oxides first took place at the beginning of the 5th millennium BC in Anatolia (Yalçın 2000, 115). Knowing the existence of copper oxides and where to find them, Anatolian people first collected oxide ores near the surface and smelted them in clay crucibles. It was then discovered that improvements could be achieved in the properties of the metal by smelting different types of ores. In alloys melted from arsenic-bearing ores, positive effects on workability were observed, such as a decreased formation of

Fig. 9 Graph showing the deviation of hardness in the cross-section of the samples. – (Ü. Güder).



gas porosity in the casting stage and an increase in the metal's hardness through cold forging. Although even 0.5 % arsenic content contributes to the easier processing of copper tools, the hardness of the material increases only with higher rates of arsenic (Eaton/McKerrell 1976, 169). For example, the effect of an arsenic content of 2 % on alloy hardness is just 6 % compared to pure copper (Lechtman 1996, 488).

The amount of arsenic and the composition of intermetallic phases provide information about the metallurgical origin of the copper from which the Gülpınar samples were produced. It is proposed that, due to the low rate of arsenic, i. e. around 1 % detected in the chemical analyses of the metal body, a process of vaporizing arsenic was applied in the production. In addition, copper sulphide and iron oxide inclusions as intermetallic phases indicate that sulphurous ores were used after heating them, instead of directly smelting the copper oxide ores. In the intermetallic phases, cobalt, lead and nickel metals were found to be at most 10.1 %, 7.8 % and 0.5 % respectively. Cobalt, lead and nickel are common elements in Fahlerz ores (Craddock 2010, 28). Although it is possible to produce arsenical copper by the co-smelting of Fahlerz ores together with copper oxides, it has been reported in laboratory experiments that arsenic can be obtained in these products at levels as high as between 7 % and 26 % (Lechtman/Klein 1999, 525). Arsenic content in polymetallic ores decreases not only during pre-heating but also during the smelting process (Boscher 2016, 32). In conclusion, the metallurgical production scenario in which the Fahlerz ore was heated first, while the arsenic was removed from the ore with sulphur and was then smelted, is consistent with the results obtained from the analysis of the Gülpınar tools.

Çanakkale and its environs are rich in iron and sulphur-containing copper mines bearing traces of ancient operations, in addition to the multiple modern copper mines operated today (Ryan 1960, 25-27; Pernicka et al. 2002). On the contrary, in the Troad the location of any ancient mines with arsenic-bearing ore deposits remains unknown (Lehner/Yener 2014, 532).

Arsenical copper is a type of copper alloy, encountered in Anatolia and the Near East since the 4th millennium BC (Yalçın 2008, 22). The first polymetallic ores were extracted in Mersin, Değirmentepe and Norşuntepe. The presence of arsenic at 1 % and higher in these finds, which are thought to be the first experimental alloys, is seen as a sign of the start of secondary sulphurous ore smelting (Yener 2000, 32). Arsenical copper was common during the Chalcolithic period and it was frequently used during the 3rd millennium BC (Yener 2000, 29). On the other hand, in the Iranian Tepe Yahya in the Near East, among finds dated to the end of the 5th millennium BC, arsenic was found at a rate of 1.24 % in a nail/needle with a rectangular cross-section. The metallographic examination of this object shows that the material used was not native copper. Also, there is contemporary evidence of arsenic content related to crucible smelting in Tal-i Iblis, 150 km north of Tepe Yahya (Thornton et al. 2002, 1456). There is also archaeological evidence

for the use of arsenical copper during the late 5th millennium in the Caucasus, with ratios around 1 % (e.g. Gambaschidze et al. 2010; Courcier 2014).
Even if copper artifacts are present at many of the Chalcolithic western Anatolian sites, no clear evidence has been found demonstrating whether metal artifacts were produced at regional metal manufacturing centres or were manufactured locally by itinerant craftsmen. In addition, at Gülpınar there is no archaeological evidence (such as ore, crucibles, smelting slag) suggesting the smelting of the metal from which the copper tools were formed. However, this data alone does not allow us to state with certainty that copper was not smelted on the site. There is archaeological evidence for a copper slag at the 5th millennium BC marble workshop site of Kulaksızlar in central western Anatolia (Takaoğlu in print, fig. 14b), which implies that certain sites of this period may have been places of copper smelting activities. On-site smelting of copper may not always be the case in western Anatolia. Considering similar chemical compositions of examined artifacts, it is possible to argue that already smelted copper was introduced to Gülpınar and was then heated and formed according to the desired shape.

