# Patterns of metal procurement, manufacture and exchange in Early Bronze Age northwestern Anatolia: Demircihüyük and beyond

# Michele Massa, Orlene McIlfatrick and Erkan Fidan

Bilecik Şeyh Edebali University, Turkey, British Institute at Ankara, UK, and Bilecik Şeyh Edebali University, Turkey michele.massa@bilecik.edu.tr

## Abstract

This paper adds a new interpretive layer to the already extremely well-investigated site of Demircihüyük, a small Early Bronze Age settlement at the northwestern fringes of the central Anatolian plateau. It presents a reassessment of the evidence for prehistoric mining in the region, as well as a new programme of chemical composition analysis integrated with an object functional and technological typology of the site's metal assemblages. The results reveal complex manufacturing techniques (such as bivalve mould casting, plating and lost wax) and the co-occurrence of several alloying types, including the earliest tin bronzes in the region. Object typology further indicates that the Demircihüyük community was at the intersection of two distinct metallurgical networks: one centred on the western Anatolian highlands, the other spanning the northern part of the central plateau. Additionally, several strands of evidence suggest that the beginning of interregional exchanges, linking central Anatolia to northern Levantine and Mesopotamian societies, may have started at an earlier date than the commonly assumed ca 3000–2800 BC.

# Özet

Bu makale, Orta Anadolu platosunun kuzeybatısında yer alan, oldukça iyi araştırılmış küçük ölçekli bir İlk Tunç Çağı yerleşmesi olan Demircihüyük'e yeni bir yorum getirmektedir. Makale ile bölgedeki tarih öncesi döneme ilişkin madencilik kanıtlarının yeniden değerlendirilmesinin yanı sıra, yerleşmedeki metal eserlerin işlevsel ve teknolojik tipolojisine dayalı yeni bir kimyasal bileşim analizi sunulmaktadır. Sonuçlar, çift kalıp döküm tekniği, kaplama ve kayıp balmumu tekniği gibi karmaşık üretim tekniklerinin bilindiğini ve ayrıca birkaç alaşımın beraber kullanıldığı bilgilerinin yanında bölgedeki en eski bakır-kalay karışımı (tunç) eserlerin yerleşmede olduğunu kanıtlamaktadır. Yerleşmedeki metal eserlerin tipolojisi ise Demircihüyük'ün Batı Anadolu eşiği ve Orta Anadolu platosunun kuzeyindeki iki farklı metalürjik ağın kesişim noktası olduğunu göstermektedir. Buna ek olarak, birkaç kanıt sayesinde, Batı ve Orta Anadolu ile kuzey Levant ve Mezopotamya toplumları arasındaki uzak mesafeli bölgeler arası ticaret, yaygın olarak kabul edilenlerden daha erken bir tarih olan M.Ö 3000–2800 yıllarında başlamış olabileceği varsayılmaktadır.

Demircihüyük, a small settlement at the northwestern edge of the central Anatolian plateau (fig. 1), was excavated by Manfred Korfmann between 1975 and 1978, and is at present one of the best-excavated and most thoroughly published Bronze Age sites in Turkey (Korfmann 1983; 1987; Seeher 1987; 2000; Efe 1988; Kull 1988; Baykal Seeher, Obladen Kauder 1996; also Massa 2014: 74–76 for a summary in English). The site is composed of a mounded settlement and its associated burial ground, and witnessed a long albeit discontinuous occupation between

the Chalcolithic and Hellenistic periods. This paper focuses on the metal assemblages associated with the Early Bronze Age levels, dated ca 2870–2500 BC (table 1; Weninger 1987), and which have already been the focus of two previous archaeo-metallurgical analyses (Bachmann et al. 1987; Pernicka 2000). Through metal composition analysis with a portable x-ray fluorescence spectrometer (pXRF), functional and technological object typologies, and a reassessment of the evidence for prehistoric mining in the region, we hope to shed light on patterns of metal procure-

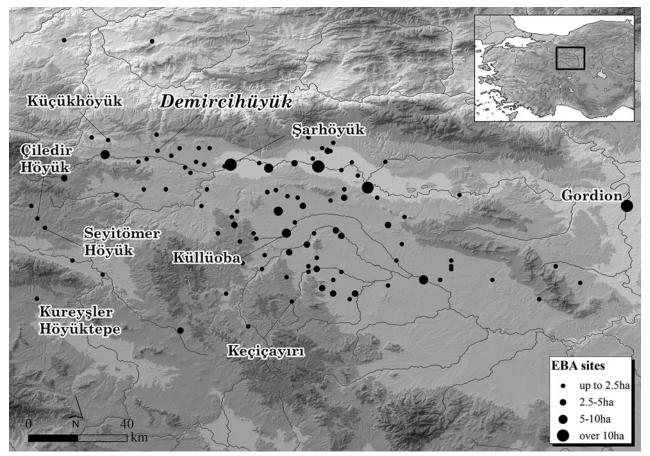


Fig. 1. Map of the region around Demircihüyük, showing excavated (labelled) and surveyed Early Bronze Age sites.

ment, manufacture and exchange at the site. In particular, we are interested in understanding the employment of different metal alloys diachronically and the application of different metallurgical techniques for object manufacture. Thanks to the excellent stratigraphic record and a large set of radiocarbon dates, the tight chronological sequence can be employed to date diachronic changes as accurately as possible. The results are contextualised within the Anatolian metallurgical panorama of the early to mid third millennium BC, with the aim of understanding how the small community of Demircihüyük participated in the Early Bronze Age long-distance exchange networks.

From a methodological standpoint, we are also interested in exploring the potential of portable x-ray fluorescence spectrometers for the analysis of prehistoric metals. PXRF is a technique that allows for relatively cheap, very fast and non-destructive chemical-composition studies on a range of different artefact classes. It has, however, two major shortcomings. The first is that, in its non-destructive use, pXRF is only able to analyse the surface of an object, which generally has a different composition from the rest of the artefact (see more below). The second is that, compared to other (destructive) techniques for undertaking chemical-composition analysis, it has low accuracy and precision. In order to assess the feasibility of pXRF analysis for prehistoric metals, we experimented with a detailed routine of data acquisition to maximise its advantages and reduce its shortcomings, and we also compared our results against earlier results obtained by Ernst Pernicka via the destructive instrumental neutron activation analysis (INAA) technique (Pernicka 2000).

The relative and absolute chronology of Demircihüyük A detailed chrono-typology of the Demircihüyük ceramic assemblages (Seeher 1987; Efe 1988) and a set of 64 radiocarbon dates covering phases E to M (Weninger 1987; Manning 1995: 156) allow us to circumscribe the stratified Early Bronze Age occupation (levels D to P) between ca 2870 and 2570 cal. BC, and to place the unstratified surface materials (termed as 'Q') within a few generations later (table 1). Thanks to detailed work on ceramic chronotypology associated with stratigraphic analysis and four radiocarbon dates, the more recent excavations at Küllüoba (ca 50km away as the crow flies) have further confirmed the validity of the Demircihüyük sequence (Efe, Ay Efe 2000; Efe, Fidan 2008; Sarı 2009; 2012; Türkteki 2012). In addition, Demircihüyük can be quite easily linked with the Trojan sequence which, despite the long-standing problems of relating Carl Blegen's results with those of the renewed excavations of Manfred Korfmann, still represents the most important 'stratigraphic pillar' in western Anatolia (Bachhuber 2008: 24). With our current knowledge, Demircihüyük levels D to P run parallel to the various levels of Troy I, while phase 'Q' is broadly contemporary with Troy IIa–b (table 1).

With regard to the cemetery of Demircihüyük-Sarıket, the tight ceramic chrono-typology carried out on the settlement's materials has allowed Jürgen Seeher to date the Early Bronze Age occupation of the necropolis from levels K/L to the early horizon of 'Q' (2000: 222): i.e. to approximately two centuries between ca 2700 and 2550/2500 BC. Moreover, Seeher has identified a number of ceramic fossil guides that could be more finely dated to one to three levels in the settlement (2000: 32-50). While he has not explicitly used this information to attempt further subdivision of the occupation of Sarıket, 100 graves (out of 497, i.e. 20% of the total) that contain one or more fossil guides can be attributed to a shorter chronological span within this period. In particular, the dated graves cluster in one of two groups, that have been thus defined as 'early' (settlement levels K/L to N) and 'late' (levels O to 'Q') phases of the cemetery (table 2). The early phase of the cemetery covers approximately 2700-2600 BC, while the late phase spans ca 2600-2500 BC. This is an important result that will be discussed below in relation to the diachronic changes in the observed patterns of metal exchange.

#### Demircihüyük's metal assemblage

Despite the extensive excavations targetting the settlement, only 29 metal items were found; all are copper-based with the exception of a single lead fragment (table 3; Obladen Kauder 1996: 313). Conversely, a total of 257 metal objects (159 copper, 37 lead, 44 gold and 17 silver) were retrieved from closed funerary contexts and the general cemetery area (Seeher 2000: 66-132). The much higher number of metal objects found at Demircihüyük-Sarıket and, particularly, the presence of silver and gold clearly reflect different patterns of deposition. Most of the artefacts from the settlement were in all likelihood accidentally lost, and not purposefully discarded, since - if they were broken, for example – they could have been recyled and reshaped into new objects. Conversely, all the items found in the burials were intentionally deposited. This difference is also highlighted by the small range of metal artefacts found in domestic contexts; this is limited to small copper-based tools, rings and pins, i.e. items that are more likely to be lost than larger objects. These observations are important because they show that what we retrieve from habitation levels is generally only a small fraction of the quantity and range of metal items likely circulating at any one time. Only specific contexts (graves, sudden settlement destructions, hoards) that act as 'metal recovery traps' (see Nakou 1997: 635 for the concept) can

| Demircihöyük | No. of 14C<br>samples | Estimated date    | Troy | Küllüoba        | Karataş | Anatolian<br>periodisation |
|--------------|-----------------------|-------------------|------|-----------------|---------|----------------------------|
| Phase D      | -                     | 2870–2850 cal. BC |      | West Tr. 3/ V C |         | Early Bronze I             |
| Phase E1–2   | 30                    | 2850–2830 cal. BC | Ia–c | West Tr. 2/VB   | -       |                            |
| Phase F1     | 1                     | 2830–2810 cal. BC |      | VA              | I–II    |                            |
| Phase F2     | -                     | 2810–2790 cal. BC |      |                 |         |                            |
| Phase F3     | _                     | 2790–2770 cal. BC | _    |                 |         |                            |
| Phase G      | -                     | 2770–2750 cal. BC | Id–e | _               | III     |                            |
| Phase H      | 25                    | 2750–2730 cal. BC | -    | IV F            |         | Early Bronze II early      |
| Phase I      | _                     | 2730–2710 cal. BC | _    |                 |         |                            |
| Phase K1     | -                     | 2710–2690 cal. BC | Ig-k | IV E            | IV      |                            |
| Phase K2     | 2                     | 2690–2670 cal. BC |      |                 |         |                            |
| Phase L      | 4                     | 2670–2650 cal. BC |      |                 |         |                            |
| Phase M      | 2                     | 2650–2630 cal. BC |      | IV D            | V:1     | Early Bronze II middle     |
| Phase N      | -                     | 2630–2610 cal. BC |      |                 |         |                            |
| Phase O      | _                     | 2610–2590 cal. BC | 1    | IV C            | V:2     |                            |
| Phase P      | -                     | 2590–2570 cal. BC | 1    |                 |         |                            |
| Phase Q      | _                     | 2570–2550 cal. BC | IIa  | IV B            | V:3     | Early Bronze II late       |

Table 1. Chonological sequence of the Early Bronze Age occupation of Demircihüyük, showing contemporary levels of Troy, Küllüoba and Karataş (from Massa 2014: table 1).

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| Ceramic type   | Settlement<br>level(s) | Cemetery<br>phase | Grave nos   | References         |
|--|------------------------|-------------------|---|--------------------|
| Amphora  | Pre-K?                 | Early             | 422   | Seeher 2000: 46    |
| Bottle with spherical body, elongated neck and everted rim | H-I-K                  | Early             | 62, 100, 118, 141   | Seeher 2000: 35–36 |
| B1 Jug   | K                      | Early             | 85, 105, 280, 298, 313, 357,<br>448, 456, 569   | Seeher 2000: 40    |
| C1 Jug   | Pre-K?                 | Early             | 25, 39, 40, 53, 148, 161, 167,<br>183, 219, 235, 271, 289, 352,<br>386, 469, 497            | Seeher 2000: 42    |
| C2 Jug   | Κ                      | Early             | 45, 149, 278  | Seeher 2000: 42    |
| Jug with lateral spout                                     | L                      | Early             | 370   | Seeher 2000: 44    |
| Efe 6 bowl (footed)  | ʻQ'                    | Late              | 19, <b>368</b>  | Seeher 2000: 34    |
| Efe 6 bowl (loop-handled)                                  | 'Latest phases'        | Late              | <b>37</b> , 568   | Seeher 2000: 34    |
| Efe 14k S-profile bowl                                     | O–'Q'                  | Late              | 106, 274, 275, 315, 327, 426, 468   | Seeher 2000: 34    |
| A1 Jug   | N–P                    | Late              | <b>95</b> , 112, 205, 229, 305, 372   | Seeher 2000: 38    |
| A4 Jug   | 0–'Q'                  | Late              | <b>26</b> , 35, 38, 58, 101, <b>117</b> , 144, 145, 210, 216, 220, 233, 300, 307, 367B, 400 | Seeher 2000: 39    |
| B2 Jug   | P–'Q'                  | Late              | 463, 494, 546   | Seeher 2000: 40    |
| B3 Jug   | 'Latest phases'        | Late              | <b>37</b> , 83, <b>95</b> , 97, 190, <b>202</b> , <b>213</b> , 463                          | Seeher 2000: 40    |
| B6 Jug   | ʻQ'                    | Late              | 299, <b>321</b> , <b>350</b> , 479  | Seeher 2000: 41    |
| C3 Jug   | 'Latest phases'        | Late              | 8, 82, 88, 131, 149, <b>321, 350</b> , 392, 513, 530, 552                                   | Seeher 2000: 42    |
| Omphalos bottom in jugs                                    | 'Latest phases'        | Late              | <b>117</b> , <b>202</b> , 211, <b>213</b> , 320, 361, 418                                   | Seeher 2000: 45    |
| Three-footed jug   | ʻQ'                    | Late              | 275   | Seeher 2000: 45    |
| Tripod jar   | 'Q'                    | Late              | <b>26</b> , 151, <b>368</b>   | Seeher 2000: 46    |
| Tankard  | ʻQ'                    | Late              | 294, 317  | Seeher 2000: 46    |
| 'Teapot'   | ʻQ'                    | Late              | 247, 452  | Seeher 2000: 47    |

Table 2. Synoptic table showing the Demircihüyük-Sarıket graves associated with ceramic materials directly comparable to specific settlement levels, and their affiliation to one of two phases of the cemetery ('early' and 'late'). Grave numbers in bold indicate that more than one fossil type is present in the same grave.

provide a more realistic glimpse into the amount, range and quality of metalwork that circulated within prehistoric communities.

