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ELEMENTAL ANALYSIS OF PRE-POTTERY NEOLITHIC B COPPER FINDS FROM GRE FILLA

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ABSTRACT

Twenty-eight copper-based artefacts, including unworked lumps, ornaments, and tools, recovered from Pre-Pottery Neolithic B layers of Gre Fılla, located in the southeast of Anatolia, were analysed by hand-held, portable X-ray fluorescence spectrometer to understand the feasibility of instrument in identifying the type of copper minerals available at the settlement. The bulk analysis of eight lumps was further performed by inductively coupled plasma atomic emission spectroscopy and inductively coupled mass spectrometry. The results revealed important differences between the two approaches. According to the elemental composition obtained by bulk analysis, the lumps appeared to be malachite. The presence of lumps suggests that manufacturing of the objects was achieved at the site. The chisel axes, one with a bone handle, present the earliest examples of metal axes, although they reflect lithic manufacturing technology in contrast to postdated axes. A comparison with the contemporary settlement at Çayönü, Aşıklı, and Tel Halula reflects the model of copper metallurgy in the region at the beginning of pyrotechnology.

KEYWORDS: Gre Fılla, ICP-MS, PPNB, malachite, copper metallurgy, Turkey, Anatolia, Upper Tigris Region.

1. INTRODUCTION

The emergence of copper-based metallurgy in Anatolia during the Neolithic Period has been extensively studied through archaeological studies and archaeometric analysis in the last decades. We know that the earliest evidence of using copper from Anatolia dates to around the late ninth millennium (Yalçın 2008; Nordqvist et al. 2012). It is not surprising that Neolithic settlements in Anatolia, where copper resources were relatively abundant, present the earliest metallurgical activities, although the proximity to sources does not ensure technological development (Yener 2000; Muhly 2011).

Chemical analysis, in conjunction with microanalysis, can reveal information on the production and provenance of copper-based objects. The technology for producing copper through annealing or smelting can be best observed by metallography, exposing the microstructure of artefacts. However, because of the rarity of earlier metal finds and local regulations, it is not always possible to analyse metal artefacts using Scanning Electron Microscope- Energy Dispersive X-Ray (SEM-EDX).

Since the 60s, various scholars have discussed the problems of archaeometallurgy on the reconstruction of ancient metallurgical activities. Hauptmann (2000) described the metallurgical chain from ore to metal, including mining, smelting, trade, and use. Different factors controlled each step of manufacturing, and chemical analysis aims to detect the elemental fractionations associated with these factors. The consumption of copper, the possible source, and technological procedures applied during the manufacturing were dependent and associated with the regional organization and technological innovations (Bourgarit and Mille 2003). Obsidian characterization studies have suggested the modelled pathways for obsidian supply to the settlements (Chataigner, Barge and Hansen 2010; Barge et al. 2018; Frahm and Tryon 2018; Abedi et al. 2018; Orange et al. 2021) and models of exchange systems in Anatolia and the Near East (Carter et al. 2015; Ibanez et al. 2016; Campbell and Healey, 2018). Likewise, understanding the chemical properties of the metal finds and technological aspects of production will eventually lead us to identify the social and economic dynamics within the settlement and the settlement's role between the trade routes and cultural interaction in the area.

The beginning of pyrotechnology (Period II) in the development stages of metallurgy suggested by Yalçın (2008) can be described as applying annealing to the metal in the form of malachite or native copper. Studies on the copper objects found at Aşıklı Höyük (Esin 1995; 1999), Çayönü (Maddin et al. 1999; Özdoğan and Özdoğan 1999), Çatalhöyük (Birch et al. 2013), and Tell Halula (Molist et al. 2009) indicated that native copper was heated up to a few hundred degrees Celsius, and then shaped by hammering at this stage (Yalçın 2000; 2017, Radivojević et al. 2010). The cold hammering and annealing of copper minerals are considered as the processes similar to the heat treatment of lithic objects, therefore this phase is also described as an experimentation stage prior to the metallurgical activities (Siklósi et al. 2012, 57; Radivojević et al. 2010, 276; Lehner and Yener 2014, 538).

Native copper could be best identified by its distinctive metallographic structure (Wayman and Duke 1999; Craddock 2000; Wayman 2004). When such analysis is impossible to perform, native copper can be characterized by its high purity and easy to detect by chemical analysis. However, copper's smelting process from malachite or other copper ores produces copper metal as pure as native copper (Maddin et al. 1980, Kuleff and Pernicka 1995; Pernicka 1999, Pernicka 2014). It was also suggested that "ancient low-volume smelting of highly enriched copper ores that may also contain low concentrations of impurities" (Kuleff and Pernicka 1995). Consequently, it could be challenging to distinguish native copper from metal smelted from copper ores by elemental analysis. Pernicka (1999) suggested that some trace elements could be used as provenance indicators, while those affected by copper-alloys and technological processing are useful for interpreting technology such as smelting. He pointed out that trace elements including Fe, Sn, Zn, Mg, Nb, Ti, and Zr reflect the efficiency of smelting and Au, Ag, Ni, Os, Pd, Pt, Rh, Ru may act as indicators of provenance (Pernicka 2014). The earliest cast copper objects produced by controlled heat treatment - smelting- in Anatolia were known at Yumuktepe in the early 5th millennium BC (Yalçın 2000). Following the above stated explanations by Pernicka, the elevated Sn, Ni, Sb, Fe, As, and Ag contents compared to main values of Anatolian copper indicated the smelting technology for Yumuktepe artefacts.

Trace element analysis by various techniques, including Atomic Absorption Spectrometry (AAS), Neutron Activation Analysis (NAA), Inductively Coupled Mass Spectrometry (ICP-MS), and LA-ICP-MS (Laser ablation Inductively Coupled Mass Spectrometry) can reveal information on ancient metallurgy and the provenance, based on chemical compositions. The popularity of portable X-ray Fluorescence (pXRF) has increased in archaeometallurgical studies in recent years, mainly because it provides non-destructive *in-situ* analysis for various archaeological and historical periods (Liritzis et al. 2020; Kousouni et al., 2021; Helmi et al., 2019). The main limitations of the technique are the lower sensitivity for some elements that could be helpful as provenance indicators, and because pXRF measures the surface of artefacts, the elemental distribution on the surface, which may differ from that of bulk composition, or layers of surface corrosion may give misleading results (Lutz and Pernicka 1996; Martinón-Torres et al. 2014; Dussubieux and Walder 2015). Although the accuracy and the precision of the measurements can be improved using certified reference materials or secondary standards (Ferguson 2013) and surface treatment to remove corrosion, it is important to understand how surface analysis contribute to the identification of the copper minerals used in the production of archaeological objects. Therefore, the question for this study is, what we can detect with pXRF analysis for copper-based objects dated to the Neolithic period recovered from Gre Fılla:

- Surface analysis: Identification of cold/warm hammered native copper or smelting based on element composition. Maybe not suitable for precise comparison for sourcing, but pXRF could be considered as a tool to simply differentiation between native copper and smelted copper artefacts.
- The corrosion layer on the surface: Due to the size of copper artefacts, the chemical properties of copper and the burial conditions of the archaeological settlement, the thickness and the distribution of oxidized material could vary. The element composition of the corrosion layer is usually depleted in copper and could be enriched in some trace elements when compared to core metal (Dussubieux et al. 2008; Fernandez et al. 2013; Orfanou and Rehren 2015; Dussubieux and Walder 2015). Similar burial environments have similar effects on copper artefacts leading to similar corrosion mechanisms (Oudbashi 2018; Li et al. 2019). Therefore, element variability on the surface is a quantitative problem, although the corrosion products still carry archaeological information.