Manufacturing Technique

As can be understood from the pores and copper oxide forms observed in the microstructure of the Gülpınar arsenical copper tools, the copper obtained by the smelting process was melted in suitable clay crucibles and cast into moulds. Furthermore, in the SEM examination of object 3's coded sample, it was found that the intermetallic residues with copper sulphide were concentrated in the wall and the iron oxide residues were concentrated in the centre of the object, which is interpreted as a situation related to the post-casting solidification stage. The main reason arsenic content promotes casting is that it prevents or reduces the number of casting pores in the metal due to its de-oxidant properties (Charles 1967, 21). In the microstructure of the Gülpınar tools, the number of voids and the copper oxide formations are not at a value critical enough to affect the forming process.
The final forms of the tools were obtained by applying forging, cold forging and annealing (holding at low temperatures) cycles on the initial forms coming from the moulds. The traces of this cycle were recognized from the twinned grain structures, which formed after deformation of the grains during cold forging and then recrystallization by annealing. Forming was carried out by repeating the forging and annealing process in the early native copper samples recovered from the Neolithic period at Çayönü (Stech 1990, 57). This pyrotechnological information was applied to arsenical copper obtained from sulphurous ore in Gülpınar, instead of native copper. In contrast to tin bronzes, the arsenical copper does not lose its workability after the repetition of forging and annealing processes (Charles 1967, 23). Therefore, arsenical copper is a very suitable material for forming a thin form such as a pin from a larger cast-blank form. On the outside of the samples, the edges formed by the hammer strokes and the flat surface (e.g. a stone anvil) on which the instrument was placed are clearly visible in the microscope photographs. The grains deformed during forging increasing the hardness of the material while also increasing the brittleness. Therefore, during the annealing, the intent was to allow the recrystallization of deformed grains through the application of heat. The necessity of annealing is well-defined by the cracks formed in the surface during forging in native or tinned copper.
The deformation and size reduction of the grains during cold forging are factors that increase the hardness of the object. Annealing allows the grains to recover and grow by recrystallization: the larger the grain size, the less the hardness. This effect is evident in the internal structures and micro-hardness measurements of objects 3 and 4. Coarser grain sizes in object 4 resulted in hardness readings close to almost pure, unworked

copper of about 50 HV. On the other hand, object 3's hardness values reach 122 HV. Since deformation has a hardening effect on grain forms after forging, annealing is not applied after forming to maintain the hardness of the tool. Alternatively, final cold forging may be applied at the desired hardness areas of the tool (Charles 1980, 161). In object 3, the increase in hardness, especially close to the surface, and the elongation observed in the grains indicate that the last cold forging was applied to this needle, or that intentionally there was no annealing applied after the last forming stage. A significant increase in hardness due to grain deformations in object 3 is directly related to the presence of arsenic. To achieve such hardness in pure copper, cold forging is required to reduce the grain size by 70 %, while 1 % arsenic reduced this rate by up to 35-40 % in the region near the surface (Lechtman 1996, 494-495).

CONCLUSION

The raw material used in the production of the Gülpınar copper objects is not native copper. This fact is supported by the amount of arsenic and lead in the chemical composition of the metal and the distribution of various non-metallic inclusions in the microstructure (Maddin / Wheeler / Muhly 1980; Wayman et al. 1985). The copper was obtained by heating and smelting sulphur-bearing polymetallic ore, which is a more complex metallurgical process than the smelting of oxide-containing ores. During heating and smelting the ore, much of the arsenic was lost and only 1 % of it remained in the metal. The low arsenic content has a limited effect on the colour and mechanical properties of copper (Yener 2000, 21). It is not possible to say that copper with 1 % or similar levels of arsenic is even an intentional alloy (Gale / Stos-Gale / Gilmore 1985, 154). The lack of evidence of either slag or crucibles for smelting in Gülpınar suggests that the metal of the tools might have been brought to the location as ingots or rod forms with rectangular cross-sections, where they might have been shaped by applying heating-forging-annealing cycles to obtain tools with the necessary mechanical properties. After the shaping process, one sample was left after annealing (4), while the hardness of another one (3) was further increased by a final cold-working process. The harder tool could have been used for piercing, while the other one could have been preferred for knitting.

The copper tools from the phase IIIa settlement at Gülpınar are enormously significant, since they are the earliest known arsenical copper specimens of north-western Anatolia and bear traces of smelting from polymetallic ores and mechanical treatments applied on smelted copper.