Typologically, the vast majority of the artefacts retrieved from the necropolis are personal ornaments (78%), with different shapes of pins forming the lion's share of this category (30% of the total assemblage), followed by small diadems worn on foreheads (21%) and then rings worn on fingers, on ears and in hair (8.5%). With very few exceptions, such items are very small and weigh only a few grams (0.1–8gr). Small lead vessels,

probably containing oils or perfumes, are also frequent (12%) and are much heavier (240–620gr). In contrast, the metal assemblage from the settlement is dominated by tools (52%; in the necropolis they account for 6% of the total assemblage). With the exception of the three hatchets (86–290gr), the tools are also light in weight. Weapons represent only 4% of the total funerary assemblage and include one spearhead, one battleaxe, one crescentic axe, three round maceheads, three knobbed maceheads and one possible arrowhead. The cumulative weight of these weapons (between 180gr and 350gr each) far exceeds that

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| Class              | Туре              | Settle | ement | Λ   | lecro | poli | \$ | Stray | v (ne | crop | olis) | Total | Manufacturing                             |
|--------------------|-------------------|--------|-------|-----|-------|------|----|-------|-------|------|-------|-------|---|
|                    |                   | Си     | Pb    | Cu  | Pb    | Ag   | Au | Cu    | Pb    | Ag   | Au    |       | technologies                              |
|                    | Needle            | 3      |       | 7   |       |      |    | 1     |       |      |       | 11    | Open mould casting                        |
| Tools              | Flat axe/hatchet  |        |       | 2   |       |      |    | 1     |       |      |       | 3     | Open mould casting                        |
| Too                | Awl/punch         | 10     |       |     |       |      |    | 1     |       |      |       | 11    | Open mould casting                        |
|                    | Knife/blade       | 2      |       | 5   |       |      |    |       |       |      |       | 7     | Open mould casting                        |
| 2                  | Razor             |        |       | 2   |       |      |    |       |       |      |       | 2     | Open mould casting                        |
| Toiletry           | Spatula           |        |       | 1   |       |      |    |       |       |      |       | 1     | Open mould casting                        |
| $T_{C}$            | Tattoo needle(?)  |        |       | 4   |       |      |    |       |       |      |       | 4     | Bivalve mould casting                     |
|                    | Battleaxe         |        |       | 1   |       |      |    |       |       |      |       | 1     | Lost wax                                  |
|                    | Crescentic axe    |        |       | 1   |       |      |    |       |       |      |       | 1     | Bivalve mould casting                     |
| su                 | Round macehead    |        |       | 2   |       |      |    | 1     |       |      |       | 3     | Bivalve mould casting                     |
| Weapons            | Knobbed macehead  |        |       | 3   |       |      |    |       |       |      |       | 3     | Lost wax                                  |
| We                 | Spearhead         |        |       | 1   |       |      |    |       |       |      |       | 1     | Bivalve mould casting                     |
|                    | Dagger            |        |       | 1   |       |      |    | 1     |       |      |       | 2     | Open mould casting                        |
|                    | Arrow             | 1      |       |     |       |      |    |       |       |      |       | 1     | Bivalve mould casting                     |
| Vessels            | Bottle            |        |       |     | 28    |      |    |       | 3     |      |       | 31    | Lost wax/coating(?)                       |
|                    | Jug               |        |       |     | 1     |      |    |       |       |      |       | 1     | Lost wax/coating(?)                       |
|                    | Hair ring         |        |       | 4   |       |      |    |       |       |      |       | 4     | Open mould casting,<br>hammering          |
| s                  | Ring/earring      | 1      |       | 5   |       | 3    | 3  | 6     |       |      |       | 18    | Open mould casting,<br>hammering          |
| nent               | Diadem            |        |       | 21  | 2     | 5    | 23 |       |       | 2    | 2     | 55    | Hammering, repoussé                       |
| irnai              | Earstud           |        |       |     |       |      | 3  |       |       |      |       | 3     | Hammering, chasing                        |
| nal o              | Bead              |        |       | 1   | 3     | 1    | 12 |       |       |      |       | 17    | Hammering                                 |
| Personal ornaments | Pin               | 6      |       | 66  |       | 4    | 1* | 6     |       | 1    |       | 84    | Bivalve mould casting, gilding*           |
|                    | Bracelet          |        |       | 8   |       |      |    | 1     |       |      |       | 9     | Open mould casting,<br>hammering, chasing |
|                    | Applique          |        |       | 1   |       | 1    |    | 1     |       |      |       | 3     | Hammering                                 |
|                    | Pin or needle     | 1      |       |     |       |      |    |       |       |      |       | 1     | Open/bivalve mould casting                |
| и                  | Too fragmentary   | 3      |       |     |       |      |    | 1     |       |      |       | 4     |   |
| Uncertain          | Strip with rivets |        |       | 1   |       |      |    |       |       |      |       | 1     | Hammering, punching                       |
| Unc                | Wire              |        |       |     |       |      |    | 2     |       |      |       | 2     | Open mould casting                        |
|                    | Bowl(?)           |        | 1     |     |       |      |    |       |       |      |       | 1     |   |
|                    | Dagger(?)         | 1      |       |     |       |      |    |       |       |      |       | 1     |   |
|                    | Total             | 28     | 1     | 137 | 34    | 14   | 42 | 22    | 3     | 3    | 2     | 286   |   |

Table 3. Functional typology of all metal artefacts found at Demircihüyük (in the settlement, in closed funerary contexts and in the general necropolis area). The possible metallurgical technologies employed in their manufacture are also indicated, as well as the metal with which they were produced. Cu = copper; Pb = lead; Ag = silver; Au = gold. \*Gilding is present on just one piece (S119).

of all the other items combined, suggesting that, in the small community of Demircihüyük, weaponry may have been employed as a significant show of metal wealth. In addition, the three knobbed maceheads are possibly items of status rather than, or in addition to, having a practical function since they have a close association with burials of significant individuals both at Demircihüyük and Alacahöyük, the Alacahöyük piece is made of gold and they are depicted on ceremonial standards associated with rich burials at Alacahöyük and Horoztepe (Zimmermann 2008: 342–45; Massa 2014: 85–86).

#### **Previous analyses**

The analysis carried out by Pernicka focused on a total of 24 objects from the Early Bronze Age contexts of the necropolis: 18 copper-based artefacts were studied with destructive, high-precision INAA, while two silver-based, two gold-based and two lead artefacts were investigated with non-destructive laboratory-based XRF (Pernicka 2000). Pernicka's results are employed as a benchmark against which we can compare our own analytical results (below) and will be integrated into the analysis of alloying practices. An earlier study on Demircihüyük's metal artefacts was carried out with a quartz prism spectrograph on the corrosion crust of 17 samples from the settlement. This is a semi-quantitative technique that can provide only approximate estimates regarding the proportion of elements present in the metal (Bachmann et al. 1987). We were able to reanalyse five of these samples (S207, S217, S218, S226 and S228) and compare the new results with those of the original study. As table 4 demonstrates, there is very little agreement between our results and those of H.G. Bachmann and colleagues. Since quartz prism spectrography has only very rarely been employed in the study of prehistoric metals, and given that our pXRF results are to a large extent confirmed by Pernicka's INAA analysis (though less accurate and precise), the results of Bachmann and colleagues have been deemed unreliable and are not employed in the remainder of this current analysis.

## Analytical methodology

For this study we employed a Bruker Tracer IV-SD handheld portable x-ray fluorescence spectrometer. Over the last decade, pXRF analysis has been widely applied in the field of archaeology, not only for the analysis of metal artefacts (for example Yalçın 2011; Zimmermann, Yıldırım 2011; Yalçın, Yalçın 2013; Geniş, Zimmermann 2014; Lehner et al. 2015), but also for pottery (Forster et al. 2011; Kealhofer et al. 2015; McIlfatrick 2015), chipped stone (obsidian: Milič 2014; chert: Nazaroff et al. 2014), marble (Zöldföldi 2011), pigments and paints (Mantler, Schreiner 2000). When considering analytical costs, pXRF is much cheaper than any destructive technique, and is also able to analyse artefacts much faster than any other technique (Frahm, Doonan 2013). In addition, its small size allows the instrument to be fully portable - making it ideal for fieldwork and museum visits. The non-destructive nature of pXRF analysis allows for the assessment of

| Sample no. | Exc. no. | Reading no. | As% | Sn% | Ag% | Ni% | Bachmann et al. 1987 results         |
|------------|----------|-------------|-----|-----|-----|-----|--------------------------------------|
| S207       | K8.152   | S207-1      | 1.4 | 0.2 | 1.5 | 0.1 | 'Cu-Ag alloy with As and without Ni' |
|            |          | S207-2      | 1.0 | 0.2 | 1.0 | 0.1 | -                                    |
|            |          | S207-3      | 1.8 | 0.2 | 1.4 | 0.1 | -                                    |
| S217       | G8.356   | S217-1      | 0.4 | 0.1 | 0.2 | 0.1 | 'Cu-Ag alloy with As and without Ni' |
|            |          | S217-2      | 0.4 | 0.1 | 0.3 | 0.1 | _                                    |
|            |          | S217-3      | 0.2 | 0.2 | 0.3 | 0.1 | -                                    |
| S218       | G8.481   | S218-1      | 0.6 | 0.2 | 0.2 | 0.1 | 'Cu-Ag alloy with As and without Ni' |
|            |          | S218-2      | 1.3 | 0.1 | 0.1 | 0.1 | -                                    |
| S226       | K8.1179  | S226-1      | 0.5 | 0.2 | 0.2 | 0.1 | 'Arsenical copper without tin'       |
|            |          | S226-2      | 0.4 | 0.2 | 0.2 | 0.1 | -                                    |
|            |          | S226-3      | 0.6 | 0.2 | 0.2 | 0.1 | -                                    |
| S228       | K7.127   | S228-1      | 1.7 | 0.2 | 0.2 | 0.1 | 'Cu-Ag alloy with As and Ni'         |
|            |          | S228-2      | 1.8 | 0.1 | 0.2 | 0.1 |                                      |
|            |          | S228-3      | 1.1 | 0.2 | 0.3 | 0.1 |                                      |

Table 4. Comparison between the analytical results of quartz prism spectrography (Bachmann et al. 1987: table 1) and pXRF (the current study). Values shaded in light grey might indicate intentional alloy; the last column reports the qualitative assessment of Bachmann and colleagues.

artefacts which would not be chemically analysed if such action would subject them to destruction or damage. The technique can also be used to obtain multiple samples from the same item. Because of these factors, its use makes it much easier to obtain research permits, particularly in Turkey where the export of archaeological samples is severely limited and strict rules apply to analyses undertaken in museums.

As already mentioned, a major drawback of pXRF is that, contrary to destructive techniques that analyse powdered samples extracted from cores drilled through an object, pXRF cannot analyse an artefact's bulk composition, in fact it can analyse to a depth of only a few tens of microns (ca 0.05mm) from the surface of any given object (unless, of course, a prepared sample from a drilled core is available for pXRF analysis, in which case, however, the technique is destructive). This limitation is a particular problem in the analysis of prehistoric metals, whose structure is always heterogeneous because of the metallurgical techniques employed, post-depositional processes and the very nature of metal materials themselves (Scott 1991b: 5-32). For instance, during casting certain elements tend to sink towards the centre of an artefact while others float to the outer layers (surface segregation), with the result that, on the surface, some alloyed metals are more or less abundant than others (Pollard, Bray 2014: 225). For complex three-dimensional objects, there can also be selective segregation in different parts of an artefact, related to the speed of casting and the cooling environment. Furthermore, the process of hammering artefacts when hot (in order to harden the edges and shape objects) selectively brings to the surface some elements more than others (Hauptmann et al. 2002: 52). Additionally, most metal objects are covered by a corrosion patina that changes the surface's chemical composition, with depletion of some alloyed metals, particularly in smaller objects (Lehner et al. 2015: 196; Philip 2015: 137). It is thus the case that there are significant differences in terms of chemical composition between the surface and the bulk structure of prehistoric metal items, and that pXRF results will therefore normally differ from those retrieved via destructive techniques, careful sample preparation and rigorous quantitative methods.

In addition, pXRF has a relatively low accuracy and precision when compared to destructive techniques like atomic absorption spectroscopy or neutron activation analysis, particularly when the sample is not pretreated in a laboratory (as in our case); its results also suffer from poor inter-laboratory reproducibility (Lutz, Pernicka 1996; Heginbotham et al. 2011; Frahm 2013; Speakman, Shackley 2013; Lehner 2015: 134–40). Therefore, pXRF results cannot be employed for sophisticated analysis of provenance (employing trace elements).

However, the question asked here is whether pXRF can serve as a reliable tool to understand prehistoric alloying practices. In order to investigate this, we reanalysed all the artefacts from Pernicka's analyses that we could access in the Eskişehir Museum (a total of nine pieces). We took several readings for each object, in different locations. The results show that the pXRF correctly detected the presence of all the major alloying components and identified the native copper artefact as such (S089). As expected, however, the pXRF results tend to overestimate the proportion of secondary metals in the alloy and present a significant range of values between readings, as a consequence of heterogeneous surfaces (table 5). This notwithstanding, the results do show that pXRF analysis is successful in identifying the major alloyed elements and thus can be employed to shed light on alloying practices. These observations also helped us to devise an analytical strategy to account for such shortcomings and to integrate them into the interpretive process. For each sample, we took two to seven readings, depending on an object's size, and took into account the degree of heterogeneity of the sample as well as the degree of corrosion of the object (we tried as much as possible to target clean or cleaner surfaces). Regarding the latter, given the absence of complex laboratory facilities we were unable to estimate accurately in a quantitative manner the depth and nature of the corrosion crust, but we tried nonetheless to qualitatively assess it by providing several categories of severity of corrosion (table 5). Multiple readings from the same object (shown in tables 6 and 7) provided the opportunity to compare different areas of the sample surface and make a better assessment of how the object had been manufactured, and whether it may have been manufactured from multiple parts (such as pins with elaborate heads). We also took note of the sample location on the object and the conditions of the surface within the sampled radius, in order to assess results better.

Regarding our analytical strategy, we tried as much as possible to analyse a representative sample (out of 286 artefacts) based on the following aims:

- to cover the whole third millennium BC occupation of the site, from phase D to 'Q';
- 2. to choose samples with an accurate dating within the site's well-defined stratigraphy;
- 3. to choose samples with relatively little surface corrosion;
- 4. to choose samples covering the whole range of types represented at the site;
- 5. to target gold and silver objects in addition to copperbased ones.