In this study, the elemental compositions of 28 copper-based artefacts are presented, including lumps, ornaments, and tools found at Gre Fılla. The objects recovered from levels dated to PPNB are among the earliest metal finds in Anatolia and the Near East. Because of the location of the settlement, approximately 90 km to the east of Çayönü, the Neolithic site yielded the earliest metal objects and lumps in the form of malachite and native copper, Gre Fılla metal finds are of particular significance. Identifying copper minerals and potential pyrometallurgical activities could improve our knowledge relating to the stages applied during the manufacturing of the copper from raw material to the final object during the PPNB phase for this region. Archaeological evidence and contextual information contributing to the analysis provide a more holistic understanding of the results. The study also evaluates the applicability of pXRF to the non-destructive surface analysis of copper-based finds and the impacts of corrosion layers.

2. MATERIAL AND METHODS

2.1. *Archaeological Site and Metal Finds*

Gre Fılla, located in the Kocaköy district of Diyarbakır, has been excavated under the direction of A. Tuba Ökse and Diyarbakır Archaeological Museum as part of the archaeological salvage project of the sites to be affected by the Ambar Dam, including Ambar Höyük and Kendale Hecala since 2018. The mound is over 10 m high and about 0.5 ha in extent. Excavations have revealed a settlement occupied from the Pre-Pottery Neolithic (PPN) to Pottery Neolithic (PN). The PN levels were destroyed by a Late Antique and Medieval Cemetery (Ökse 2021). The cultural sequence classified for Gre Fılla is given in Table 1. Archaeological studies revealed the superimposed rectangular or cell plan buildings and oval structures in the mound's northern slope (Fig. 1). Calibrated 14C dates for an oval subterranean structure (Building 8) and two rectangular buildings (Building 5 and 2) suggest they had been contemporarily used during the PPNB (Table 2).

Table 1. Occupation periods of Gre Fılla

Gre Fılla Periods	Archaeological Periods
GF I	Late Antique-Medieval Cemetery
GF II	Medieval Levels
GF III	Destroyed Pottery Neolithic Levels
GF IV	Pre-Pottery Neolithic B Levels
GF V	Pre-Pottery Neolithic A Levels

Figure 1. Arial photograph of the northern operation of Gre Fılla (excavation archive, 2020).

The metal artefacts, including unworked lumps, ornaments, and tools, were found during the 2020 excavation season (Table 2). Copper-based lumps with a total weight of 139.48 gr were more frequently discovered in the rubble deposits (N8/064/M) of Structure 8, along with animal bones, obsidian, and flint tools (Fig 2). The archaeological data indicates that the structure could have been buried with rubble, "sealed," and finally abandoned after being re-used for a long time period between 8349-7599 cal. BC.

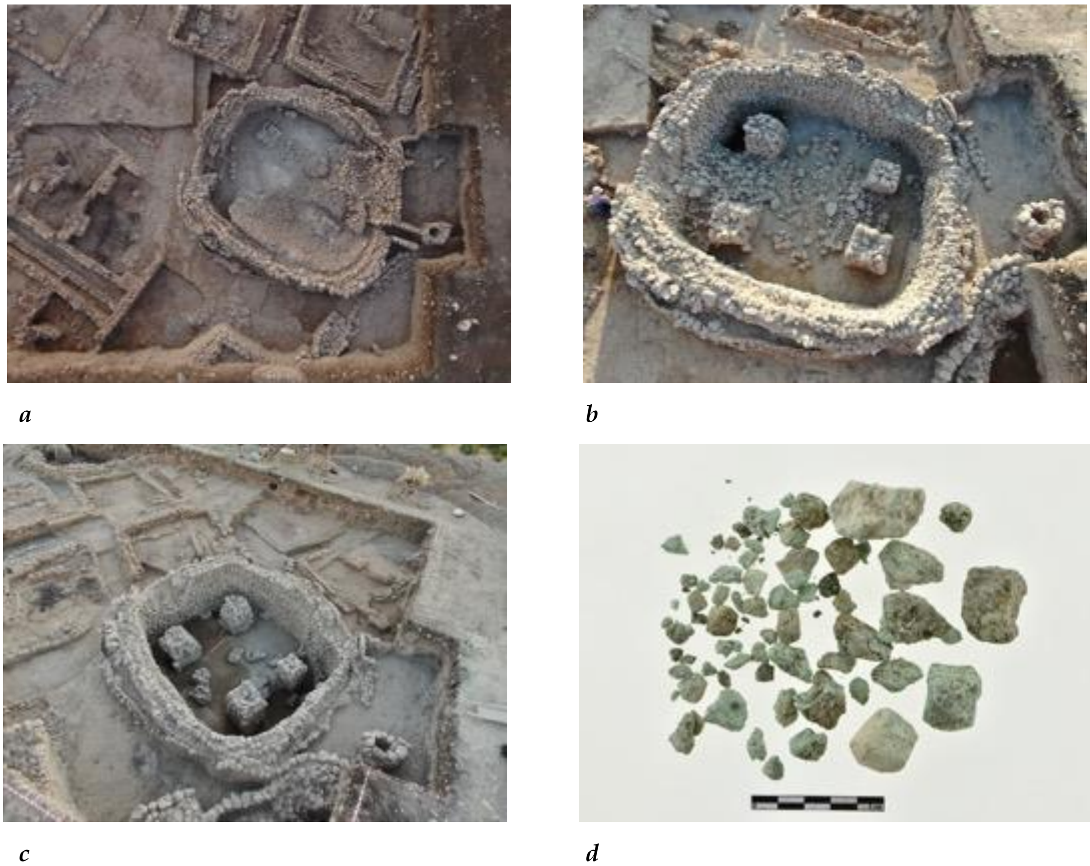

Fig 2. Different layers of the filling debris of Structure 8 (N8/064/M) where the lumps were recovered (a-c) Lump samples found in the filling debris (d) (excavation archive).

Table 2. Contextual information for the analysed finds from Gre Fılla, sorted by contextual unit.