Acknowledgements

The sample preparation processes and archaeometric analyses of the Middle Chalcolithic Gülpınar copper artifacts were carried out at the ÇOBİLTUM Archaeometry Laboratory of Çanakkale Onsekiz Mart University, Turkey. Archaeometallurgical studies at the Max-Planck-Institut für Eisenforschung are supported by the Alexander von Humboldt-Stiftung. For his contribution to the interpretation of the results of the analysis, we would like to thank Prof. Ünsal Yalçın from Deutsches Bergbau-Museum, Archaeometallurgy Research section (Bochum). We are also grateful to the editor and the two anonymous reviewers for their feedback to improve this manuscript.

References

Boscher 2016: L. C. Boscher, Reconstructing the Arsenical Copper Production Process in Early Bronze Age Southwest Asia [PhD thesis Univ. College London 2016].

Charles 1967: J. Charles, Early Arsenical Bronzes – A Metallurgical View. American Journal of Archaeology 71, 1967, 21-26.

1980: J. Charles, The Coming of Copper and Copper-base Alloys and Iron: A Metallurgical Sequence. In: T. E. Wertime / J. Muhly (eds), The Coming Age of Iron (Yale 1980) 151-181.

Courcier 2014: A. Courcier, Ancient Metallurgy in the Caucasus from the Sixth to the Third Millennium BCE. In: B. W. Roberts /

C. P. Thornton (eds), Archaeometallurgy in Global Perspective: Methods and Syntheses (New York 2014) 579-664.

Craddock 2010: P. Craddock, Early Metal Mining and Production (London 2010).

Eaton/McKerrell 1976: E. R. Eaton/H. McKerrell, Near Eastern Alloying and Some Textual Evidence for the Early Use of Arsenical Copper. World Archaeology 8, 1976, 169-191.

Gabriel 2006: U. Gabriel, Ein Blick zurück – das fünfte Jahrtausend vor Christus in der Troas. In: M. Korfmann (ed.), Troia: Archäologie eines Siedlungshügels und seiner Landschaft (Mainz 2006) 355-360.

Gale/Stos-Gale/Gilmore 1985: N. Gale / Z. A. Stos-Gale / G. R. Gilmore, Alloy Types and Copper Sources of Anatolian Copper Alloy Artifacts. Anatolian Studies 35, 1985, 143-173.

Gambaschidze et al. 2010: I. Gambaschidze / G. Mindiaschwili / G. Gogotschuri / K. Kachiani / I. Dschaparidze, Die Arten von Metallartefakten und deren Verbreitung in Georgien. In: I. Gambaschidze / G. Mindiaschwili / G. Gogotschuri / K. Kachiani / I. Dschaparidze (eds), Alte Metallurgie und Bergbau in Georgien im 6.-3. Jt. v. Chr. (Tbilissi 2010) 146-229.

Garstang 1953: J. Garstang, Prehistoric Mersin Yümüktepe in Southern Turkey (Oxford 1953).

Grammenos 1997: D. Grammenos, Neolithiki Makedonia (Athens 1997).

Hellström 1987: P. Hellström, Paradeisos. A Late Neolithic Settlement in Aegean Thrace (Stockholm 1987).

Lechtman 1996: H. Lechtman, Arsenic Bronze: Dirty Copper or Chosen Alloy? A View from the Americas. Journal of Field Archaeology 23, 1996, 477-514.

Lechtman/Klein 1999: H. Lechtman / S. Klein, The Production of Copper-arsenic Alloys (Arsenic Bronze) by Cosmelting: Modern Experiment, Ancient Practice. Journal of Archaeological Science 26, 1999, 497-526.

Lehner/Yener 2014: J. W. Lehner / K. A. Yener, Organization and Specialization of Early Mining and Metal Technologies in Anatolia. In: B. W. Roberts / C. P. Thornton (eds), Archaeometallurgy in Global Perspective: Methods and Syntheses (New York 2014) 529-557.

Maddin/Wheeler/Muhly 1980: R. Maddin / T. S. Wheeler / J. D. Muhly, Distinguishing Artifacts Made of Native Copper. Journal of Archaeological Science 7, 1980, 211-225. DOI: 10.1016/S0305-4403(80)80025-2.