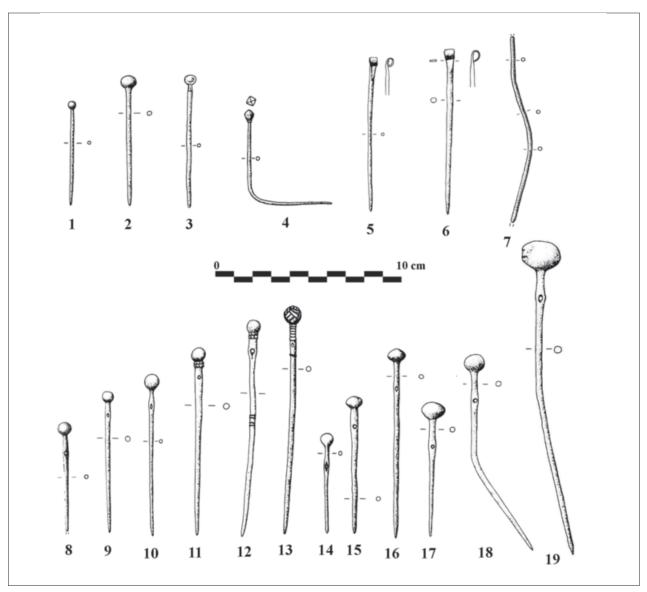
Due to unforeseen administrative circumstances, it was however not possible to access the whole metal collection held at the Eskişehir Museum and, in particular, we could

| Object               | Lab. no. | Cu%    | Sn%    | As%    | Pb%  | Sb%    | Ni%    | Ag%    | Au%    | Fe%    | Zn%    |
|----------------------|----------|--------|--------|--------|------|--------|--------|--------|--------|--------|--------|
| S046                 | HDM 2471 | 87.00  | 0.0035 | 4.9000 | n.a. | 0.0390 | 0.0272 | 0.0243 | 0.0060 | 0.3520 | 0.0049 |
| Crescentic axe       | S046-1   | 86.1   | bdl    | 12.5   | bdl  | bdl    | 0.1    | bdl    | 0.1    | 0.2    | 0.2    |
|                      | S046-2   | 86.5   | bdl    | 12.2   | bdl  | bdl    | 0.1    | bdl    | 0.1    | 0.1    | 0.2    |
|                      | S046-3   | 90.6   | bdl    | 8.0    | bdl  | 0.1    | 0.1    | 0.1    | bdl    | 0.2    | 0.2    |
|                      | S046-4   | 89.9   | bdl    | 8.7    | bdl  | bdl    | 0.1    | bdl    | 0.1    | 0.3    | 0.2    |
|                      | S046-5   | 83.7   | bdl    | 15.0   | bdl  | bdl    | 0.1    | bdl    | 0.1    | 0.2    | 0.2    |
|                      | S046-6   | 86.8   | bdl    | 11.7   | bdl  | bdl    | 0.1    | 0.1    | 0.1    | 0.3    | 0.2    |
| S056                 | HDM 2491 | 97.00  | 5.8000 | 0.0480 | n.a. | 0.0107 | 0.0294 | 0.0179 | 0.0037 | 0.0140 | 0.0008 |
| Knobbed mace         | S056-1   | 74.6   | 13.8   | 0.4    | 8.3  | 0.2    | bdl    | bdl    | 0.2    | 0.3    | 0.2    |
|                      | S056-2   | 63.6   | 18.7   | 0.8    | 9.9  | 0.1    | bdl    | bdl    | 0.4    | 0.2    | 0.2    |
|                      | S056-3   | 83.4   | 9.1    | 0.2    | 6.0  | 0.1    | bdl    | bdl    | 0.1    | 0.4    | 0.2    |
|                      | S056-4   | 75.1   | 12.4   | 0.6    | 9.2  | 0.1    | bdl    | bdl    | 0.2    | 0.3    | 0.2    |
|                      | S056-5   | 75.8   | 11.9   | 0.6    | 9.2  | 0.1    | bdl    | bdl    | 0.2    | 0.5    | 0.2    |
| S089                 | HDM 2473 | 101.00 | 0.0025 | 0.0214 | n.a. | 0.0018 | 0.0560 | 0.0141 | 0.0009 | 0.0380 | 0.0008 |
| Round mace           | S089-1   | 98.6   | bdl    | bdl    | bdl  | bdl    | 0.1    | bdl    | bdl    | 0.3    | 0.2    |
|                      | S089-2   | 98.6   | bdl    | bdl    | bdl  | bdl    | 0.1    | bdl    | bdl    | 0.2    | 0.2    |
|                      | S089-3   | 98.6   | bdl    | bdl    | bdl  | bdl    | 0.1    | bdl    | bdl    | 0.2    | 0.2    |
|                      | S089-4   | 98.6   | bdl    | bdl    | bdl  | bdl    | 0.1    | bdl    | bdl    | 0.2    | 0.2    |
| S093                 | HDM 2472 | 92.00  | 7.7000 | 0.0910 | n.a. | 0.0158 | 0.0143 | 0.0390 | 0.0110 | 0.0190 | 0.0093 |
| Poker spear          | S093-1   | 80.1   | 13.9   | 0.2    | 3.8  | 0.1    | bdl    | bdl    | 0.2    | 0.2    | 0.2    |
|                      | S093-2   | 72.9   | 17.2   | 0.2    | 5.7  | 0.1    | bdl    | 0.1    | 0.2    | 0.2    | 0.2    |
|                      | S093-3   | 78.6   | 17.2   | 0.3    | 3.8  | 0.1    | bdl    | bdl    | 0.3    | 0.1    | 0.2    |
|                      | S093-4   | 75.9   | 15.0   | 0.2    | 5.9  | 0.1    | bdl    | bdl    | 0.2    | 0.3    | 0.2    |
|                      | S093-4   | 73.9   | 15.0   | 0.4    | 6.0  | 0.1    | bdl    | 0.1    | 0.2    | 0.2    | 0.2    |
| S122                 | HDM 2475 | 88.00  | 5.2000 | 0.0154 |      | 0.0150 | 0.0277 | 0.0241 | 0.0049 | 0.2375 | 0.2    |
| Knobbed mace         | S122-1   | 87.1   |        | bdl    | n.a. |        | 0.0277 | bdl    | 0.0049 | 0.2373 |        |
|                      |          |        | 11.0   |        | 0.6  | 0.1    |        |        |        |        | 0.2    |
|                      | S122-2   | 82.5   | 15.2   | bdl    | 0.8  | 0.2    | 0.1    | bdl    | 0.1    | 0.4    | 0.2    |
|                      | S122-3   | 88.6   | 9.5    | bdl    | 0.7  | 0.1    | 0.1    | bdl    | 0.1    | 0.3    | 0.2    |
|                      | S122-4   | 88.1   | 10.0   | bdl    | 0.7  | 0.1    | 0.1    | bdl    | 0.1    | 0.3    | 0.3    |
|                      | S122-5   | 85.1   | 12.8   | bdl    | 0.8  | 0.1    | 0.1    | bdl    | 0.1    | 0.3    | 0.3    |
|                      | S122-6   | 87.5   | 10.5   | bdl    | 0.7  | 0.1    | 0.1    | bdl    | 0.1    | 0.4    | 0.3    |
| S134<br>Knobbed mace | HDM 2474 | 100.00 | 0.0040 | 3.3000 | n.a. | 0.0270 | 0.0156 | 0.0229 | 0.0000 | 0.0148 | 0.0013 |
| Knobbed mace         | S134-1   | 92.8   | 0.1    | 5.2    | 0.1  | 0.1    | bdl    | 0.1    | 0.1    | 0.9    | 0.2    |
|                      | S134-2   | 95.3   | bdl    | 3.2    | bdl  | 0.1    | 0.1    | 0.1    | 0.1    | 0.3    | 0.2    |
|                      | S134-3   | 95.6   | bdl    | 2.9    | bdl  | 0.1    | 0.1    | 0.1    | 0.1    | 0.3    | 0.2    |
|                      | S134-4   | 93.8   | 0.1    | 4.6    | 0.1  | 0.1    | 0.1    | 0.1    | 0.1    | 0.4    | 0.2    |
|                      | S134-5   | 94.9   | bdl    | 3.6    | bdl  | 0.1    | 0.1    | 0.1    | 0.1    | 0.3    | 0.2    |
|                      | S134-6   | 93.3   | 0.1    | 5.0    | 0.1  | 0.1    | 0.1    | 0.1    | 0.1    | 0.5    | 0.2    |
| S146                 | HDM 2478 | 95.00  | 9.6000 | 0.0073 | n.a. | 0.0083 | 0.0015 | 0.0350 | 0.0084 | 0.0450 | 0.0023 |
| Pin                  | S146-1   | 93.8   | 5.1    | bdl    | bdl  | 0.1    | 0.1    | bdl    | 0.1    | 0.2    | 0.2    |
|                      | S146-2   | 91.2   | 7.8    | bdl    | bdl  | 0.1    | 0.1    | bdl    | 0.1    | 0.2    | 0.2    |
|                      | S146-3   | 92.3   | 6.7    | bdl    | bdl  | 0.1    | 0.1    | bdl    | 0.1    | 0.2    | 0.2    |
|                      | S146-4   | 88.6   | 10.3   | bdl    | 0.1  | 0.1    | 0.1    | bdl    | 0.1    | 0.2    | 0.2    |
| S157                 | HDM 2479 | 70.00  | 0.0060 | 1.9700 | n.a. | 0.0330 | 0.0022 | 0.1100 | 0.0025 | 0.3200 | 0.0015 |
| Razor                | S157-1   | 92.2   | bdl    | 6.3    | bdl  | 0.1    | 0.1    | 0.2    | 0.1    | 0.3    | 0.2    |
|                      | S157-2   | 91.3   | bdl    | 7.2    | bdl  | 0.1    | 0.1    | 0.2    | 0.1    | 0.3    | 0.2    |
|                      | S157-3   | 89.1   | bdl    | 9.5    | bdl  | 0.1    | 0.1    | 0.2    | 0.1    | 0.2    | 0.2    |
| S181                 | HDM 2481 | 97.00  | 0.0060 | 4.3000 | n.a. | 0.1060 | 0.0020 | 0.0500 | 0.0003 | 0.0190 | 0.0006 |
| Shaft-hole axe       | S181-1   | 94.1   | 0.1    | 4.4    | 0.2  | 0.2    | 0.1    | 0.1    | 0.1    | 0.3    | 0.2    |
|                      | S181-2   | 91.2   | 0.1    | 7.5    | 0.1  | 0.2    | bdl    | 0.1    | 0.1    | 0.1    | 0.2    |
|                      | S181-3   | 90.7   | 0.1    | 8.0    | 0.1  | 0.1    | bdl    | 0.1    | 0.1    | 0.1    | 0.2    |
|                      | S181-4   | 94.0   | 0.1    | 4.5    | 0.1  | 0.2    | bdl    | 0.1    | 0.1    | 0.2    | 0.2    |
|                      | 5101 4   |        |        |        |      |        |        |        |        |        |        |

Table 5. Comparison between the analytical results of INAA (readings starting with 'HDM'; Pernicka 2000: table 1) and pXRF (starting with 'S'; the current study) on the same copper-based artefacts. Note that INAA analysis did not account for lead (Pb). Total can be more or less than 100%. Note: bdl = below detection limit; n.a. = not analysed.

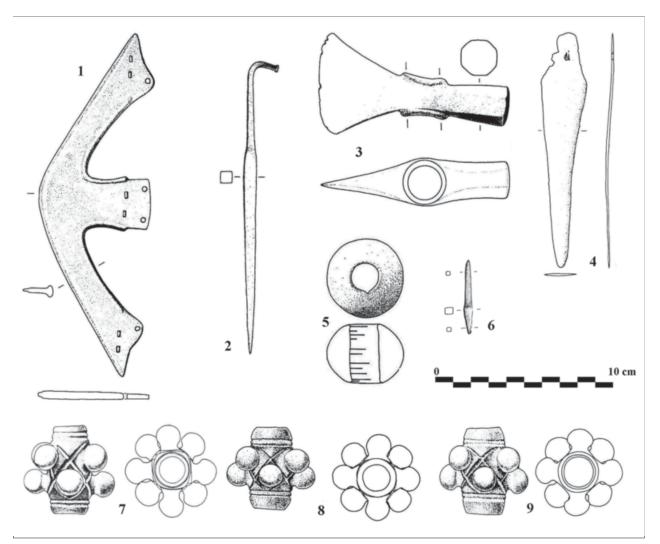
only sample a limited number of items from the settlement. With these limitations in mind, we analysed a total of 59 metal objects: seven from the settlement and 52 from the cemetery (figs 2–5, tables 6, 7). Out of these 59 artefacts, 38 could be dated with accuracy (one to three stratigraphic levels), while 21 grave goods could only be attributed to the K/L to 'Q' period. While copper-based objects form the majority of the samples (42 items), gold-based ones were also well represented (16), though we were able to analyse only one silver-based object and no lead artefacts (the latter due to heavy corrosion on all the lead pieces). In addition to these, we also included in the analysis artefacts sampled by Pernicka and not resampled by us – three gold/silver diadems and nine copper-based pieces – bringing the total number of analysed pieces to 71.

The Bruker Tracer IV-SD instrument used in this study is equipped with a  $10 \text{mm}^2 \text{ XFlash}^{\circledast} \text{ SDD}$  (silicon drift detector): typical resolution 145 KeV at 100,000 cps. The multichannel analyser has a 1,024 channel configuration. The x-ray tube type is a rhodium target with a maximum voltage of 40Kv at a current of 15µA. The instrument has a five-position computer-controlled filter changer. The filter used in this study was an A1-Ti filter of composition 0.012" (0.3048mm) aluminum and 0.001" (0.0254mm) titanium, which is the Bruker standard filter for metal alloy analysis, including copper alloys. Our settings were optimised at 40Kv and 15.6 µA. The instrument's detector window measures 5mm × 4mm, which allows for small fragments to be analysed. Analysis time was 90 seconds per reading.