Sample Nr.	Period	Trench	Building - Level	Context	Description	Calibrated Dates (BC)
GRE-C001	GF IV	N8	Oval Structure 8, Level 3	O8/064/M	Small irregularly shaped	
GRE-C002	GF IV	N8	Oval Structure 8, Level 3	O8/064/M	Small irregularly shaped	
GRE-C003	GF IV	N8	Oval Structure 8, Level 3	O8/064/M	Small irregularly shaped	
GRE-C004	GF IV	N8	Oval Structure 8, Level 3	O8/064/M	Small irregularly shaped	
GRE-C005	GF IV	N8	Oval Structure 8, Level 3	O8/064/M	Small irregularly shaped	
GRE-C006	GF IV	N8	Oval Structure 8, Level 3	O8/064/M	Small irregularly shaped	
GRE-C007	GF IV	N8	Oval Structure 8, Level 3	O8/064/M	Small irregularly shaped	
GRE-C008	GF IV	N8	Oval Structure 8, Level 3	O8/064/M	Small irregularly shaped	
GRE-C009	GF IV	N8	Oval Structure 8, Level 3	O8/064/M	Small irregularly shaped	8349-8242
GRE-C010	GF IV	N8	Oval Structure 8, Level 3	O8/064/M	Small irregularly shaped	
GRE-C011	GF IV	N8	Oval Structure 8, Level 3	O8/064/M	Small irregularly shaped	
GRE-C012	GF IV	N8	Oval Structure 8, Level 3	O8/064/M	Small irregularly shaped	
GRE-C013	GF IV	N8	Oval Structure 8, Level 3	O8/064/M	Small irregularly shaped	
GRE-C014	GF IV	N8	Oval Structure 8, Level 3	O8/064/M	Small irregularly shaped	
GRE-C015	GF IV	N8	Oval Structure 8, Level 3	O8/064/M	Small irregularly shaped	
GRE-C016	GF IV	N8	Oval Structure 8, Level 3	O8/064/M	Small irregularly shaped	

GRE-C018	GF IV	O8	Rectangular Building 2, Level 8	N8/115/M	Chisel-Axe	7586-7502
GRE-C019	GF IV	O8	Rectangular Building 2, Level 8	N8/115/M	Chisel-Axe	
GRE-C020	GF IV	O8	Rectangular Building 13, Level 2	O8/153/M (exterior)	Pendant	
GRE-C021	GF IV	O8	Rectangular Building 13, Level 2	O8/174/M	Folded sheet	
GRE-C023	GF IV	O8	Rectangular Building 2, Level 8	N8/115/M	Small irregularly shaped	
GRE-C024	GF IV	O8	Rectangular Building 14, Level 2	O8/176/M	Small irregularly shaped	
GRE-C025	GF IV	P9	Rectangular Building 5, Level 1	P9/042/M (exterior)	Chisel-Axe	8296-8197
GRE-C026	GF IV	P9	Rectangular Building 5, Level 1	P9/042/M (exterior)	Fishhook	
GRE-C027	GF IV	N9		Cultural Fill	Ear-labret	
GRE-C028	GF V?	P8		Burial P8/607/G	Bead	

The rectangular Building 2, Level 8, Room O8/115/M revealed two copper chisel-axes, one of which was hafted into a well-preserved bone handle (Fig. 3). The chisel-axes were uncovered along with flat stone axes; one was fixed into a similar bone handle as the copper axe (Fig. 4). The fishhook and the third chisel-axe were found in an area by the rectangular Building 5, Level 1, Room P9/042/M (Fig. 5).

Two more unworked lumps were recovered from Building 2, Level 8, Room O8/119/M and Building 14, Level 2, Room O8/176/M. An oval-shaped pendant and an ear-labret were uncovered from Building 13, Level 1, Room O8/153/M and cultural fill respectively (Fig. 6). The folded sheet copper-based artefact was found in the rectangular Building 13, Level 2, Room O8/174/M (Fig. 7). Underneath the PPNB levels in Trench P8, in burial P8/607/G dug into the lowest debris on the virgin soil, dating to PPNA (GF Period V), a copper bead has been found (Fig. 8). In general, the metal artefacts from Gre Fılla could be classified as unworked raw material, tools, and ornaments. Although they have been found in well-defined contexts, so far, the spatial distribution of metal finds does not reveal a clear relationship between the structures relevant to metal manufacturing or usage. Whereas the number of untreated lumps along with the lithic material and bones suggest, the function of the Oval Structure 8, Chamber N8/064/M was distinctive, in comparison with rectangular planned buildings.

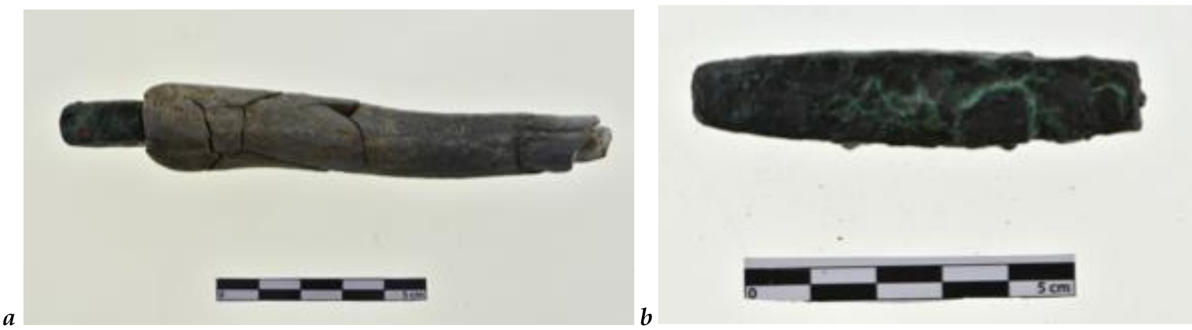

Figure 3. Chisel-axes from Building 2, Room O8/115/M a) GRE-C018 and b) GRE-C019 (excavation archive).

Figure 4. The archaeological context of GRE-C018 and GRE-C019 (excavation archive).

Figure 5. The fishhook and the chisel-axe recovered from the northern side of Building 5, Room P9/042/M (excavation archive).

Figure 6. The oval-shaped pendant and the ear-labret from Rectangular Building 13and Cultural Fill, respectively (excavation archive).

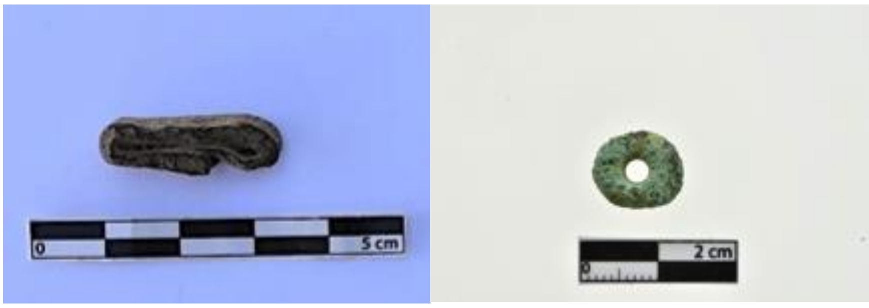

Figure 7. The folded sheet artefact and the bead recovered from Burial P8/607/G (excavation archive).