Maxwell et al. 2018: V. Maxwell / A. Sampson / N. Skaerpelis / R. M. Ellam, An Archaeological and Archaeometric Analysis of Early Metal Finds from Ftelia, Mykonos. In: A. Sampson / T. Tsouruni (eds), Ftelia on Mykonos: Neolithic Networks in the Southern Aegean Basin. Vol. II (Rhodes 2018) 153-186.

McGeehan-Liritzis 1996: V. McGeehan-Liritzis, The Role and Development of Metallurgy in the Late Neolithic and Early Bronze Age of Greece. Studies in Mediterranean Archaeology 12 (Jonsered 1996).

Özdemir 2017: A. Özdemir, The Architecture and Spatial Use of the Prehistoric Settlement at Gülpınar (Smintheion) [unpubl. PhD thesis Univ. Çanakkale 2017].

Özgünel 2003: C. Özgünel, Das Heiligtum des Apollon Smintheus und die Ilias. Studia Troica 13, 2003, 261-291.

Pernicka 2006: E. Pernicka, Metalle machen Epoche. Bronze und Eisen als Werkstoffe und Handelsware. In: M. Korfmann (ed.), Troia: Archäologie eines Siedlungshügels und seiner Landschaft (Mainz 2006) 349-352.

Pernicka et al. 2002: E. Pernicka / C. Eibner / Ö. Öztunalı / G. A. Wagner, Early Bronze Age Metallurgy in the North-east Aegean. In: G. A. Wagner / E. Pernicka / H. P. Uerpmann (eds), Troia and the Troad: Scientific Approaches (Berlin, Heidelberg, New York 2002) 143-172.

Renfrew/Slater 1986: C. Renfrew / E. A. Slater, Metal Artifacts and Metallurgy. In: C. Renfrew / M. Gimbutas / E. S. Elster (eds), Excavations at Sitagroi. A Prehistoric Village in Northeast Greece. Vol. II (Los Angeles 1986) 301-322.

2003: C. Renfrew / E. A. Slater, Metal Artifacts and Metallurgy. In: E. S. Elster / C. Renfrew (eds), Prehistoric Sitagroi: Excavations in Northeast Greece, 1968-1970. 2: The Final Report (Los Angeles 2003) 301-320.

Ryan 1960: C. W. Ryan, A Guide to the Known Minerals of Turkey (Ankara 1960).

Schoop 1995: U. Schoop, Die Geburt des Hephaistos: Technologie und Kulturgeschichte neolithischer Metallverwendung im Vorderen Orient (Espelkamp 1995).

Seferiades 1992: M. Seferiades, Le metal. In: R. Treuil (ed.), Dikili Tash: village préhistorique de Macédoine orientale. I: Fouilles de Jean Deshayes (1961-1975). Bulletin de correspondance hellénique suppl. 24 (Athènes 1992) 113-119.

Stech 1990: T. Stech, Neolithic Copper Metallurgy in Southwest Asia. Archaeomaterials 4, 1990, 55-61.

Takaoğlu in print: T. Takaoğlu, Kulaksızlar Revisited: Excavations towards the Context of a Marble Workshop. In: S. Steadman / G. McMahon (eds), The Archaeology of Anatolia. Recent Discoveries (2019-2020). Vol. IV (Cambridge in print).

Takaoğlu/Özdemir 2018: T. Takaoğlu / A. Özdemir, The Middle Chalcolithic Period in the Troad: A New Look from Gülpınar. In: S. Dietz / F. Mavridis / Z. Tankosic / T. Takaoğlu (eds), Communities in Transition: The Circum-Aegean Later Neolithic Stage (ca. 5000/4800-3200/3000 BC) (Oxford 2018) 479-490.

Thornton/Lamberg-Karlovsky 2004: C. P. Thornton / C. C. Lamberg-Karlovsky, A New Look at the Prehistoric Metallurgy of Southeastern Iran. Iran 42, 2004, 47. DOI: 10.2307/4300662.

Thornton et al. 2002: C. P. Thornton / C. C. Lamberg-Karlovsky / M. Liezers / S. M. M. Young, On Pins and Needles: Tracing the Evolution of Copper-base Alloying at Tepe Yahya, Iran, via ICP-MS Analysis of Common-place Items. Journal of Archaeological Science 29, 2002, 1451-1460.

Tuncel/Şahoğlu 2018: R. Tuncel / V. Şahoğlu, The Chalcolithic of Coastal Western Anatolia: A View from Liman Tepe, İzmir. In: S. Dietz / F. Mavridis / Z. Tankosic / T. Takaoğlu (eds), Communities in Transition: The Circum-Aegean Later Neolithic Stage (ca. 5000/4800-3200/3000 BC) (Oxford 2018) 513-529.