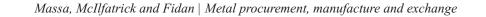


*Fig. 2. Analysed pins (1–6 and 9–19 from the necropolis, 7–8 from the settlement; for references, see table 6): (1) S076; (2) S113; (3) S119; (4) S178; (5) S055; (6) S060; (7) S211; (8) S207; (9) S015; (10) S112; (11) S117; (12) S049; (13) S051; (14) S194; (15) S011; (16) S034; (17) S114; (18) S042; (19) S146.* 

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*Fig. 3. Analysed weapons (1–5 and 7–9 from the necropolis, 6 from the settlement; for references, see table 6): (1) S046 crescentic axe; (2) S093 poker spearhead; (3) S181 shafthole battleaxe; (4) S100 dagger; (5) S089 round macehead; (6) S223 arrow(?); (7) S056 knobbed macehead; (8) S122 knobbed macehead; (9) S134 knobbed macehead.* 



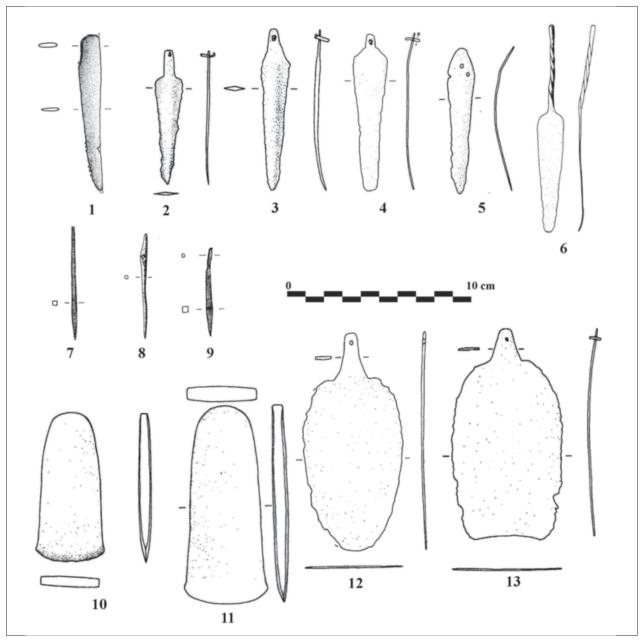


Fig. 4. Analysed tools and toiletry items (2–6, 8 and 10–13 from the necropolis, 1, 7 and 9 from the settlement; for references, see table 6): (1) S218 knife; (2) S116 knife/small dagger; (3) S172 knife/small dagger; (4) S188 knife/small dagger; (5) S174 knife/small dagger; (6) S078 spatula; (7) S217 awl; (8) S024 needle; (9) S226 awl; (10) S068 flat axe/hatchet; (11) S057 flat axe/hatchet; (12) S157 razor; (13) S141 razor.

| Bibliography               | Seeher 2000: 72, | fig. 18-G.53b |        |        | Seeher 2000: 73,<br>fig. 19-G.62b | Seeher 2000: 75, | fig. 20-G.82b |        | Seeher 2000: 77, | fig. 21-G.88c  |        |        |        | Seeher 2000: 78, | fig. 23-G.100b    |        | Seeher 2000: 78, | fig. 23-G.100f    |               |               |               |               | Seeher 2000: 79,            | fig. 23-G.105b |        | Seeher 2000: 81,            | fig. 24-G.118b |        | Seeher 2000: 82, | fig. 25-G.131b   |             | Seeher 2000: 82, | fig. 25-G.132a |        |              |              | Seeher 2000: 82, | fig. 25-G.132b |              |        |
|----------------------------|------------------|---------------|--------|--------|-----------------------------------|------------------|---------------|--------|------------------|----------------|--------|--------|--------|------------------|-------------------|--------|------------------|-------------------|---------------|---------------|---------------|---------------|-----------------------------|----------------|--------|-----------------------------|----------------|--------|------------------|------------------|-------------|------------------|----------------|--------|--------------|--------------|------------------|----------------|--------------|--------|
| Reading L<br>location      | Head S           | Shaft f       | Shaft  | Shaft  | Tip                               | Shaft S          | Shaft f       | Shaft  | Head             | Head           | Shaft  | Shaft  | Shaft  | Head             | Shaft f           | Shaft  | Side A, blade S  | Side A, blade f   | Side A, blade | Side B, blade | Side B, blade | Side B, blade | Head                        | Shaft f        | Shaft  | Head S                      | Shaft f        | Shaft  | Head             | Shaft f          | Shaft       | Rim (top) S      | Knob f         | Knob   | Rim (bottom) | Rim (bottom) | Side A S         | Side A f       | Side B       | Side B |
| Sb<br>%                    | 0.1              | 0.1           | 0.1    | 0.1    | 0.1                               | 0.1              | 0.1           | 0.2    | 0.2              | 0.2            | 0.2    | 0.2    | 0.2    | 0.1              | 0.1               | 0.1    | 0.1              | 0.1               | 0.1           | 0.1           | 0.1           | 0.1           | 0.1                         | 0.1            | 0.1    | 0.1                         | 0.1            | 0.1    | 0.1              | 0.1              | 0.1         | 0.2              | 0.1            | 0.1    | 0.1          | 0.1          | 0.1              | 0.1            |              | 0.1    |
| Bi<br>%                    | lbd              | lbd           | lbd    | lbd    | lbd                               | lbd              | lbd           | 0.1    | lbd              | lbd            | lbd    | lbd    | lbd    | lbd              | lbd               | lbd    | 0.1              | 0.1               | lbd           | 0.1           | 0.1           | 0.1           | lbd                         | lbd            | lþd    | lbdl                        | 0.1            | 0.1    | lbd              | lbd              | 0.1         | 0.1              | 0.1            | lbd    | 0.1          | 0.1          | 0.1              | 0.1            | Ipq :        | lþd    |
| Au<br>%                    | 0.1              | 0.1           | 0.1    | 0.1    | 0.1                               | 0.1              | 0.1           | 0.1    | 0.1              | 0.1            | 0.1    | 0.1    | 0.1    | 0.1              | 0.1               | 0.1    | 0.1              | 0.1               | 0.1           | 0.1           | 0.1           | 0.1           | 0.1                         | 0.1            | 0.1    | 0.1                         | 0.1            | 0.1    | 0.1              | 0.1              | 0.1         | 0.2              | 0.4            | 0.1    | 0.2          | 0.2          | 0.1              | 0.1            | 0.1          | 0.1    |
| Zn<br>%                    | 0.2              | 0.2           | 0.2    | 0.2    | 0.2                               | 0.2              | 0.2           | 0.2    | 0.2              | 0.2            | 0.2    | 0.2    | 0.2    | 0.2              | 0.2               | 0.2    | 0.2              | 0.2               | 0.2           | 0.2           | 0.2           | 0.2           | 0.2                         | 0.2            | 0.2    | 0.2                         | 0.2            | 0.2    | 0.2              | 0.2              | 0.3         | 0.2              | 0.2            | 0.2    | 0.2          | 0.2          | 0.2              | 0.2            | 0.2          | 0.2    |
| Ni<br>%                    | 0.1              | 0.1           | 0.1    | 0.1    | 0.1                               | 0.1              | 0.1           | 0.1    | 0.1              | 0.1            | 0.1    | 0.1    | 0.1    | 0.1              | 0.1               | 0.1    | 0.1              | 0.1               | 0.1           | 0.1           | 0.1           | 0.1           | 0.1                         | 0.1            | 0.1    | 0.1                         | 0.1            | 0.1    | 0.1              | 0.1              | 0.1         | 0.1              | lbd            | 0.1    | 0.1          | lbdl         | 0.1              | 0.1            | 0.1          | 0.1    |
| Fe%                        | 0.2              | 0.2           | 0.2    | 0.2    | 0.5                               | 0.2              | 0.2           | 0.2    | 0.3              | 0.2            | 0.2    | 0.2    | 0.2    | 0.3              | 0.2               | 0.2    | 0.2              | 0.1               | 0.2           | 0.3           | 0.2           | 0.3           | 0.2                         | 0.2            | 0.2    | 0.3                         | 0.3            | 0.3    | 0.2              | 0.2              | 0.1         | 0.3              | 0.2            | 0.4    | 0.3          | 0.5          | 0.2              | 0.2            | 0.3          | 0.2    |
| $^{Ag}_{\%}$               | 0.1              | 0.1           | 0.1    | 0.2    | 4.6                               | 0.2              | 0.2           | 0.2    | 0.1              | 0.1            | 0.1    | 0.1    | 0.1    | lbdl             | 0.1               | lbd    | 0.1              | 0.1               | 0.1           | 0.1           | 0.1           | 0.1           | 0.1                         | 0.1            | 0.2    | 0.2                         | 0.2            | 0.2    | 0.2              | 0.2              | 0.3         | lbd              | 0.1            | lbd    | lbdl         | lbdl         | 0.1              | 0.1            | 0.1          | 0.1    |
| Pb %                       | 0.1              | lbd           | 0.1    | 0.1    | 0.1                               | 0.1              | 0.1           | 0.2    | 0.3              | 0.2            | 0.2    | 0.6    | 0.3    | 0.2              | 0.2               | 0.1    | lbd              | lbd               | lbd           | lbd           | lbd           | lbd           | 0.1                         | 0.1            | 0.1    | 0.1                         | 0.2            | 0.1    | 0.1              | 0.2              | 0.2         | 8.3              | 9.6            | 6.0    | 9.2          | 9.2          | lbd              | lbdl           |              | lbdl   |
| Sn<br>%                    | 0.1              | 0.1           | 0.1    | 0.1    | 0.5                               | 0.1              | 0.1           | 0.2    | 0.1              | 0.1            | 0.2    | 0.2    | 0.2    | 6.7              | 7.0               | 5.8    | lbd              | lbd               | lbd           | lbd           | lbd           | lbd           | 0.1                         | 0.1            | 0.1    | 0.1                         | 0.1            | 0.1    | 0.1              | 0.1              | 0.2         | 13.8             | 18.7           | 9.1    | 12.4         | 11.9         | lbd              | 0.1            | 0.1          | lbdl   |
| $\frac{As}{\%}$            | 1.9              | 0.4           | 1.7    | 1.6    | 1.6                               | 0.4              | 0.8           | 0.3    | 2.0              | 1.7            | 1.0    | 3.3    | 1.8    | 0.8              | 0.6               | 0.3    | 12.5             | 12.2              | 8.0           | 8.7           | 15.0          | 11.7          | 3.2                         | 1.0            | 2.2    | 2.7                         | 6.2            | 3.6    | 1.7              | 2.2              | 0.9         | 0.4              | 0.8            | 0.2    | 0.6          | 0.6          | 0.6              | 0.5            | 0.5          | 0.7    |
| Cu<br>%                    | 96.7             | 98.2          | 96.8   | 96.8   | 91.9                              | 98.1             | 97.7          | 97.9   | 96.2             | 96.7           | 97.4   | 94.7   | 96.4   | 91.2             | 9.06              | 92.5   | 86.1             | 86.5              | 90.6          | 89.9          | 83.7          | 86.8          | 95.4                        | 97.5           | 96.2   | 95.6                        | 92.1           | 94.7   | 9.96             | 96.1             | 97.3        | 74.6             | 63.6           | 83.4   | 75.1         | 75.8         | 98.1             | 98.2           | 98.1         | 98.0   |
| Total                      | 99.5             | 99.5          | 99.5   | 99.6   | 99.7                              | 99.5             | 9.66          | 9.66   | 99.7             | 99.7           | 9.66   | 99.7   | 9.66   | 9.66             | 9.66              | 9.66   | 99.5             | 99.5              | 99.5          | 99.5          | 99.5          | 9.66          | 99.5                        | 99.5           | 99.5   | 9.66                        | 99.6           | 99.6   | 99.5             | 99.5             | 9.66        | 98.0             | 94.2           | 99.5   | 98.3         | 98.6         | 99.5             | 99.5           | 99.5<br>22 - | 99.5   |
| Weight Reading<br>(gr) no. | S011-1           | S011-2        | S011-3 | S011-4 | S015-1                            | S024-1           | S024-2        | S024-3 | S034-1           | S034-2         | S034-3 | S034-4 | S034-5 | S042-1           | S042-2            | S042-3 | S046-1           | S046-2            | S046-3        | S046-4        | S046-5        | S046-6        | S049-1                      | S049-2         | S049-3 | S051-1                      | S051-2         | S051-3 | S055-1           | S055-2           | S055-3      | S056-1           | S056-2         | S056-3 | S056-4       | S056-5       | S057-1           | S057-2         | S057-3       | S057-4 |
| Weight (gr)                |                  |               | • •    |        |                                   |                  |               | •      |                  | •              | •      | •      | • •    | •                | •                 |        | 184              |                   | •             |               |               | •             |                             |                |        | 11.1                        |                |        | 2.8              |                  | • •         | 232              |                | •      | • •          | •            | 287              | •              |              |        |
| Alloy                      | Unalloyed        |               |        |        | Silver-<br>copper                 | Unalloyed        |               |        | Arsenical        | copper         |        |        |        | Tin bronze       |                   |        | Arsenical        | copper            |               |               |               |               | Arsenical                   | copper         |        | Arsenical                   | copper         |        | Arsenical        | copper           |             | Tin-leaded       | bronze         |        |              |              | Unalloyed        |                |              |        |
| Surface<br>preservation    |                  | in patches    |        |        | Light corrosion                   | Corrosion patina | in patches    |        |                  | in many places |        |        |        |                  | patina in patches |        |                  | patina in patches |               |               |               |               | Toggle pin Corrosion patina | in many places |        | Toggle pin Corrosion patina | in many places |        | Light corrosion  | covering most of | the surface | Little corrosion |                |        |              |              | Little corrosion |                |              |        |
| Type                       | Toggle pin       |               |        |        | Toggle pin                        | Needle           |               |        | Toggle pin       |                |        |        |        | Toggle pin       |                   |        | Crescentic       | ахе               |               |               |               |               | Toggle pin                  |                |        | Toggle pin                  |                |        | Pin              |                  |             | Knobbed          | mace           |        |              |              | Flat axe         |                |              |        |
| Context                    | G.53             |               |        |        | G.62                              | G.82             |               |        | G.88             |                |        |        |        | G.100            |                   |        | G.100            |                   |               |               |               |               | G.105                       |                |        | G.118                       |                |        | G.131            |                  |             | G.132            |                |        |              |              | G.132            |                |              |        |
| Exc.<br>no.                |                  | Nr. 165       |        |        | DHN<br>Nr. 186                    | DHN              | Nr. 343       |        |                  | Nr. 415        |        |        |        |                  | Nr. 307           |        | -                | Nr. 305           |               |               |               |               |                             | Nr. 324        |        |                             | Nr. 341        |        |                  | Nr. 421          |             |                  | Nr. 408        |        |              |              |                  | Nr. 409        |              |        |
| Site                       | Demircihüyük     | necropolis    |        |        | Demircihüyük<br>necropolis        | Demircihüyük     | necropolis    |        | Demircihüyük     | necropolis     |        |        |        | Demircihüyük     | necropolis        |        | Demircihüyük     | necropolis        |               |               |               |               | Demircihüyük                | necropolis     |        | Demircihüyük                | necropolis     |        | Demircihüyük     | necropolis       |             | Demircihüyük     | necropolis     |        |              |              | Demircihüyük     | necropolis     |              |        |
| Sample Site<br>no.         | SO11             |               |        |        | S015                              | S024             |               |        | S034             |                |        |        |        | S042             |                   |        | S046             |                   |               |               |               |               | S049                        |                |        | S051                        |                |        | S055             |                  |             | S056             |                |        |              |              | S057             |                |              |        |