Figure 8. Burial P8/607/G, placed in hocker position (excavation archive).

2.2. *Analytical Methods*

Elemental analysis of the metal samples was conducted with a handheld EDXRF; The Olympus Innov-X Delta model analyzer. The apparatus was equipped with a silicon-drift detector (SDD) and an excitation source of X-ray tube Ta target.

Although pXRF is a non-destructive analysis and requires little sample preparation, in the case of copper-based artefacts, many researchers suggest elemental analysis should be applied on cleaned surfaces because of the corrosion layer (Lutz and Pernicka 1996; Martinón-Torres et al. 2012; Charalambous et al. 2014; Radivojevic et al. 2019). However, such cleaning is not always appropriate if the finds are too small or display any decoration or paint. Moreover, the corrosion layer may contribute to metalwork wear analysis (Dolfini and Crellin 2016). Other papers discussed the feasibility of using pXRF without any sample preparation and its ability to distinguish native copper (Dussubieux 2008; Martinón-Torres et al. 2014; Fernandez et al. 2013; Orfanou and Rehren 2015; Dussubieux and Walder 2015). Therefore, even though the unprepared surface measurements indicate the results cannot be considered fully quantitative and cannot be compared to the other bulk analysis results, we decided to use pXRF measurement on the surface mechanically cleaned to investigate the feasibility of the measurements in order to determine nature of the raw material, i.e., native copper or malachite.

The instrument was adjusted to alloy plus mode and was set to 8, 13, and 40 kV for 35 s after testing for 60 s, 120 s, 180 s, and 300 s. The measurements were performed on the flattest spots to ensure the direct contact of the instrument probe with the sample to minimize air space. To prevent effects of soil contamination of copper objects, a silicon filter was used during analysis. The data was calculated using fundamental parameters included in the instrument's software. The precision and accuracy of the method involved analysing a certified reference materials CDA 314/UNS C31400 (Table 3).

Table 3. The results for CDA 314/UNS C31400 obtained in this study (n.d. not detected, n.a. not available).

Constituent	mean values		
	Certified Values*	Found* (pXRF)	Found (ICP-OES and ICP-MS)
Ag	0.002	n.d.	15.7±0.4 †
Sb	0.006±0.002	n.d.	41±1 †
As	0.003	n.d.	n.d.
Cu	90.08±0.06	90.11	89*
Fe	0.007±0.001	n.d.	n.d.
Ni	0.004 ±0.002	0.019	21±1 †
Pb	1.99±0.06	1.7	2.2±0.1*
Si	0.002	0.01	n.a.
Sn	0.029±0.005	n.d.	226±5 †
Zn	7.81±0.05	7.89	7.9±0.2*

* w/w %, † mg/kg

ICP-MS analyses were carried out by Perkin Elmer SCIEX ELAN DRC II for the trace elements, As, Pb, Sb, Sn, Zn, Ag, Au, Bi, Ni, P, Cr, Co. Additionally, major element contents were determined by means of Perkin Elmer Optima 4300DVmodel ICP-OES at METU Central Laboratory. The powdered samples were taken by a diamond drill from the cores of the unworked lumps, which had appropriate dimensions. The drillings obtained from the patina were discarded during the sampling to prevent possible contamination. 10 mg of drillings were weighed, and 5 ml of hydrochloric acid (HCl) and nitric acid (HNO_3) mixture were added to the samples. This mixture was placed in a PTFE vessel and digested by microwave heating. The efficiency of the digestion procedure and accuracy were checked by the certified reference material, powdered CDA 314/UNS C31400. Some authors also mentioned the effect of hydrochloric acid (HCl) and nitric acid (HNO_3) mixture on the precipitation of silver chloride from aqueous solutions (Mille and Bourgarit 2000). However, the concentrations of elements in CRM measured by ICP-MS were in agreement with the certified values (Table 3).

3. RESULTS AND DISCUSSION

The surface elemental composition of the metal artefacts from Gre Fılla indicates the high purity copper having Fe, Si, and P as the major impurities (Table 4). Although the trace elements including Hg, Sb, As, Ag, Zn, Pb, Ni, Co were measured, they were found to be below the instrument's detection limit. The average copper concentration for the unworked lumps was 96.4 (wt. %), with a standard deviation of 3.09. The lower copper contents of two lumps (GRE-C001 and GRE-C010) were observed by pXRF analysis. On the other hand, the mean of the copper for the chisel axes and the other objects was 97.8 (wt. %), and the standard deviation 2.03. Iron concentration of the unworked artefacts varied significantly from 0.32 to 9.36 (wt. %). Likewise, iron was present in variable concentration, between 0.12 and 4.73 (wt. %) for the objects.

Table 4. Elemental compositions of Gre Fılla metal artefacts by pXRF (w/w %).

Sample	Cu	Fe	Si	P	Type
GRE-C001	87.8	9.36	0.91	1.12	Lump
GRE-C002	98.2	1.19	0.28	0.32	
GRE-C003	97.3	1.52	0.37	0.72	
GRE-C004	94.9	4.24	0.44	0.36	
GRE-C005	97.6	1.48	0.33	0.55	
GRE-C006	99.2	0.32	0.22	0.29	
GRE-C007	98.6	0.48	0.50	0.44	
GRE-C008	97.0	2.29	0.21	0.42	
GRE-C009	97.4	1.85	0.28	0.50	
GRE-C010	88.9	8.47	0.91	1.68	
GRE-C011	99.1	0.49	0.21	0.25	
GRE-C012	96.4	2.09	0.41	0.54	
GRE-C013	97.5	1.74	0.44	0.34	
GRE-C014	96.7	2.56	0.38	0.38	
GRE-C015	96.9	0.88	0.23	0.29	
GRE-C016	96.54	2.71	0.27	0.36	
GRE-C023	95.9	0.86	0.16	0.27	
GRE-C024	98.5	0.87	0.22	0.30	
GRE-C018	99.1	0.12	0.51	0.31	Chisel-axe
GRE-C019	98.6	0.66	0.34	0.41	
GRE-C025	93.5	4.73	0.56	0.74	
GRE-C020	98.5	0.67	0.28	0.52	Pendant
GRE-C026	99.2	0.84	0.46	0.34	Fishhook
GRE-C027	99.3	0.19	0.21	0.28	Ear-labret
GRE-C028	95.9	3.02	0.39	0.38	Bead
GRE-C021	98.4	0.84	0.27	0.32	Folded sheet

The concentration of elements silicon and phosphorous were determined to understand the effect of soil contamination during the burial. The computation of Pearson's correlation coefficients between Cu, Fe, Si, and P identified a positive correlation between Fe and Si (Table 5). An inverse correlation between Cu and Fe was also present. Although the discrepancies detected in the concentration of iron in the lump samples could depend on the different behaviour of the original copper material during corrosion, surface porosity or material heterogeneity (Orfanou and Rehren, 2015); the significant positive correlation between Si and Fe suggest the effect of environmental contamination consisting of iron-bearing clay minerals on the surface of the sample.