Yalçın 2000: Ü. Yalçın, Frühchalkolithische Metallfunde von Mersin-Yumuktepe: Beginn der extraktiven Metallurgie? Turkish Academy of Sciences Journal of Archaeology 3, 2000, 109-128.

2008: Ü. Yalçın, Ancient Metallurgy in Anatolia. In: Ü. Yalçın / H. Özbal / A. G. Paşamehmetoğlu (eds), International Conference AMITEM – Ancient Mining in Turkey and the Eastern Mediterranean (Ankara 2008) 15-40.

Yener 2000: K. A. Yener, Domestication of Metals: The Rise of Complex Metal Industries in Anatolia (Leiden 2000).

Wayman et al. 1985: M. L. Wayman / R. R. Smith / C. G. Hickey / M. J. M. Duke, The Analysis of Copper Artifacts of the Copper Inuit. Journal of Archaeological Science 12/5, 1985, 367-375. DOI: 10.1016/0305-4403(85)90065-2.

Wertime 1973: T. A. Wertime, The Beginnings of Metallurgy. Science N. S. 182/4115, 1973, 875-887. DOI: 10.1126/science.182.4115.875.

Zachos 2007: C. Zachos, The Neolithic Background: A Reassessment. In: P. M. Day / R. C. P. Doonan (eds), Metallurgy in the Early Bronze Age (Sheffield 2007) 169-206.

Zusammenfassung / Summary / Résumé

Mittelchalkolithische Kupferwerkzeuge aus Gülpınar in Nordwestanatolien – ein archäometrischer Ansatz

Die prähistorische Fundstelle von Gülpınar, die unter den Überresten des griechisch-römischen Heiligtums des Apollon Smintheus (Smintheion) in der Küstenregion der Troas liegt, ist eine jener neu ausgegrabenen Stätten, die unser Wissen über die westanatolische Küstenregion und die angrenzenden ostägäischen Inseln im 5. Jahrtausend v. Chr. erweitern. Ein Beitrag der archäologischen Ausgrabungen an der Fundstelle stammt aus dem Bereich der Kupfermetallurgie, die im Mittelpunkt dieser Studie steht. Vier Kupferwerkzeuge (Ahlen und Nadeln), die zwischen 4930 und 4455/4300 v. Chr. datiert werden, kamen in Phase III von Gülpınar zutage. Sowohl die chemische Zusammensetzung als auch die mikrostrukturellen Merkmale dieser Werkzeuge wurden untersucht, um die metallurgischen Prozesse ihrer Herstellung und Ausformung zu verstehen. Analytische Techniken, tragbare Röntgenfluoreszenzanalyse (P-RFA), Metallographie (optische Mikroskopie), energiedispersive Röntgenspektroskopie (SEM-EDS)-Untersuchung und Mikrohärteprüfung wurden an den verfügbaren Proben der Objekte durchgeführt. Die Ergebnisse der archäometrischen Analysen zeigen, dass das zur Herstellung dieser Werkzeuge verwendete Kupfer durch Erhitzen und anschließendes Schmelzen der schwefelhaltigen polymetallischen Erze gewonnen wurde. In den chemischen Zusammensetzungen wurde ein Arsengehalt von ca. 1 % nachgewiesen. Obwohl der Arsengehalt die physikalischen Eigenschaften der Werkzeuge leicht verbesserte, wurde die Menge als zu niedrig angesehen, um einen intentionellen und kontrollierten Prozess für die Arsenlegierung nachzuweisen. Das Metall für die Werkzeuge könnte in halbfertiger Form nach Gülpınar gebracht worden sein, da bei den Ausgrabungen keine auf Kupfermetallurgie hindeutenden Funde (Schlacke, Tiegel oder Düsen) angetroffen wurden. Die Objekte wurden durch Zyklen von Erhitzen, Schmieden und Glühen geformt. Darüber hinaus wurde festgestellt, dass die Härte der Werkzeuge durch einen abschließenden Kaltbearbeitungsprozess gesteigert wurde.