| Seeher 2000: 83, | fig. 25-G.141d |        | Seeher 2000: 86, | fig. 28-G.171    |               |        |        | Seeher 2000: 91, | fig. 30-G.213g |           |           | Seeher 2000: 91, | fig. 30-G.2131 |        |        |        | Seeher 2000: 94, | fig. 33-G.243b |               |        | Seeher 2000: 95, | fig. 33-G.243g  |               |               |               | Seeher 2000: 97, | fig. 34-G.266a |        | Seeher 2000:     | 100, fig. 36- | G.295h | Seeher 2000:     | 101, fig. 37- | G.299b |        | Seeher 2000:           | 101, fig. 37- | G.300a            | told > 1 wt%.   |
|------------------|----------------|--------|------------------|------------------|---------------|--------|--------|------------------|----------------|-----------|-----------|------------------|----------------|--------|--------|--------|------------------|----------------|---------------|--------|------------------|-----------------|---------------|---------------|---------------|------------------|----------------|--------|------------------|---------------|--------|------------------|---------------|--------|--------|------------------------|---------------|-------------------|---|
| Head             | Shaft          | Shaft  | Side A S         | Side A 1         | Side A        | Side B | Side B | Head             | Shaft          | Shaft     | Shaft     | Tang             | Tang           | Blade  | Blade  | Blade  |                  |                |               |        | Side A, shaft    | Side A, shaft 1 | Side B, shaft | Side B, shaft | Side C, shaft | Near rivet hole  | Blade          | Blade  | Head             | Head          | Head   | Head             | Shaft         | Shaft  | Shaft  | Head                   | Shaft         | Shaft             | Table 6. PXRF analytical results for copper-based artefacts. Elements shaded in light grey (1–2 wt%) might indicate intentional alloy, if we consider the thresh            |
| 0.1 F            | 0.1 S          | 0.1 S  | 0.1 S            | 0.1 S            | 0.1 S         | 0.1 S  | 0.1 S  | 0.5 F            | 0.3 S          | 0.7 S     | 0.5 S     | 0.3 T            | 0.2 J          | 0.1 E  | 0.1 E  | 0.1 E  | 0.1              | 0.1            | 0.1           | 0.1    | 0.1 S            | 0.1 S           | 0.1 S         | 0.1 S         | 0.1 S         | 0.1              | 0.1 E          | 0.1 E  |                  | 0.1 F         | 0.1 F  | 0.3 F            | 0.3 S         | 0.3 S  | 0.3 S  | 0.1 F                  | 0.1 S         | 0.1 S             | onsid   |
| 0.3              | 0.5            | 0.5    | lbd              | lbdl             | lþd           | lbd    | lpd    | 0.2              | 0.1            | 0.3       | 0.1       | 0.7              | 0.7            | 0.2    | 0.4    | 0.5    | 0.1              | 0.1            | 0.1           | lpd    | lbd              | lbd             | lbd           | lbd           | 0.1           | lpd              | lbd            | lbdl   | lþd              | lbd           | lbd    | 0.1              | 0.1           | 0.2    | 0.2    | lbd                    | lbd           | lbd               | we c  |
| 0.1              | 0.1            | 0.1    | 0.1              | 0.1              | 0.1           | 0.1    | 0.1    | 0.3              | 0.1            | 0.6       | 0.3       | 0.1              | 0.1            | 0.1    | 0.1    | 0.1    | 0.1              | 0.1            | 0.1           | 0.1    | 0.2              | 0.3             | 0.2           | 0.2           | 0.3           | 0.1              | 0.1            | 0.1    | 0.1              | 0.1           | 0.1    | 0.2              | 0.2           | 0.2    | 0.2    | 0.1                    | 0.1           | 0.1               | loy, ij   |
| 0.7              | 0.2            | 0.2    | 0.3              | 0.3              | 0.3           | 0.3    | 0.3    | 0.2              | 0.2            | 0.2       | 0.2       | 0.2              | 0.2            | 0.2    | 0.2    | 0.2    | 0.2              | 0.2            | 0.2           | 0.2    | 0.2              | 0.2             | 0.2           | 0.2           | 0.2           | 0.2              | 0.2            | 0.2    | 0.2              | 0.2           | 0.2    | 0.2              | 0.2           | 0.2    | 0.2    | 0.3                    | 0.2           | 0.2               | ial al  |
| 0.1              | 0.1            | 0.1    | 0.1              | 0.1              | 0.1           | 0.1    | 0.1    | 0.1              | 0.1            | 0.1       | 0.1       | 0.1              | 0.1            | 0.1    | 0.1    | 0.1    | 0.1              | 0.1            | 0.1           | 0.1    | 0.1              | 0.1             | 0.1           | 0.1           | 0.1           | 0.1              | 0.1            | 0.1    | 0.1              | 0.1           | 0.1    | 0.1              | 0.1           | 0.1    | 0.1    | 0.1                    | lbd           | 0.1               | ention  |
| 0.2              | 0.2            | 0.2    | 0.6              | 0.6              | 0.5           | 0.5    | 0.5    | 0.7              | 0.3            | 0.5       | 0.5       | 0.2              | 0.2            | 0.2    | 0.2    | 0.2    | 0.3              | 0.2            | 0.2           | 0.2    | 0.2              | 0.1             | 0.3           | 0.2           | 0.1           | 0.2              | 0.2            | 0.2    | 0.3              | 0.2           | 0.2    | 0.8              | 0.7           | 0.5    | 0.6    | 0.8                    | 0.5           | 0.2               | e inte  |
| C.U              | 0.4            | 0.3    | 0.1              | 0.1              | 0.1           | 0.1    | 0.1    | 0.1              | 0.1            | 0.2       | 0.1       | 0.5              | 0.5            | 0.3    | 0.3    | 0.4    | 0.1              | 0.1            | 0.1           | 0.1    | lbd              | 0.1             | 0.1           | 0.1           | 0.1           | 0.1              | 0.1            | 0.1    | 0.1              | 0.1           | 0.1    | 0.1              | lbdl          | lbd    | 0.1    | 0.1                    | 0.1           | 0.1               | Idicai  |
| C.U              | 0.7            | 1.4    | lbd              | lbdl             | lbd           | lbd    | lpd    | 6.1              | 1.9            | 5.4       | 6.2       | 1.7              | 2.3            | 1.4    | 1.3    | 2.7    | lpq              | lpd            | lpd           | lpd    | 3.8              | 5.7             | 3.8           | 5.9           | 6.0           | lbd              | lbd            | lbdl   | 0.1              | 0.1           | 0.1    | 0.7              | 0.7           | 0.7    | 0.6    | 0.1                    | 0.1           | 0.1               | ght in  |
| 0.1              | 0.1            | 0.2    | 0.1              | 0.1              | 0.1           | lbd    | 0.1    | 14.8             | 8.7            | 20.9      | 14.6      | 0.3              | 0.3            | 0.1    | 0.1    | 0.1    | lþd              | lþd            | lþd           | lþd    | 13.9             | 17.2            | 15.0          | 15.0          | 16.4          | 0.1              | 0.0            | 0.0    | 0.1              | 0.1           | 0.1    | 21.6             | 16.5          | 16.6   | 18.3   | 0.1                    | 0.1           | 0.1               | 6) mi   |
| 1.1              | 0.9            | 1.0    | 0.6              | 0.6              | 0.5           | 0.5    | 0.5    | 3.5              | 1:1            | 6.3       | 3.6       | 0.9              | 5.3            | 1.6    | 1.0    | 2.1    | lpq              | lpq            | lpq           | lpq    | 0.2              | 0.5             | 0.2           | 0.4           | 0.5           | 1.8              | 3.1            | 2.6    |                  | 0.2           | 0.2    | 1.5              | 1.0           | 1.1    | 1.0    | 2.3                    | 5.1           | 1.4               | 2 wt%   |
| 20.1             | 9.96           | 96.0   | 97.6             | 97.7             | 97.8          | 97.9   | 98.0   | 70.8             | 86.8           | 55.4      | 71.1      | 95.4             | 90.7           | 95.6   | 96.1   | 93.9   | 98.6             | 98.6           | 98.6          | 98.6   | 80.1             | 72.9            | 78.6          | 75.9          | 73.6          | 96.8             | 95.5           | 96.0   |                  | 98.2          | 98.1   | 73.4             | 79.9          | 79.4   | 77.8   | 95.9                   | 93.2          | 97.3              | y (1  |
| 77.0             | 99.9           | 100.0  | 9.66             | 9.66             | 9.66          | 9.66   | 9.66   | 97.3             | 99.7           | 90.5      | 97.3      | 100.3            | 100.5          | 9.99   | 100.0  | 100.3  | 99.5             | 99.5           | 99.5          | 99.5   | 98.8             | 97.2            | 98.6          | 98.0          | 97.4          | 99.5             | 99.5           | 99.5   | 99.5             | 99.5          | 99.5   | 99.0             | 99.5          | 99.4   | 99.4   | 99.7                   | 9.66          | 99.5              | ht gre.   |
| 1-0000           | S060-2         | S060-3 | S068-1           | S068-2           | S068-3        | S068-4 | S068-5 | S076-1           | S076-2         | S076-3    | S076-4    | S078-1           | S078-2         | S078-3 | S078-4 | S078-5 | S089-1           | S089-2         | S089-3        | S089-4 | S093-1           | S093-2          | S093-3        | S093-4        | S093-5        | S100-1           | S100-2         | S100-3 | S112-1           | S112-2        | S112-3 | S113-1           | S113-2        | S113-3 | S113-4 | S114-1                 | S114-2        | S114-3            | d in ligh   |
|                  |                |        |                  |                  |               |        |        |                  |                |           |           | 4.1              |                |        |        |        | 264              |                |               |        |                  |                 |               |               |               | 18.6             |                |        | 6.8              |               |        |                  |               |        |        |                        |               |                   | shadea  |
| Unalloyed        |                |        | Unalloyed        |                  |               |        |        | Tin-             | arsenic-       | lead cop- | per alloy | Arsenic          | lead           | copper | alluy  |        | Native           | copper         |               |        | Tin-leaded       | bronze          |               |               |               | Arsenical        | copper         |        | Unalloyed        |               |        | Tin bronze       |               |        |        | Arsenical              | copper        |                   | Elements  |
| а                | in many places |        |                  | corrosion patina | everywhere on |        |        | patina           | in patches     |           |           | Almost no        | corrosion      | -      | _      |        |                  |                | small patches |        |                  | corrosion       |               |               |               | Light corrosion  | patina         |        | Corrosion patina | in patches    |        | Small patches of | corrosion     |        |        | Toggle pin Most of the |               | darker than usual | Table 6. PXRF analytical results for copper-based artefacts. Elements shaded in light grey (1–2 wt%) might indicate intentional alloy, if we consider the threshold > 1 wt% |
| Pin              |                |        | Flat axe         |                  |               |        |        | Pin              |                |           |           | Spatula          |                |        |        |        | Round            | mace           |               |        | Poker            | spear           |               |               |               | Dagger           |                |        | Toggle pin       |               |        | Pin              |               |        |        | Toggle pin             |               |                   | or copper-  |
| G.141            |                |        | G.171            |                  |               |        |        | G.213            |                |           |           | G.213            |                |        |        |        | G.243            |                |               |        | G.243            |                 |               |               |               | G.266            |                |        | G.295            |               |        | G.299            |               |        |        | G.300                  |               |                   | esults fo   |
| NHU              | Nr. 486        |        |                  | Nr. 497          |               |        |        | DHN              | Nr. 829        |           |           | DHN              | Nr. 838        |        |        |        |                  | Nr. 795        |               |        |                  | Nr. 794         |               |               |               | DHN              | Nr. 605        |        | DHN              | Nr. 662       |        |                  | Nr. 697       |        |        |                        | Nr. 772       |                   | ytical r  |
| Demircihüyük     | necropolis     |        | Demircihüyük     | necropolis       |               |        |        | Demircihüyük     | necropolis     |           |           | Demircihüyük     | necropolis     |        |        |        | Demircihüyük     | necropolis     |               |        | Demircihüyük     | necropolis      |               |               |               | Demircihüyük     | necropolis     |        | Demircihüyük     | necropolis    |        | yük              | necropolis    |        |        | yük                    | necropolis    |                   | S. PXRF anal  |
| S060             |                |        | S068             |                  |               |        |        | S076             |                |           |           | S078             |                |        |        |        | S089             |                |               |        | S093             |                 |               |               |               | S100             |                |        | S112             |               |        | S113             |               |        |        | S114                   |               |                   | Table (   |