Table 5. Pairwise Pearson Correlations for the data obtained from metal finds.

Sample 1	Sample 2	N	Correlation	95% CI for ρ	P-Value
Fe	Cu	26	-0.974	(-0.989; -0.943)	<0.001
Si	Cu	26	-0.796	(-0.904; -0.590)	<0.001
P	Cu	26	-0.836	(-0.924; -0.664)	<0.001
Si	Fe	26	0.828	(0.649; 0.920)	<0.001
P	Fe	26	0.837	(0.666; 0.925)	<0.001
P	Si	26	0.829	(0.650; 0.921)	<0.001

Principal component analysis (PCA) was applied on the data set of twenty-six artefacts and four variables using a correlation matrix with no rotation axis. The first two principal components explain around 95% of the cumulative variance. We observe a large positive loading for Si, P, and Fe in the PC1 in Fig. 9. Therefore, especially GRE-C001 and GRE-C010 are distinguished from the remaining by the higher Fe contents. PCA confirms that Fe variation is mostly due to the corrosion that occurred on the samples.

Table 6. The element compositions of lump samples measured by ICP-OES (Cu and Fe) and ICP-MS (trace elements) and LOD are presented. Results in *wt %, otherwise mg/kg (n.d. not detected, n.a. not available).

Sample	Cu*	Fe*	Zn*	Cr	Co	Ni	As	Ag	Sn	Sb	Pb
GRE-C001	54	0.40±0.01	0.24±0.01	24±2	12.3±0.5	21±1	n.d.	n.d.	226±5	1.56±0.04	32±1
GRE-C002	55	0.36±0.01	0.30±0.01	22±2	48±1	16±1	n.d.	1.9±0.1	0.59±0.05	n.d.	69±2
GRE-C003	38	0.63±0.01	0.17±0.01	47±3	6.4±0.6	47±4	n.d.	34±1	n.d.	n.d.	13.9±0.6
GRE-C004	49	1.89±0.01	0.26±0.01	110±3	17±1	64±1	56±5	63±2	n.d.	0.85±0.05	195±3
GRE-C008	45	2.9±0.01	0.82±0.01	74±3	675±20	217±12	197±16	6.7±0.3	0.51±0.04	6.4±0.4	136±2
GRE-C010	37	1.18±0.01	0.17±0.01	52±1	n.d.	29±1	10.1±0.4	n.d.	n.d.	0.36±0.02	6.8±0.4
GRE-C012	45	0.77±0.01	0.43±0.01	143±1	475±22	0.16±0.01*	n.d.	n.d.	1.4±0.1	0.69±0.02	117±2
GRE-C013	55	0.38±0.01	0.24±0.01	22±2	n.d.	125±5	n.d.	18±1	2.3±0.1	0.44±0.04	24±1
LOD	n.a.	0.003	n.a.	0.2	0.1	n.a.	0.7	0.02	0.1	0.03	n.a.

The elemental compositions of the eight lump samples analysed with ICP-OES and ICP-MS are compiled in Table 6. Although fourteen elements regularly used in analysing ancient copper finds were measured, eleven of them are reported. Bismuth, phosphorous, and silver concentrations were found below detection limits, while copper values are given for informational purposes by METU Central Laboratory. Bulk analysis of the lumps revealed malachite with varying amounts of iron, zinc, and other trace elements. Malachite minerals are known to be more heterogonous in chemical compositions. Therefore, a larger amount of sampling or drilling is suggested for analysis to represent the chemical characteristics of the material (Pernicka and Begemann 1993 23). However, the lumps from Gre Fılla are not suitable for such sampling because of their dimensions. Therefore, it is not clear whether the lumps have a common origin or not.

When the results obtained from the surface by pXRF are compared to the values of drillings measured by ICP-OES and ICP-MS, important differences are observed (Table 4 and 6). There was a copper enrichment in the surface analysis for all the samples, while trace elements were found below the detection limits of pXRF device. The iron values on the surface were defined as related to corrosion processes, and chemical analysis also revealed a non-systematic iron enrichment on the surface. The elemental composition determined by pXRF is influenced by the effects of corrosion, heterogeneity of copper mineral, surface geometry, and porosity (Dussubieux et al. 2008; Oudbashi 2015; Nicholas and Manti 2014; Nørgaard 2017). The calibration and data processing methods of pXRF could also impact the measured values.

The presence of the raw material in the form of lumps at the site designates that the production process should have been completed at the site; however, a workshop has not been identified so far. The archaeological data also shows no trace of activity relating to smelting or casting. Previous studies on the stone materials showed the differential distribution of obsidian tools based on their provenance among the structures. Still, an apparent reason for the differentiation is not yet apparent (Muşkara and Konak 2021).

Unworked lumps of malachite were found at Çayönü from the Grill-Planned Buildings' sub-phases (PPNA) and workshops for manufacturing various types of native copper and malachite objects dated to the PPNB (Table 7, Fig. 10). We know that copper beads were produced by hammering unworked copper lumps into thin foils that were rolled up and cut (Özdoğan and Özdoğan, 1999; Esin 1995; Pernicka, 2014). In comparison, Franklin (1982) proposed a folding technique, which involved beating unworked lumps into sheets then folded into the bulk material for native copper production in the North American Arctic. The folded sheet artefact (GRE-C021) seems to belong to a similar manufacturing technique. Consequently, GRE-C021 implies the presence of metal production at the settlement.

Three chisel-axes are the most peculiar objects among the copper artefacts recovered at Gre Fılla. Archaeological and archaeometallurgical studies present numerous small objects, mostly beads, pins, and basic tools, including fishhooks found at Çayönü and Aşıklı Höyük, made of native copper and malachite at the beginning of the pyrotechnology during the PPNB (Table 7, Fig. 10). Whereas the half-moon (lunula) pendant recovered in a burial as a part of a necklace at Tell Halula, dated to the late PPNB phases of occupation, is unusual for its large size (9 cm long, 1.01 cm wide, and 0.2 cm thick, Molist et al., 2009).