Middle Chalcolithic Copper Tools from Gülpınar in North-Western Anatolia – an Archaeometric Approach

The prehistoric site of Gülpınar, located beneath the remains of the Graeco-Roman Sanctuary of Apollo Smintheus (Smintheion) in the coastal Troad, is one of those newly excavated sites that enhances our knowledge of the western Anatolian littoral and the adjacent eastern Aegean islands during the 5th millennium BC. One of the contributions of the archaeological excavations at the site is in the category of copper metallurgy, which is the point of focus of this study. Four copper tools (awls and pins) were revealed in phase III of Gülpınar, dated to between 4930 and 4455/4300 BC. Both the chemical composition and the microstructural features of these tools were examined to understand the metallurgical processes applied for their production and forming. Analytical techniques, portable X-ray fluorescence (p-XRF) analysis, metallography (optical microscopy), energy-dispersive X-ray spectroscopy (SEM-EDS) examination and microhardness testing were conducted on the available samples from the objects. The results of the archaeometric analyses demonstrated that the copper used to form these tools was obtained by heating and then smelting the sulphur-bearing polymetallic ores. In the chemical compositions, an amount of around 1 % arsenic was detected. Although the arsenic content provided a moderate improvement in the physical properties of the tools, the amount was considered too low to demonstrate an intentional, controlled process for arsenic alloying. The metal of the tools may have been brought in semi-finished forms to Gülpınar, since no finds relating to the copper metallurgy (slag, crucibles, tuyeres) were encountered during the excavations. The forming was determined by applying cycles of heating, forging and annealing. Moreover, increasing the hardness of the tools by a final cold working process was also detected.

Objets en cuivre du Chalcolithique moyen de Gülpınar dans le Nord-Ouest de l'Anatolie – une approche archéométrique

Le site préhistorique de Gülpınar, situé à proximité des vestiges du sanctuaire gréco-romain d'Apollon Smintheus (Smintheion) dans la zone côtière de la Troade, est l'un des sites fouillés récemment qui élargit nos connaissances du littoral anatolien occidental et des îles voisines de l'Égée orientale du 5e millénaire av. J.-C. Les fouilles de ce site apportent une contribution toute particulière dans le domaine de la métallurgie du cuivre qui retiendra notre attention dans cette étude. Quatre artefacts en cuivre (alênes et épingles) furent identifiés à la phase III de Gülpınar, datés entre 4930 et 4455/4300 av. J.-C. On a examiné la composition chimique et les caractéristiques microstructurelles de ces objets afin de comprendre les processus métallurgiques utilisés pour la production et le façonnage. Les échantillons prélevés sur ces objets furent soumis à des techniques analytiques, une analyse par détecteur portable de fluorescence X, une métallographie (MO), un examen par spectrométrie de rayons X à dispersion d'énergie (SEM-EDS) et des tests de microdureté. Les résultats des analyses archéométriques ont révélé que le cuivre utilisé pour ces objets a été obtenu en chauffant, puis en fondant les minerais polymétalliques contenant du souffre. Une quantité d'environ 1 % d'arsenic a été détectée. Certes, cette teneur d'arsenic procurait une légère amélioration des propriétés physiques des objets, mais elle restait tout de même trop faible pour prouver un processus d'alliage à l'arsenic contrôlé intentionnellement. Le métal de ces objets est peut-être arrivé à Gülpınar sous forme de demi-produits, car l'on a trouvé aucun élément lié à la métallurgie du cuivre (scories, creuset, tuyère) durant les fouilles. Le façonnage était obtenu en ayant recours à des cycles de chauffe-forgeage-recuit. On a en outre constaté un processus final de travail à froid pour augmenter la dureté des objets.

Traduction: Y. Gautier

Schlüsselwörter / Keywords / Mots clés

Nordwestanatolien / Gülpınar / 5. Jahrtausend v. Chr. / Kupferwerkzeuge / Archäometrie
North-Western Anatolia / Gülpınar / 5th millennium BC / copper tools / archaeometry
Nord-Ouest de l'Anatolie / Gülpınar / 5e millénaire av. J.-C. / objets en cuivre / archéométrie

Ümit Güder
Max-Planck-Institut für Eisenforschung
Max-Planck-Str. 1
D - 40237 Düsseldorf
u.guder@mpie.de

Turan Takaoğlu
Çanakkale Onsekiz Mart Üniversitesi
Department of Archaeology
Terzioğlu Kampüsü
TR - 17020 Çanakkale
takaoglu@comu.edu.tr

Abdulkadir Özdemir
Fırat Üniversitesi
Department of Archaeology
TR - 23119 Elazığ
akadir23@gmail.com