| 5      Daget      Carceion patina      Areancial      8/9      11/6      9/9      9/1      10     <   | Exc.<br>no. | Conte. | Context Type | Surface<br>preservation | Alloy            | Weight<br>(gr) | Reading<br>no. | Total | Cu<br>% | As<br>%  | Sn H<br>% | Pb / | Ag<br>%  | Fe N<br>% | Ni<br>% 9 | Zn Au<br>% % |          | Bi Sb<br>% % | Reading location  | Bibliography   |
|---|-------------|--------|--------------|-------------------------|------------------|----------------|----------------|-------|---------|----------|-----------|------|----------|-----------|-----------|--------------|----------|--------------|-------------------|--|
| In publics      coppet      S116-2      995      64.      21      0.1      0.2      0.1      0.2      0.1      0.2      0.1      0.2      0.1      0.2      0.1      0.2      0.1      0.2      0.1      0.1      0.2      0.1      0.2      0.1      0.2      0.1      0.2      0.1      0.1      0.2      0.1      0.1      0.1      0.2      0.1      0.1      0.1      0.1      0.2      0.1  | G.305       |        | Dagger       |                         |                  | 8.9            | S116-1         |       |         |          |           |      |          |           |           |              |          |              | 1 Near rivet hole |  |
| Image: consisting line basis      SI16-3      995      964      21      01      02      01      03      01  | Nr. 740     |        |              |                         | copper           |                | S116-2         |       |         |          |           |      |          |           |           |              |          |              | 1 Blade           | 102, fig. 37-  |
| International point      Silidad      Silidad <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>S116-3</td> <td></td> <td>BCUC.D</td>   |             |        |              |                         |                  |                | S116-3         |       |         |          |           |      |          |           |           |              |          |              |                   | BCUC.D   |
| jiii Curresion putina      Arsenical      8.4      S1172      99.5      95.4      21      0.1      0.1      0.2      0.1      bull        In patchess      copper      S1172      99.6      95.7      56      0.1      0.1      0.0      0.1  |             |        |              |                         |                  |                | S116-4         | -     |         |          | _         |      |          | _         | _         |              | _        | _            | 2 Near rivet hole | 0  |
| In parches      copper      S1172      99.6      97.7      56      0.1      0.1      0.6      0.1      0.2      0.1      built        Uniform      Uniform      Unallyed      28      117.2      99.5      97.0      1.5      0.1 <td< td=""><td>G.305</td><td></td><td>Toggle pi</td><td></td><td>Arsenical</td><td>8.4</td><td>S117-1</td><td></td><td></td><td></td><td>_</td><td>_</td><td>_</td><td></td><td></td><td></td><td>_</td><td></td><td></td><td>Seeher 2000:</td></td<>   | G.305       |        | Toggle pi    |                         | Arsenical        | 8.4            | S117-1         |       |         |          | _         | _    | _        |           |           |              | _        |              |                   | Seeher 2000:   |
| Image: bit in the part of the p   | Nr. 741     |        |              |                         | copper           |                | S117-2         |       |         | _        | -         | _    | _        |           | _         |              | _        |              |                   | 102, fig. 37-  |
| Image      SI17-4      996      953      2.8      0.2      0.3      0.1      0.1      0.1        networksion in glided      Unalloyed      2.8      S119-1      1004      0.6      n.d.      n.d. <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>S117-3</td> <td></td> <td>l Shaft</td> <td>UC.DU</td>   |             |        |              |                         |                  |                | S117-3         |       |         |          |           |      |          |           |           |              |          |              | l Shaft           | UC.DU  |
|   |             |        |              |                         |                  |                | S117-4         |       | _       |          |           |      |          |           |           |              |          |              | 2 Shaft           |  |
| corresion on<br>shaft<br>(held)      (bit)<br>(bit)<br>(held)      (bit)<br>(bit)<br>(bit)<br>(held)      (bit)<br>(bit)<br>(bit)<br>(held)      (bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit)<br>(bit) | DHN G.309   |        | Pin          |                         | Unalloyed        | 2.8            | S119-1         |       | -       | <u> </u> | <u> </u>  |      |          |           | <u> </u>  |              |          | <u> </u>     | l. Head           | Seeher 2000:   |
| Bibit<br>(bead)      guided<br>(bead)      S119-3      99.8      97.6      bdl      0.2      0.8      0.1      0.3      0.1      0.1        d      Verylight<br>corresionian<br>(evortisionian      Tim bronze      215.4      512.2-1      99.7      87.1      bdl      0.5      0.1      0.2      0.3      0.1      0.2      0.1      bdl      bdl      bdl      0.3      0.1      0.2      0.1      bdl      bdl      bdl      bdl      0.1      0.2      0.1      0.1      bdl      b  | Nr. 764     |        |              | sion on                 | (shaft)/         |                | S119-2         |       |         |          |           |      |          |           |           |              |          | -            | 1. Head           | 102, fig. 38-  |
| Image: constraint in the constratend of the constraint in the constraint in the constraint in the   |             |        |              |                         | gilded<br>(head) |                | S119-3         |       |         |          |           |      |          |           |           | <u> </u>     |          |              | 2 Shaft           | G.309c   |
| Impondent      Timbronze      Tisk      Sizz-2      99.7      87.1      bit      Dis      Dis <thdis< th="">      Dis      Dis</thdis<>   |             |        |              |                         | (IICaU)          |                | S119-4         |       |         |          |           |      |          |           |           |              |          |              | 2 Shaft           |  |
| corresion in a<br>few of the knobs      space  | DHN G.316   |        | Knobbed      |                         | Tin bronze       | 215.4          | S122-1         |       |         |          |           |      |          |           |           |              |          |              | 1 Rim (top)       | Seeher 2000:   |
| lew of the knobs      size      bold      9.5      0.7      bold      0.2      0.1      0.2      0.1      bold        A      very of the knobs      212.4      997      88.1      bold      0.0      0.1      0.1      0.3      0.1      bold      bold        212.4      99.7      88.1      bold      0.1      0.1      0.3      0.1      0.3      0.1      bold      bold <td< td=""><td>Nr. 951</td><td></td><td>mace</td><td>corrosion in a</td><td></td><td></td><td>S122-2</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>2 Knob</td><td>103, fig. 38-</td></td<>  | Nr. 951     |        | mace         | corrosion in a          |                  |                | S122-2         |       |         |          |           |      |          |           |           |              |          |              | 2 Knob            | 103, fig. 38-  |
| 4      Cronsion in patches      S1224      997      88.1      bd1      0.7      bd1      0.3      0.1      0.3      0.1      bd1        4      Cronsion in patches      Arsenical      207.5      99.7      85.1      0.1      10.3      0.1      0.3      0.1      0.1      bd1      bd1        5122-5      99.7      87.5      bd1      0.1      0.1      0.1      0.1      0.1      0.1      0.1      0.1      0.1      bd1      bd1 <td></td> <td></td> <td></td> <td>few of the knobs</td> <td></td> <td></td> <td>S122-3</td> <td></td> <td>l Knob</td> <td>G.316b</td>  |             |        |              | few of the knobs        |                  |                | S122-3         |       |         |          |           |      |          |           |           |              |          |              | l Knob            | G.316b   |
|   |             |        |              |                         |                  |                | S122-4         |       |         |          |           |      |          |           |           |              |          |              | l Knob            |  |
|   |             |        |              |                         |                  |                | S122-5         |       |         |          |           |      |          |           |           |              |          |              | 1 Rim (bottom)    |  |
| d      Corrosion in<br>patches      Arsenical<br>copper      207.6      S13.4.1      99.7      92.8      52.      0.1      0.1      0.3      0.1      0.2      0.1      bdl        patches      copper      S13.4.2      99.6      95.3      3.2      0.1      0.1      0.3      0.1      0.2      0.1      bdl      bdl        S13.4.2      99.6      95.3      3.2      0.1      0.1      0.3      0.1      0.2      0.1      bdl      bdl        S13.4.4      99.5      99.5      99.5      99.6      99.6      91.7      0.1      0.1      0.3      0.1  |             |        |              |                         |                  |                | S122-6         |       |         |          | -         |      |          |           |           |              |          |              | 1 Rim (bottom)    |  |
| patches      copper      S1342      99.6      95.3      3.2      0.1      0.1      0.2      0.1   | DHN G.335   |        | Knobbed      | Corrosion in            | Arsenical        | 207.6          | S134-1         | -     |         | -        | -         |      |          |           |           |              |          |              | 1 Rim (top)       | Seeher 2000:   |
| Rise      Si34-3      995      95.6      95.9      96.1      06.1      07.1      07.3      07.1      07.3      07.1 <t< td=""><td>Nr. 725</td><td></td><td>mace</td><td></td><td>copper</td><td></td><td>S134-2</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>l Knob</td><td>106, fig. 40-</td></t<>   | Nr. 725     |        | mace         |                         | copper           |                | S134-2         |       |         |          |           |      |          |           |           |              |          |              | l Knob            | 106, fig. 40-  |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$   |             |        |              |                         |                  |                | S134-3         |       |         |          |           |      |          |           | <u> </u>  | <u> </u>     |          |              | 1 Knob            |  |
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$   |             |        |              |                         |                  |                | S134-4         |       |         | _        |           |      |          |           |           |              |          |              | 1 Rim (bottom)    |  |
|   |             |        |              |                         |                  |                | S134-5         |       |         |          |           |      |          |           |           |              |          |              | l Knob            |  |
|   |             |        |              |                         |                  |                | S134-6         |       |         |          |           |      |          |           |           |              |          |              | 1 Rim (bottom)    |  |
|   | DHN G.350   |        | Razor        |                         | Arsenical        | 40.1           | S141-1         |       |         |          |           |      |          |           |           |              |          |              | 1 Side A          | Seeher 2000:   |
|   | Nr. 898     |        |              |                         | copper           |                | S141-2         |       |         |          |           |      |          |           |           |              |          |              | 1 Side B          | 108, fig. 41-  |
|   |             |        |              |                         |                  |                | S141-3         |       |         |          |           |      |          |           |           |              |          |              | 1 Side B          | G.350f   |
| $ \begin{array}{c c c c c c c c c c c c c c c c c c c $   | DHN G.372   |        | Ring         | n in                    | Silver-          | 1.7            | S144-1         |       |         |          |           |      |          |           |           |              |          |              | Ŧ                 | Seeher 2000:   |
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$   | 901         |        |              |                         | copper           |                | S144-2         |       |         |          | _         | _    |          |           |           |              |          |              | 1.                | $\begin{bmatrix} 109, \text{fig. 43-} \\ 6, 273 \end{bmatrix}$ |
| $ \begin{array}{ccccc} Toggle pin \\ Toggle pin \\ throughout, with \\ a few free \\ patches \\ patche$   |             |        | _            |                         |                  |                | S144-3         | _     | _       | _        | -         | _    | _        | -         | _         | _            | -        | -            | 1.                | 07/C.D   |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$   | DHN G.376   |        |              | n Quite corroded        | Tin bronze       | 53.2           | S146-1         |       |         |          |           |      |          |           |           |              |          |              | 1 Head            | Seeher 2000:   |
| $ \begin{array}{c c c c c c c c c c c c c c c c c c c $   | Nr. 942     |        |              | throughout, with        |                  |                | S146-2         |       |         | _        |           |      |          |           |           |              |          |              | 1 Head            | 111, fig. 43-  |
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$   |             |        |              | a tew tree              |                  |                | S146-3         |       |         |          |           |      | <u> </u> |           | <u> </u>  | <u> </u>     | <u> </u> |              | 1 Shaft           | G.3/6c   |
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$   |             |        |              | parentes                |                  |                | S146-4         |       |         | _        | _         |      |          |           |           |              |          |              | 1 Shaft           |  |
| $ \begin{array}{c c c c c c c c c c c c c c c c c c c $   | DHN G.421   |        |              | ni in                   | Arsenical        | 29.4           | S157-1         |       |         |          |           |      |          |           |           |              |          |              | 1 Side A          | Seeher 2000:   |
| $ \begin{array}{ c c c c c c c c c c c c c c c c c c c$   | Nr. 916     |        |              |                         | copper           |                | S157-2         |       |         |          |           |      |          |           |           |              |          |              | 1 Side A          | 115, fig. 45-  |
| Dagger      Corrosion in      Unalloyed      4.3      S172-1      99.7      97.0      1.2      0.1      0.3      0.2      0.1      0.2      0.1      0.2      0.1      0.2      0.1      0.2      0.1      0.1      0.2      0.1      0.1      0.2      0.1      0.1      0.2      0.1 </td <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>S157-3</td> <td></td> <td>1 Side B</td> <td>G.421b</td>  |             |        |              |                         |                  |                | S157-3         |       |         |          |           |      |          |           |           |              |          |              | 1 Side B          | G.421b   |
| S172-2      99.6      97.0      1.3      0.1      0.2      0.2      0.1      0.1      0.2      0.1      0.   | DHN G.479   | -      |              | Corrosion in            | Unalloyed        | 4.3            | S172-1         |       |         |          |           |      |          |           |           |              |          |              | 1 Near shoulder   |  |
| 99.6 96.9 1.4 0.1 0.2 0.2 0.1 0.1 0.1 0.2 0.1 0.1   | Nr.<br>1070 |        |              | patches                 |                  |                | S172-2         |       |         |          |           |      |          |           |           |              |          |              |                   | 120, fig. 48-  |
|   | 0           |        |              |                         |                  |                | S172-3         |       |         |          |           |      |          |           |           |              |          |              | 1 Blade           | 06/+.0   |