The size of chisel-axes of Gre Fılla is compatible with the lunula pendant, which was shaped from native copper by alternating treatments of cold hammering and annealing. Although drillings were not taken from chisel-axes and only surface measurements were performed by pXRF, it can be concluded from the pattern of the major elements that they were also made of malachite mineral (Table 4 and 6). However, further analysis is required. Besides the dimensions, the function of the chisel-axes as a tool also makes them significant for this period. While the contemporary metal objects formed by annealing were mainly ornaments and basic tools, chisel-axes from

Gre Fılla were made with a different purpose and imitated the stone industry, as is evident from their context (Fig. 4). According to the *in-situ* chisel-axe found attached to a horn handle, indicate that such objects were used as tools. Five axes made of malachite and recovered from the PPNB levels of Yiftahel in Israel were classified as prestigious items used as votive offerings (Khalaily, Milevski, and Barzilai 2013, 226). The archaeological context suggested that these votive objects were stored together at roof level. The axes ranging in size from 1 to 5 cm long have similar dimensions with Gre Fılla chisel axes; on the other hand, they have an elongated trapeze shape. The metal axes found at Yumuktepe dating to c. 5000 BC present the earliest examples of cast objects produced from smelted copper (Yalçın 2000). Kuruçay (Duru, 1983; Umurtak 1996), Barçın Höyük (Gerritsen et al., 2010), Ilıpınar (Begemann et al., 1994) and Bakla Tepe (Şahaoğlu and Tuncel, 2014) are the other late Chalcolithic settlements in Anatolia yielding flat axes with flared cutting edges manufactured from smelted copper. So far, the chisel-axes uncovered at Gre Fılla appear unique for being made of malachite as a tool.

The earliest stage of copper metallurgy is generally associated with changes in early Neolithic, PPNB, whereas the metal finds of previous periods are considered mainly as luxury items (Yener 2000; Muhly 2011). Yalçın (2003, 2017) proposed a model of the development of metallurgy in five stages for Anatolia. The metal finds dated to the PPNB from various sites correspond to his Phase II or Beginning Phase (8200–7300 BC). The beginning phase is characterized by the use of native copper and malachite and shaping by cold and hot/warm working (annealing). A comparative list of metal finds of the Beginning Phase given in Table 6 presents the artefacts from Gre Fılla, which fit well into this stage, although we were not able to determine the methods of treatment yet. The timescale sets Gre Fılla among the earliest settlements as examples of the emergence of copper metallurgy in Anatolia (Fig. 10).

Table 7. A comparative analysis of early metal finds represents the early stage of copper metallurgy (n.d. not determined).

Settlement (^{14}C dates)				**Metal finds**
Çayönü 8200-7500 BC (Yalçın 2000)	**Aşıklı** 7800-7600 BC (Muhly 2011)	**Tel Halula** 7580-7320 cal. BC (Molist et al. 2009)	**Gre Fılla** 8349-7502 cal. BC	
Anatolia, SE	Anatolia, Central	Syria, Euphrates Valley	Anatolia, SE	**Location**
Native copper Malachite	Native Copper Malachite	Native Copper Galena	Malachite	**Copper form**
Annealing, cold-working	Annealing, cold-working	Annealing, cold-working	n.d.	**Treatment**
Status/cult area, workshops, burial	Burial, residential structures	Burials	Oval structures and rectangular buildings	**Context**
Lumps, beads, pendants, awls, hooks, borers, inlays	Beads	Pendant, beads	Lumps, bead, pendant, fishhook, labret, chisel-axes	**Type**

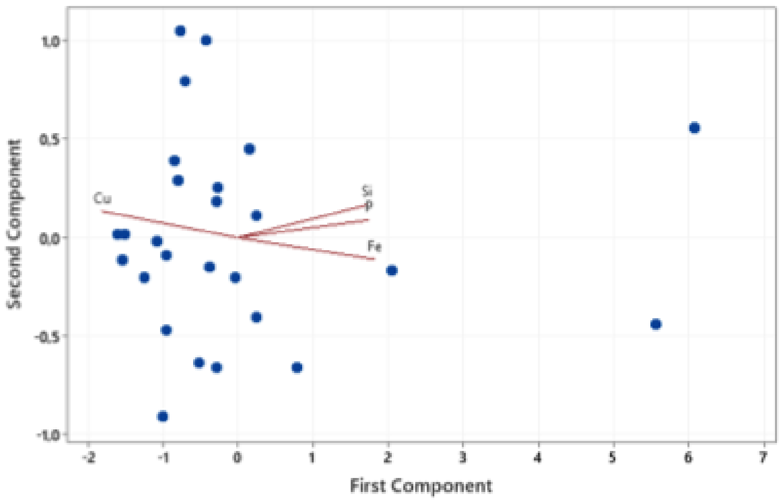

Figure 9. Principal components 1 and 2 of the dataset a) bivariate plot and b) score and loadings plot.

Figure 10. Map showing the locations of Gre Fılla, Çayönü, Tell Halula and Aşıklı Höyük (Google Earth image).

4. CONCLUSION

The element composition of artefacts by pXRF indicated the copper content with some impurities in variable amounts, including Fe, Si and P. Statistical analysis with PCA shows a strong correlation between Fe and Si; therefore, we conclude that the impurities occurred as a result of soil contamination containing iron bearing minerals during the burial. The trace elements accompanying the smelting process and considered as indicators of casting were found below the detection limits. However, significant differences in element values were observed when drillings obtained from some lumps were analysed by ICP-OES and ICP-MS. The bulk analysis of unworked lumps revealed that the malachite is the single form of mineral available during the PPNB. The result also indicates that even though pXRF is not a suitable method for corroded malachite artefacts, it could give informative results which contribute to the data obtained by bulk analysis. The calibration method should also be improved using similar secondary standards and application of corrections; on the other hand, qualitative data produced by net peak areas could be effective in defining the copper mineral or copper alloy (Nicholas and Manti 2014).

The settlement at Gre Fılla is located in south-eastern Anatolia, approximately 90 km to the east of Çayönü. The archaeological studies at Çayönü, an important site for the PPNA and PPNB, provided insights into the emergence of the copper industry for the region. During the Round Building phase dated to the PPNA, only a few unworked lumps of malachite were recovered, whereas worked metal was found abundantly in the PPNB phases of Grill-Planned and Cell-Planned Buildings. The amount of malachite, along with bone ornaments and stone found in a courtyard, is suggested a possible crafting activity (Yener 2000). The types of metal finds were also increased, including tools such as awls and hooks. However, the temporal distribution suggested that most of the metal finds came from the intermediate sub-phases. Yener (2000) proposed, "The implication is that the utilization of copper did not develop steadily, progressively or continuously."