| Seeher 2000: | 121, tig. 48- | 0C04.D | Seeher 2000: | 122, fig. 49- | G.492b             | Seeher 2000:     | 122, fig. 49- | G.494b |         |        | Seeher 2000:  | 125, fig. 51-    | 0/10.0     |        | Seeher 2000:     | 127, fig. 52- | G.552b | Obladen      | Kauder 1996: | 382, pl. 156.3 | Obladen  | Kauder 1996: | 382, pl. 130./ | Obladen      | Kauder 1996: | 382, pl. 155.1 | Obladen Kauder      | 1996: 382,<br>pl. 155.2      | Obladen Kauder | 1996: 382, | pl. 155.7 | Obladen Kauder             | 1996: 382,    | pl. 155.10  | Obladen Kauder      | 1996: 382,    | pl. 155.12  | Table 6 (continued). PXRF analytical results for copper-based artefacts. Elements shaded in light grey (1–2 wt%) might indicate intentional alloy, if we consider the threshold |
|--------------|---------------|--------|--------------|---------------|--------------------|------------------|---------------|--------|---------|--------|---------------|------------------|------------|--------|------------------|---------------|--------|--------------|--------------|----------------|----------|--------------|----------------|--------------|--------------|----------------|---------------------|------------------------------|----------------|------------|-----------|----------------------------|---------------|-------------|---------------------|---------------|-------------|---|
| shoulder     |               | Blade  | Head         | Head          | Shaft              | Near shaft-hole  | Blade         | Blade  | On butt | Blade  | Near shoulder | Blade            | Blade      | Rivet  | Head             | Shaft         | Shaft  | Head         | Shaft        | Shaft          | Shaft    | Shaft        | Shaft          | Shaft        | Shaft        | Shaft          | Blade               | Blade                        | Shaft          | Shaft      | Shaft     | Shaft                      | Shaft         | Shaft       | Blade               | Blade         | Blade       | we consider   |
| -            |               | 0.2    | 0.2          | 0.2           | 0.2                | 0.2              | 0.2           | 0.1    | 0.2     | 0.2    | 0.3 ]         | 0.2              | 0.3 ]      | 0.6 ]  | 0.1              | 0.1           | 0.2    | 0.1          | 0.1          | 0.1            | 0.1      | 0.1          | 0.1            | 0.1          | 0.1          | 0.1            | 0.2                 | 0.1                          | 0.1            | 0.1        | 0.1       | 0.2                        | 0.2           | 0.2         | 0.3 ]               | 0.2           | 0.2 ]       | oy, if  |
| pq           | lbd           | lbdl   | 0.1          | lbd           | 0.1                | lbd              | lbd           | lbd    | lbd     | lbd    | 0.1           | 0.1              | 0.1        | 0.3    | lbd              | lbd           | 0.1    | lbd          | lbd          | 0.1            | 0.1      | 0.1          | 0.1            | lbd          | lbd          | lbd            | lbd                 | lþd                          | lbd            | lbd        | lbd       | 0.1                        | 0.1           | 0.1         | lbd                 | lbd           | lbd         | al all  |
| 0.1          | 0.1           | 0.1    | 0.1          | 0.1           | 0.1                | 0.1              | 0.1           | 0.1    | 0.1     | 0.1    | 0.3           | 0.2              | 0.2        | 0.4    | 0.1              | 0.1           | 0.1    | 0.1          | 0.1          | 0.1            | 0.1      | 0.1          | 0.1            | 0.1          | 0.1          | 0.1            | 0.1                 | 0.1                          | 0.1            | 0.1        | 0.1       | 0.1                        | 0.1           | 0.1         | 0.1                 | 0.1           | 0.1         | ntion   |
| 0.2          | 0.2           | 0.2    | 0.2          | 0.2           | 0.2                | 0.2              | 0.2           | 0.2    | 0.2     | 0.3    | 0.2           | 0.2              | 0.2        | 0.2    | 0.2              | 0.2           | 0.2    | 0.6          | 0.3          | 0.2            | 0.2      | 0.2          | 0.2            | 0.2          | 0.2          | 0.2            | 0.4                 | 0.4                          | 0.6            | 0.6        | 0.7       | 0.3                        | 0.3           | 0.3         | 0.3                 | 0.3           | 0.3         | te inte   |
| 0.1          | 0.1           | 0.1    | 0.1          | 0.1           | 0.1                | 0.1              | lbdl          | lbd    | lbd     | 0.1    | 0.1           | 0.1              | 0.1        | 0.4    | 0.1              | 0.1           | 0.1    | 0.1          | 0.1          | 0.1            | 0.1      | 0.1          | 0.1            | 0.1          | 0.1          | 0.1            | 0.1                 | 0.1                          | 0.1            | 0.1        | 0.1       | 0.1                        | 0.1           | 0.1         | 0.1                 | 0.1           | 0.1         | ıdicat  |
| 7.0          | 0.2           | 0.3    | 0.3          | 0.6           | 0.3                | 0.3              | 0.1           | 0.1    | 0.2     | 0.3    | 0.2           | 0.2              | 0.2        | 0.6    | 0.2              | 0.2           | 0.2    | 0.2          | 0.2          | 0.2            | 0.1      | 0.1          | 0.1            | 0.2          | 0.2          | 0.2            | 0.2                 | 0.2                          | 0.4            | 0.4        | 0.6       | 0.2                        | 0.2           | 0.2         | 0.2                 | 0.3           | 0.2         | ght ir  |
| 7.N          | 0.1           | 0.2    | 0.2          | 0.1           | 0.2                | 0.1              | 0.1           | 0.1    | 0.1     | 0.1    | 0.2           | 0.2              | 0.2        | lþd    | 0.1              | 0.1           | 0.2    | 1.5          | 1.0          | 1.4            | 3.1      | 0.7          | 2.4            | 0.2          | 0.3          | 0.3            | 0.2                 | 0.1                          | 0.1            | 0.2        | 0.2       | 0.2                        | 0.2           | 0.2         | 0.2                 | 0.2           | 0.3         | (o) mi  |
|              | 0.1           | 0.1    | 0.6          | 0.3           | 0.8                | 0.2              | 0.1           | 0.1    | 0.1     | 0.1    | 0.2           | 0.4              | 0.4        | 0.3    | 0.7              | 0.8           | 0.8    | 0.1          | 0.1          | 0.2            | 0.2      | 0.2          | 0.2            | 0.1          | 0.1          | 0.1            | 0.2                 | 0.1                          | 0.1            | 0.1        | 0.1       | 0.2                        | 0.2           | 0.3         | 0.1                 | 0.1           | 0.1         | -2 wt%  |
| 1.0          | lbd i         | 0.1    | 0.1          | 0.1           | 0.1                | 0.1              | 0.1           | 0.1    | 0.1     | 0.1    | 29.2          | 25.1             | 26.1       | 37.9   | 0.1              | 0.1           | 0.2    | 0.2          | 0.2          | 0.2            | 0.3      | 0.2          | 0.3            | 0.1          | 0.1          | 0.2            | 0.2                 | 0.1                          | 0.1            | 0.1        | 0.2       | 0.2                        | 0.2           | 0.2         | 0.2                 | 0.1           | 0.2         | y (1-   |
| 0.0          | 11.6          | 3.9    | 4.0          | 4.8           | 3.9                | 4.4              | 7.5           | 8.0    | 4.5     | 3.2    | 1.1           | 0.0              | 1.1        | 1.6    | 4.5              | 3.5           | 1.8    | 1.4          | 1.0          | 1.8            | 3.3      | 2.9          | 2.6            | 0.4          | 0.4          | 0.2            | 0.6                 | 1.3                          | 1 0.5          | 1 0.4      | 0.5       | 0.5                        | 0.4           | 9.0         | 1.7                 | 1.8           | 1.1         | ht gre  |
| 0.7.0        | 87.1          | 94.4   | 93.9         |               | 93.8               | 94.1             | 91.2          | 90.7   | 94.0    | 95.2   | 67.3          | : 71.9           | 70.2       | 56.5   | 93.6             | 94.4          | 95.9   | 95.3         | 96.5         | 95.0           | 91.8     | 94.7         | 93.3           | 98.0         | 98.0         | 98.1           | 97.5                | 97.0                         | 97.4           | 97.4       | 97.0      | 97.7                       | 97.6          | 97.3        | 96.5                | 96.5          | 97.2        | in lig  |
| 1.76         | 99.6          | 99.7   | 99.7         | 99.7          | 99.7               | 9.66             | 9.66          | 9.66   | 9.66    | 9.66   | 99.1          | 99.4             | 99.0       | 98.9   | 9.66             | 99.7          | 99.7   | 99.5         | 99.5         | 9.66           | 9.66     | 99.5         | 99.5           | 99.5         | 99.5         | 9.66           | 99.5                | 99.5                         | 99.5           | 99.5       | 99.5      | 9.66                       | 99.7          | 99.7        | 9.66                | 9.66          | 9.66        | aded  |
| 1-+/10       | S174-2        | S174-3 | S178-1       | S178-2        | S178-3             | S181-1           | S181-2        | S181-3 | S181-4  | S181-5 | S188-1        | S188-2           | S188-3     | S188-4 | S194-1           | S194-2        | S194-3 | S207-1       | S207-2       | S207-3         | S211-1   | S211-2       | S211-3         | S217-1       | S217-2       | S217-3         | S218-1              | S218-2                       | S223-1         | S223-2     | S223-3    | S226-1                     | S226-2        | S226-3      | S228-1              | S228-2        | S228-3      | ents shu  |
| ں<br>ا       |               |        | 2.9          |               | 1                  | 346              |               |        |         |        | 4.7           |                  |            |        | 2.7              | 1             |        | 2.6          |              |                | ы        |              |                |              |              |                |                     | 1                            |                | 1          |           |                            |               | 1           |                     | 1             |             | . Elem  |
| Arsenical    | copper        |        | Arsenical    | copper        |                    | Arsenical        | copper        |        |         |        | Tin bronze    |                  |            |        | Arsenical        | copper        |        | Unalloyed    |              |                | Arsenic- | silver cop-  | per alloy      | Unalloyed    |              |                | Unalloyed           |                              | Unalloyed      |            |           | Unalloyed                  |               |             | Unalloyed           |               |             | ed artefacts  |
| COLLOSION    | patina        |        |              |               | a tew tree patches | Little corrosion |               |        |         |        | -             | covering most of | the object |        | Corrosion patina | in patches    |        | Uniform dark | patina       |                |          | few free     | patches        | patina       | in patches   |                | Corrosion almost Ur | everywhere on<br>the surface | patina         | in patches |           | Corrosion almost Unalloyed | everywhere on | the surface | Corrosion almost Ur | everywhere on | the surface | Table 6 (continued). PXRF analytical results for copper-based   |
| Dagger       |               |        | Pin          |               |                    | Shafthole        | ахе           |        |         |        | Dagger        |                  |            |        | Toggle pin       |               |        | Toggle pin   |              |                | Pin      |              |                | Awl          |              |                | Awl                 |                              | Arrow          |            |           | Awl                        |               |             | Knife               |               |             | cal results   |
| C.480        |               |        | G.492        |               |                    | G.494            |               |        |         |        | G.517         |                  |            |        | G.552            |               |        |              |              |                |          |              |                |              |              |                |                     |                              |                |            |           |                            |               |             |                     |               |             | analytiv  |
|              | Nr.           | 6/01   | DHN          | Nr.           | 1171               | DHN              | Nr.           | 1015   |         |        | DHN           | Nr.              | / 211      |        | DHN              | Nr.           | 1133   | K8.152       |              |                | I10.217  |              |                | G8.356       |              |                | G8.481              |                              | I10.27         |            |           | K8.1179                    |               |             | K7.127              |               |             | PXRF (  |
|              | necropolis    |        | Demircihüyük | necropolis    |                    | Demircihüyük     | necropolis    |        |         |        | yük           | necropolis       |            |        | Demircihüyük     | necropolis    |        | Demircihüyük | settlement   |                | yük      | settlement   |                | Demircihüyük | settlement   |                | Demircihüyük G8.481 | settlement                   | Demircihüyük   | settlement |           | Demircihüyük K8.1179       | settlement    |             | yük                 | settlement    |             | (continued).  |
| 51/4         |               |        | S178         |               |                    | S181             |               |        |         |        | S188          |                  |            |        | S194             |               |        | S207         |              |                | S211     |              |                | S217         |              |                | S218                |                              | S223           |            |           | S226                       |               |             | S228                |               |             | Table 6   |

= not detected.

| Sample | Site                       | Exc.           | Context | Туре   | Surface                           | Weight | Reading | Total | Au<br>% | Ag<br>% | Cu<br>% | Bibliography                        |
|--------|----------------------------|----------------|---------|--------|-----------------------------------|--------|---------|-------|---------|---------|---------|-------------------------------------|
| no.    | D · · · · · · · ·          | no.            | 0.25    | D' 1   | preservation                      | (gr)   | no.     | 00.1  |         |         |         | G 1 2000 50                         |
| S006   | Demircihüyük<br>necropolis | DHN<br>Nr. 132 | G.37    | Diadem | No corrosion                      |        | S006-1  | 99.1  | 68.4    | 29.7    | 1.0     | Seeher 2000: 70,<br>fig. 18-G.37a   |
| 0010   |                            |                | G 30    | 5.1    |                                   |        | S006-2  | 99.0  | 67.5    | 30.5    | 0.9     | e                                   |
| S010   | Demircihüyük<br>necropolis | DHN<br>Nr. 209 | G.38    | Diadem | No corrosion                      |        | S010-1  | 101.0 | 99.6    | 1.1     | 0.3     | Seeher 2000: 71,<br>fig. 18-G.38c   |
|        | necropolis                 | INF. 209       |         |        |                                   |        | S010-2  | 100.7 | 99.2    | 1.1     | 0.3     | lig. 18-0.580                       |
|        |                            |                |         |        |                                   |        | S010-3  | 100.6 | 99.2    | 1.1     | 0.3     |                                     |
| S013   | Demircihüyük               | DHN            | G.57    | Diadem | Light black                       |        | S013-1  | 98.2  | 60.1    | 35.8    | 2.3     | Seeher 2000: 72,                    |
|        | necropolis                 | Nr. 194        |         |        | corrosion patina                  |        | S013-2  | 98.3  | 59.9    | 36.2    | 2.3     | fig. 19-G.57f                       |
|        |                            |                |         |        |                                   |        | S013-3  | 98.2  | 59.2    | 36.9    | 2.1     |                                     |
| S014   | Demircihüyük               | DHN            | G.58    | Diadem | No corrosion                      | 0.6    | S014-1  | 101.2 | 99.8    | 1.1     | 0.2     | Seeher 2000: 73,                    |
|        | necropolis                 | Nr. 242        |         |        |                                   |        | S014-2  | 100.9 | 99.5    | 1.1     | 0.3     | fig. 19-G.58a                       |
|        |                            |                |         |        |                                   |        | S014-3  | 101.1 | 99.8    | 1.1     | 0.2     |                                     |
| S023   | Demircihüyük               | DHN            | G.79    | Diadem | Light dark-red                    | 0.7    | S023-1  | 100.9 | 97.2    | 3.1     | 0.6     | Seeher 2000: 75,                    |
|        | necropolis                 | Nr. 297        |         |        | corrosion patina                  |        | S023-2  | 99.8  | 96.0    | 3.2     | 0.6     | fig. 20-G.79q                       |
|        |                            |                |         |        |                                   |        | S023-3  | 100.1 | 96.7    | 3.0     | 0.4     |                                     |
| S028   | Demircihüyük<br>necropolis | DHN<br>Nr. 268 | G.83    | Diadem | Black corrosion patina in patches |        | S028-1  | 98.9  | 61.9    | 36.1    | 0.8     | Seeher 2000: 76,<br>fig. 21-G.83g   |
| S029   | Demircihüyük               | DHN            | G.83    | Diadem | No corrosion                      |        | S029-1  | 99.1  | 65.5    | 32.7    | 0.9     | Seeher 2000: 76,                    |
|        | necropolis                 | Nr. 255        |         |        |                                   |        | S029-2  | 98.9  | 63.4    | 34.7    | 0.9     | fig. 21-G.83h                       |
| S033   | Demircihüyük               | DHN            | G.88    | Diadem | No corrosion                      |        | S033-1  | 100.6 | 99.0    | 1.2     | 0.4     | Seeher 2000: 77,                    |
|        | necropolis                 | Nr. 414        |         |        |                                   |        | S033-2  | 100.8 | 99.2    | 1.2     | 0.4     | fig. 21-G.88a                       |
|        |                            |                |         |        |                                   |        | S033-3  | 100.8 | 99.1    | 1.3     | 0.4     | -                                   |
| S040   | Demircihüyük               | DHN            | G.95    | Diadem | No corrosion                      |        | S040-1  | 100.8 | 97.7    | 2.7     | 0.4     | Seeher 2000: 78,                    |
|        | necropolis                 | Nr. 352        |         |        |                                   |        | S040-2  | 101.2 | 98.2    | 2.6     | 0.4     | fig. 22-G.95c                       |
| S107   | Demircihüyük               | DHN            | G.295   | Diadem | No corrosion                      |        | S107-1  | 100.9 | 97.4    | 3.3     | 0.3     | Seeher 2000: 100,                   |
|        | necropolis                 | Nr. 665        |         |        |                                   |        | S107-2  | 100.5 | 96.9    | 3.3     | 0.3     | fig. 36-G.295b                      |
|        |                            |                |         |        |                                   |        | S107-3  | 100.8 | 97.1    | 3.4     | 0.3     |                                     |
| S130   | Demircihüyük-              | DHN            | G.326   | Diadem | No corrosion                      | 0.1    | S130-1  | 100.5 | 93.2    | 6.4     | 0.8     | Seeher 2000: 105,                   |
|        | Necropolis                 | Nr. 786        |         |        |                                   |        | S130-2  | 100.5 | 93.1    | 6.5     | 0.8     | fig. 40-G.326d                      |
| S143   | Demircihüyük<br>necropolis | DHN<br>Nr. 887 | G.367B  | Diadem | No corrosion                      | 0.05   | S143-1  | 100.4 | 96.1    | 3.7     | 0.6     | Seeher 2000: 109,<br>fig. 42-G.367B |
| S152   | Demircihüyük               | DHN            | G.398   | Ring   | No corrosion                      | 0.9    | S152-1  | 95.1  | 50.6    | 31.1    | 13.4    | Seeher 2000: 113,                   |
|        | necropolis                 | Nr. 911        |         | -      |                                   |        | S152-2  | 94.8  | 49.3    | 31.0    | 14.6    | fig. 44-G.398b                      |
|        |                            |                |         |        |                                   |        | S152-3  | 95.0  | 50.6    | 31.0    | 13.3    | -                                   |
| S186   | Demircihüyük               | DHN            | G.511   | Bead   | No corrosion                      | 0.3    | S186-1  | 100.7 | 97.0    | 3.4     | 0.3     | Seeher 2000: 124,                   |
|        | necropolis                 | Nr. 1150       |         |        |                                   |        | S186-2  | 99.8  | 96.5    | 3.0     | 0.3     | fig. 51-G.511b                      |
| S197   | Demircihüyük               | DHN            | G.582   | Ring   | No corrosion                      | 3      | S197-1  | 100.4 | 97.1    | 3.1     | 0.3     | Seeher 2000: 128,                   |
|        | necropolis                 | Nr. 1199       |         | 3      |                                   |        | S197-2  | 100.2 | 96.9    | 3.0     | 0.3     | fig. 53-G.582b                      |
|        |                            |                |         |        |                                   |        | S197-3  | 100.5 | 96.9    | 3.4     | 0.2     | 1                                   |
| S200   | Demircihüyük               | DHN            | G.583   | Diadem | No corrosion                      |        | S200-1  | 100.3 | 97.7    | 1.7     | 1.0     | Seeher 2000: 128,                   |
|        | necropolis                 | Nr. 1245       |         |        |                                   |        | S200-2  | 100.2 | 97.6    | 1.7     | 1.0     | fig. 53-G.583b                      |
|        | _                          |                |         |        |                                   |        | S200-2  | 100.2 | 98.0    | 1.7     | 1.0     | -                                   |

Table 7. PXRF analytical results for gold-based artefacts. Elements shaded in light grey (1-2 wt%) might indicate intentional alloy, if we consider the threshold > 1 wt%. Elements shaded in dark grey (above 2 wt%) indicate the probable intentional addition of metal in order to produce an alloy.