Unworked lumps of Gre Fılla indicate that, as at Çayönü, the manufacturing of copper was performed at the settlement. The unfinished folded sheet sample could be an indication of such activity. Even though the majority of the lumps were found within the oval building's deposits, chamber N8/064/M of Structure 8, which is distinctive due to its plan and the timespan of use, a definite indication of a workshop is not detected. Ökse (2021, 9) defined the oval subterranean structures as public areas surrounded by quadrangular buildings and described, "The grouping of quadrangular structures around each oval structure left the impression of subgroups, each making use of the subterranean structure in the middle of their residential circle." The archaeological context of the lumps suggests that they were used as offerings during burial activities of the chamber with rubble along with other items (Fig. 2). The layout of the settlement and the context of the lumps implies that, if metal manufacturing was achieved at Gre Fılla, it should have been located in one of the quadrangular buildings.

While lithic tool manufacturing was still abundant at Gre Fılla during the PPNB (Muşkara and Konak 2021), the copper industry reflects the lithic tradition. GRE-C018 is especially significant evidence for this type of manufacturing. This chisel axe hafted into a bone handle resembles the flat stone axe with a bone handle, which were found together. Even though the number of tools and ornaments at Gre Fılla are not comparable to Çayönü, the diversity of types and the presence of chisel-axes may be related to a continuous process of the copper industry and reflect interaction for technology between settlements.

The chemical composition determined in this study is not sufficient for sourcing. Likewise, it is not apparent yet, how malachite materials reached Gre Fılla. Future work will focus on lead isotope analysis to identify provenance and metallurgical analysis to understand the method of treatment.

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REFERENCES

Abedi, A., Mohammadi, V. D., Steiniger, D., and Glascock, M. D. (2018). The provenance of Kul Tepe obsidian artifacts: Syunik and the highlands of Armenia as possible seasonal pastureland. *Journal of Archaeological Science: Reports*, 21, 406-412.

Barge, O., Kharanaghi, H. A., Biglari, F., Moradi, B., Mashkour, M., Tengberg, M., and Chataigner, C. (2018). Diffusion of Anatolian and Caucasian obsidian in the Zagros Mountains and the highlands of Iran: Elements of explanation in 'least cost path' models. *Quaternary International*, 467, 297-322.

Bourgarit, D. and Mille, B. (2003). The elemental analysis of ancient copper-based artefacts by inductively-coupled-plasma atomic-emission spectrometry: an optimized methodology reveals some secrets of the Vix crater. *Measurement Science and Technology*, 14(9), 1538-1555.

Campbell, S., and Healey, E. (2018). Diversity in obsidian use in the prehistoric and early historic Middle East. *Quaternary International*, 468, 141-154.

Charalambous, A., Kassianidou, V., and Papasavvas, G. (2014). A compositional study of Cypriot bronzes dating to the Early Iron Age using portable X-ray fluorescence spectrometry (pXRF). *Journal of archaeological science*, 46, 205-216.

Chataigner, C. and Barge, O. (2010). GIS (Geographic Information System) and obsidian procurement analysis: pathway modelisation in space and time. *Hansen*, S, 1-14.

Craddock, P.T. (2000). From hearth to furnace: evidences for the earliest metal smelting technologies in the eastern Mediterranean. *Paléorient*, 26(2), 151-165.

Dolfini, A., and Crellin, R. J. (2016). Metalwork wear analysis: The loss of innocence. *Journal of Archaeological Science*, 66, 78-87.

Dussubieux, L., Deraisme, A., Frot, G., Stevenson, C., Creech, A. and Bienvenu, Y. (2008). LA–ICP–MS, SEM–EDS and EPMA analysis of Eastern North American copper based artefacts: impact of corrosion and heterogeneity on the reliability of the LA–ICP–MS compositional results. *Archaeometry*, 50(4), 643-657.

Dussubieux, L. and Walder, H. (2015). Identifying American native and European smelted coppers with pXRF: a case study of artifacts from the Upper Great Lakes region. *Journal of Archaeological Science*, 59, 169-178.

Esin, U. (1995). Early copper metallurgy at the pre-pottery site of Aşıklı. Reading in Prehistory. Studies Presented to Halet Çambel, Istanbul, 61-79.

Esin, U. (1999). Copper objects from the pre-pottery neolithic site of Aşıklı (Kızılkaya village, Province of Aksaray, Turkey). In (eds.) A. Hauptmann, Pernicka, Th Rehren, and U̇. Yalçın, *The Beginnings of Metallurgy*, Der Anschnitt, Beiheft 9, 23–30.

Ferguson, J.R. (2012). X-ray fluorescence of obsidian: approaches to calibration and the analysis of small samples. In A.N. Shugar and J.L. Mass (eds.), *Handheld XRF for art and archaeology (Vol. 3)*. Leuven University Press. 401-422.

Fernandes, R., van Os, B.J., and Huisman, H.D. (2013). The use of Hand-Held XRF for investigating the composition and corrosion of Roman copper-alloyed artefacts. *Heritage Science*, 1(1), 1-7.

Frahm, E. and Tryon, C. A. (2018). Origins of Epipalaeolithic obsidian artifacts from Garrod's excavations at Zarzi cave in the Zagros foothills of Iraq. *Journal of Archaeological Science: Reports*, 21, 472-485.

Hauptmann, A. (2007). *The archaeometallurgy of copper: evidence from Faynan, Jordan*. Springer Science & Business Media.

Helmi, F.M., Abu Ayana, Y.M., Omar, S.M. (2019) Nano-copper composite conservation of an Egyptian bronze sacred ibis bird statue: case study. *Mediterranean Archaeology and Archaeometry*, Vol. 19, No 1, (2019), 61-69, DOI: 10.5281/zenodo.2585957

Ibáñez, J. J., Ortega, D., Campos, D., Khalidi, L., Méndez, V., and Teira, L. (2016). Developing a complex network model of obsidian exchange in the Neolithic Near East: Linear regressions, ethnographic models and archaeological data. *Paléorient*, 9-32.

Khalaily, H., Milevski, I., and Barzilai, O. (2013). Caching and depositing in the pre-pottery Neolithic B of Yiftahel, Israel. Stone tools in transition: From hunter gatherers to farming societies in the Near East, In: Ferran Borrell, Juan JoséIbáñez, Miquel Molist (eds.), Bellaterra (Barcelona), Universitat Autònoma de Barcelona. Servei de Publicacions, 219-230.

Kousouni, C.K., Gkanetsos, T., Panagopoulou, A., (2021) Non – destructive XRF analysis of metallic objects from Benaki museum of Islamic art. *SCIENTIFIC CULTURE,* Vol. 7, No. 2, 69-79. DOI: 10.5281/zenodo.4465536

Kuleff, I., and Pernicka, E. (1995). Instrumental neutron activation analysis of native copper: some methodological considerations. *Journal of Radioanalytical and Nuclear Chemistry*, 191(1), 145-161.

Lehner, J. W., and Yener, K. A. (2014). Organization and specialization of early mining and metal technologies in Anatolia. Archaeometallurgy in Global Perspective, 529-557.

Li, J., Guériau, P., Bellato, M., King, A., Robbiola, L., Thoury, M. and Bertrand, L. (2019). Synchrotron-based phase mapping in corroded metals: Insights from early copper-base artifacts. *Analytical chemistry*, 91(3), 1815-1825.

Liritzis, I., Laskaris, N., Vafiadou, A., Karapanagiotis, I., Volonakis, P., Papageorgopoulou, C., and Bratitsi, M. (2020). Archaeometry: an overview. *Scientific Culture*, 6(1), 49-99.

Lutz, J. and Pernicka, E. (1996). Energy dispersive Xray fluorescence analysis of ancient copper alloys: empirical values for precision and accuracy. *Archaeometry*, 38(2), 313-323.

Maddin, R., Wheeler, T. S., and Muhly, J. D. (1980). Distinguishing artifacts made of native copper. *Journal of Archaeological Science*, 7(3), 211-225.

Maddin, R., Stech, T., and Muhly, J.D. (1991). Cayonu Tepesi: The Earliest Archaeological Metal Artifacts. In (eds.) J.-P. Mohen and C. Éluère, *Découverte du Métal*, Paris, 375-386.

Martinón-Torres, M., Li, X.J., Bevan, A., Xia, Y., Zhao, K., and Rehren, T. (2014). Forty thousand arms for a single emperor: from chemical data to the labor organization behind the bronze arrows of the Terracotta Army. *Journal of Archaeological Method and Theory*, 21(3), 534-562.

Mille, B., and Bourgarit, D. (2000). L'analyse des alliages anciens à base de cuivre: état des connaissances et développement d'un protocole d'analyse par ICP-AES. *ArchéoSciences, revue d'Archéométrie*, 24(1), 13-26.

Molist, M., Clop, X., Guerrero, E., Anfruns, J., Montero-Ruiz, I. and Rovira, S. (2009). New metallurgy findings from the pre-pottery Neolithic: Tell Halula (Euphrates Valley, Syria). *Paléorient*, 33-48.

Muhly, J.D. (2011). Metals and metallurgy. In S.R. Steadman and G. McMahon *(eds.), The Oxford Handbook of Ancient Anatolia:(10,000-323 BCE).* Oxford University Press,

Nicholas, M., and Manti, P. (2014). Testing the applicability of handheld portable XRF to the characterisation of archaeological copper alloys. *ICOM-CC, 17th Triennial Conference*, 2014 Melbourne, 1-13.

Nordqvist, K., Herva, V.P., Ikäheimo, J., and Lahelma, A. (2012). Early copper use in Neolithic north-eastern Europe: an overview. *Estonian Journal of Archaeology*, 16(1), 3-25.

Nørgaard, H. W. (2017). Portable XRF on prehistoric bronze artefacts: limitations and use for the detection of Bronze Age metal workshops. *Open Archaeology*, 3(1), 101-122.

Orange, M., Le Bourdonnec, F.X., Berthon, R., Mouralis, D., Gratuze, B., Thomalsky, J., Abedi, A. and Marro, C. (2021). Extending the scale of obsidian studies: Towards a high-resolution investigation of obsidian prehistoric circulation patterns in the southern Caucasus and north-western Iran. *Archaeometry* 63, 5, 923–940.

Orfanou, V. and Rehren, T. (2015). A (not so) dangerous method: pXRF vs. EPMA-WDS analyses of copper-based artefacts. *Archaeological and Anthropological Sciences*, 7(3), 387-397.

Oudbashi, O. (2018). A methodological approach to estimate soil corrosivity for archaeological copper alloy artefacts. *Heritage Science*, 6(1), 1-15.

Ökse, A. T. (2021). Ambar Dam Salvage Excavations in 2018-2019: Ambar Höyük, Gre Fılla and Kendale Hecala. In (eds.) S. R. Steadman and G. McMahon, *Archaeology of Anatolia Volume* IV*: Recent Discoveries (2019-2020),* pp. 4-20. Newcastle upon Tyne, Cambridge Scholars Press.

Özdoğan, M. and Özdoğan, A. (1999). Archaeological evidence on the early metallurgy at Çayönü Tepesi. In A. Hauptmann, E. Pernicka, Th. Rehren and Ü. Yalçın (eds.), *The Beginnings of Metallurgy*, Bochum, 13–22.

Pernicka E., 1999. Trace Element Fingerprinting of Ancient Copper: Guide to technology or Provenance? In S.M.M. Young, A.M. Pollard, R. Budd, R.A. Ixer (eds.), *Metals in Antiquity*. BAR International Series, 792: 163-171.

Pernicka E. (2014) Provenance Determination of Archaeological Metal Objects. In Roberts B., Thornton C. (eds), *Archaeometallurgy in Global Perspective*. New York, 239-268.

Radivojević, M., Rehren, T., Pernicka, E., Šljivar, D., Brauns, M., and Borić, D. (2010). On the origins of extractive metallurgy: new evidence from Europe. *Journal of Archaeological Science*, 37(11), 2775-2787.

Radivojević, M., Roberts, B.W., Pernicka, E., Stos-Gale, Z., Martinón-Torres, M., Rehren, T., Bray, P., Brandherm, D., Ling, J., Mei, J. and Vandkilde, H. (2019). The provenance, use, and circulation of metals in the European Bronze Age: the state of debate. *Journal of archaeological research*, 27(2), 131-185.

Siklósi, Z., Prange, M., Kalicz, N., and Raczky, P. (2012). New data on the provenance of Early Copper finds from the Great Hungarian Plain. In: *Neolithic and Copper Age between the Carpathians and the Aegean Sea. Chronologies and Technologies from the 6th to the 4th Millennium BCE*. International Workshop Budapest, 57-92.

Yalçın, Ü. (2000). Anfänge der Metallverwendung in Anatolien. In Ü. Yalçın (ed.), *Anatolian Metal I*, Bochum, 17–30.

Yalçın, Ü. (2008). Ancient Metallurgy in Anatolia. In Ü. Yalçın, H. Özbal, and A.G. Paşamehmetoğlu (eds.) *Ancient Mining in Turkey and the Eastern Mediterranean*, International conference AMITEM 15–22 June 2008, Ankara: 15–42.

Yalçın, Ü. (2017). The Beginnings of Metal Use in West Asia. In A. Tsuneki, S. Yamada and K. Hisada (eds.), *Ancient West Asian Civilization*, Singapore, 115-130.

Yener, K.A. (2000). *The domestication of metals: the rise of complex metal industries in Anatolia*. Brill.

Wayman, M.L., and Duke, M.J.M., 1999. The effects of melting on native copper. In A. Hauptmann, Pernicka, Th Rehren, and Ü. Yalçın, *The Beginnings of Metallurgy*, Der Anschnitt, Beiheft 9, 55–63.

Wayman, M.L. (2004). *Metallography of archaeological alloys*. ASM handbook, 9, 468-477.