# **Alloying practices**

There is an ongoing debate regarding the threshold above which alloys should be considered intentional, with different authors setting limits ranging between 0.5 and 3 wt% (cf. Gale et al. 1985: 145; Lechtman 1996; de Ryck et al. 2003: 579–80; Webb et al. 2006: 274). This issue is of particular importance in Anatolia where most copper deposits are polymetallic in nature and contain substantial amounts of secondary metals. We tried to test our dataset (a total of 154 readings from 42 copper-based objects) in

this regard, and the bar charts in figure 6 show a synoptic view of the proportion of the three major secondary metals (arsenic, tin, lead) found in analysed copper-based artefacts. For tin there is a clear pattern in which it is either present only in trace (<0.3 wt%) or in significant quantities (>3.5 wt%), strongly suggesting that it was intentionally added to the alloy and was not present in large proportions in the copper ore itself (cf. Pernicka 2000: 232 for similar conclusions). The lead plot suggests instead that small proportions (up to 1 wt%) of this metal

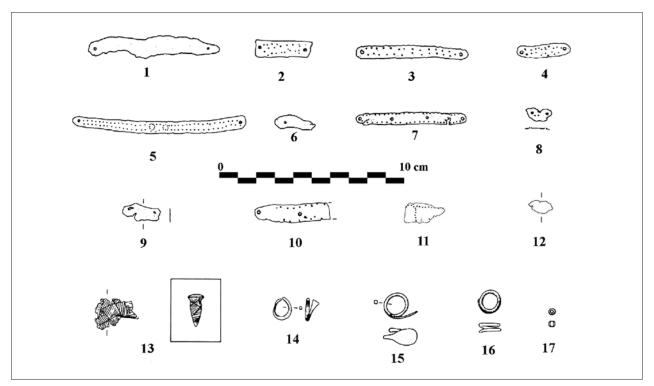


Fig. 5. Analysed gold artefacts from the necropolis (for references, see table 6): (1) S028 diadem; (2) S006 diadem; (3) S010 diadem; (4) S014 diadem; (5) S023 diadem; (6) S029 diadem; (7) S033 diadem; (8) S040 diadem; (9) S130 diadem; (10) S200 diadem; (11) S013 diadem; (12) S143 diadem; (13) S107 ear stud reworked as a diadem; (14) S152 (ear)ring; (15) S144 (ear)ring; (16) S197 (ear)ring; (17) S186 bead.

naturally occurred in the copper ores; above 5 wt% of lead is most likely intentional. Arsenic seems to behave very differently, being present in most analysed samples in varying quantities, without an apparent break in the distribution. This trend suggests that most of the copper ores employed in metallurgical production naturally contained arsenic minerals as well, and this is also hinted at by the presence of appreciable quantities of arsenic (0.3-1.5 wt%) in some of Demircihüyük's tin bronzes (for example S042, S056, S113, S188). However, high proportions (>2-3 wt%) likely represent intentional selection of arsenic-rich copper ores and/or intentional alloying of copper with arsenic ores. Intentional alloying in particular is well documented in the Aegean, Anatolia and Iran starting around the mid fourth millennium BC (Özbal et al. 2002; Doonan et al. 2007: 112-13; Thornton et al. 2009; Schoop 2011; Rehren et al. 2012; Horejs, Mehofer 2015). While the plots indicate that there is some fuzziness, as arguably one should expect from prehistoric artefacts created without modern weighing equipment and controlled laboratory environments, they also show that 2 wt% seems an appropriate (albeit to some extent artificial) threshold to set for the identification of intentionally alloyed metals. This value is also corroborated by archaeo-metallurgical experiments showing that this is approximately when differences both in colour and mechanical properties (fluidity, hardness, fragility) can be detected without specialised equipment and may thus have been recognised by prehistoric metallurgists (Northover 1989: 113; Budd, Ottaway 1991: 138–39).

Considering these observations, arsenical copper is the most common alloy employed for Demircihüyük's metalwork (39% of the sample: fig. 7), and indeed the most common alloy in early to mid third millennium BC Anatolia (Massa 2016b: 190-91, fig. 6.27). Artefacts made of unalloyed copper are also common at the site (35%); most, however, show the presence of secondary metals in their composition, and it is sometimes difficult to establish whether the presence of arsenic and lead might have been intentional. From the necropolis there are also five tin bronzes (14%), one of which (S042) was found in one of the earliest graves (grave 100) in the cemetery (table 2), indicating that small quantities of tin (either in raw form or alloyed) were already circulating in Demircihüyük from at least ca 2700 BC onward. Given the small amount of samples from the settlement, it is not possible to exclude the possibility that tin bronzes may have reached Demircihüyük in earlier phases. It is worth noting that earlier tin bronzes are found in small quantities along the northeastern Aegean seaboard at Thermi I (around 3000-2900 BC) and Beşiktepe (ca 2900-2750 cal. BC: Stos-Gale 1992; Begemann et al. 2003).

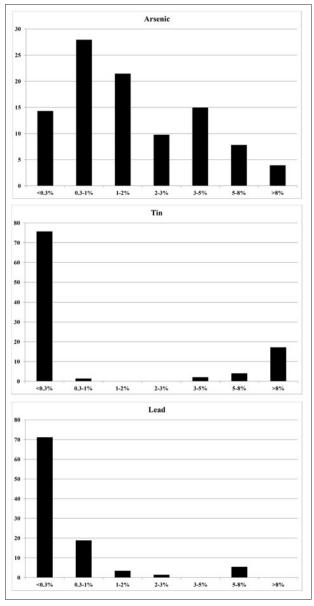
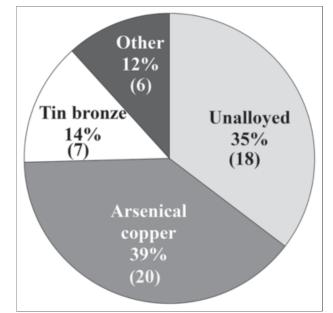


Fig. 6. Bar charts showing the aggregate amount of arsenic, tin and lead in the analysed artefacts (number of samples = 154). The analytical bins follow natural breaks in the data.

Our analysis also revealed the presence of several rarer alloys, including silver-copper and silver-arsenic-copper alloys present in a ring (S144), a toggle-pin (S015) and a pin (S211). Items S015 and S211 show low proportions of silver (4.6 wt% and 0.7–3.1 wt% respectively), and it is therefore possible that they may be accidental alloys resulting from copper ores rich in silver, like those of Balya or Gümüşköy to the west of the site (see below). However, S144 shows high silver proportions (in the 40– 70 wt% range), and it can thus be classified as an intentional alloy. Interestingly, with such alloy, annealing and hammering would selectively bring silver to the surface, producing an artefact with a silvery appearance and



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Fig. 7. Pie chart showing the proportion of different copper-based alloys in the analysed artefacts. Note: Pernicka's INAA results have also been included here.

virtually indistinguishable from an object entirely made of silver (Hauptmann et al. 2002: 52). Silver-copper alloys start appearing almost simultaneously, around the mid fourth millennium BC, across a large area spanning the Carpathians to Lower Mesopotamia (Hauptmann et al. 2002: 57; Horejs et al. 2010: 21–24). They are, for instance, present in large numbers in the Arslantepe 'Royal Grave' (ca 3000–2900 BC) and are also found at Early Bronze I Çukuriçi Höyük (2900–2750 cal. BC), the Alacahöyük 'Royal Graves', Karataş, Resuloğlu and in the Hasanoğlu figurine (Alpers-Bordaz 1978: 314; Hauptmann et al. 2002; Horejs et al. 2010: 19; Zimmermann, Yıldırım 2011; Yalçın, Yalçın 2013; Horejs, Mehofer 2015: 170; Zimmermann, Özen 2016: 20).

Two artefacts (S056 and S093) show instead the intentional addition of tin and lead in significant quantities, while S076 also shows the addition of arsenic to the tin and lead alloy (note that S056 and S093 were studied by Pernicka, but the INAA analysis did not include lead and the alloy was thus not recognised: Pernicka 2000: table 1). While lead might have deposited on the surface during post-depositional processes (i.e. whilst in contact with lead-rich soils), similar compositions are found across Anatolia and have been detected also with destructive analyses on the bulk (internal) composition of metal artefacts, and thus indicate a probably intentional alloy. Three have been found in the late Early Bronze Age 'Troadic hoard', three at Early Bronze III and Middle Bronze Age Kültepe, one at Early Bronze III Horoztepe, five at Middle Bronze Age Alişar Höyük, one at Early

Bronze III Kalınkaya, one at Poliochni Yellow and three at Resuloğlu (Esin 1969: 125–28, 134, 139–43; Pernicka et al. 1990; Zimmermann, Yıldırım 2010; 2011; Geniş, Zimmermann 2014; Lehner et al. 2015: 203). Two from Early Bronze II–III Tarsus also additionally include arsenic (Esin 1969: 131–33).

In contrast, it is uncertain whether the arsenic-leadcopper alloy of sample S078 was intentional or not. This alloy is in general very rare in Early Bronze Age Anatolia: one from the Alacahöyük 'Royal Graves', seven from Poliochni Blue-Yellow and one from Thermi IV (Esin 1969: 122–23; Pernicka et al. 1990; Begemann et al. 1992).

Lastly, our pXRF analysis has revealed that one sample (S089) is made of native copper (i.e. with impurities less than 1 wt%); this result is confirmed by the INAA analysis undertaken by Pernicka on the same object (Pernicka 2000: table 1, sample no. HDM 2473). This is interesting because, according to the available evidence, native copper deposits are only known in northern and eastern Anatolia, several hundred kilometres away from Demircihüyük (fig. 8; cf. Wagner, Öztunalı 2000; Yalçın, Maass 2013; Yalçın et al. 2015: 147–51); thus the object is likely to have arrived on site through interregional exchange. Another item (S146), a tin-bronze artefact, also shows very small traces of other secondary metals and was probably manufactured with the addition of tin to native copper, though more detailed analysis is needed to confirm this suggestion.

Turning our attention to the 16 gold-based artefacts (mostly diadems, but also two rings and one bead), table 7 shows that all contain considerable amounts of silver, ranging between 1 and 37 wt%; in a few cases there are also significant amounts of copper (1-14.5 wt%). The combination of gold and silver, called electrum, occurs naturally and is particularly widespread in Anatolia (Pernicka 2000: 234). The presence of copper is also possibly natural, though, at least in the case of \$152, it cannot be excluded as having been an intentional addition made in order to procure a red shine to the object. Compositional analyses on gold-based artefacts are still rare for Anatolian artefacts, but all show comparable results to ours, and, in particular, all gold-based items are made of electrum: for example, those from Alacahöyük and Resuloğlu, and the Hasanoğlu statuette (Zimmermann, Yıldırım 2010: table 1; Yalçın 2011; Yalçın, Yalçın 2013; Zimmermann, Özen 2016: 20).

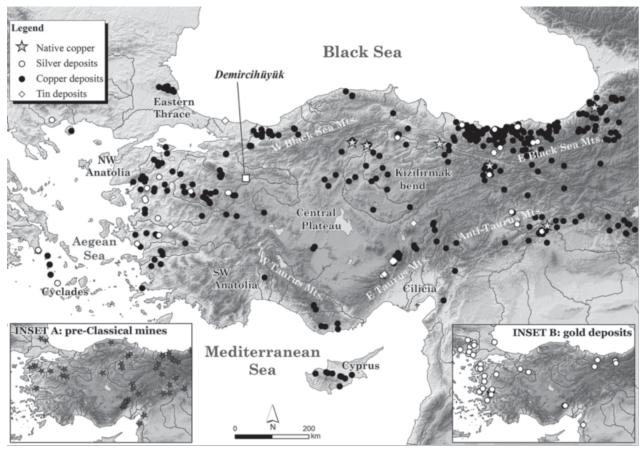


Fig. 8. Locations of known copper, native copper, silver and tin deposits in Anatolia and surrounding regions (see text for references). Inset A shows the locations of mining complexes with known pre-Classical exploitation; inset B shows the locations of gold deposits.

#### Manufacturing technologies

While microscopic analysis is needed to confirm and describe in more detail our observations, visual analysis suggests that a range of different techniques was used in the manufacture of Demircihüyük's metal assemblage (table 3). Open (single) mould casting was likely employed for simple, two-dimensional artefacts, including all the tools represented here (hatchets/flat axes, awls, punches, needles and knives/blades), as well as daggers. Bivalve (two-part) mould casting was probably employed for the manufacture of relatively simple three-dimensional items like the crescentic axe, the spearhead, the round maceheads and the arrow, as well as pins with heads. With regard to the latter, there is at present no evidence that Demircihüyük's pins were composed of different sections and assembled at a later stage. None of them have elaborate heads that would require separate moulds, there is no sign of joins between shafts and heads, and chemical composition analysis has not highlighted any significant differences in the alloys of the different parts. It is more difficult to understand how wires (used to form various types of rings, and possibly also needles and headless pins) were manufactured. The only technique known to Early Bronze Age smiths (hammering a metal rod into shape) would create a facetted surface and varying wire diameter (Oddy 1977: 83; Scott 1991a: 65); such features are not noted in our samples. It is instead more likely that wire may have been made through casting, and then shaped through annealing, hammering and polishing; moulds for wire have in fact been found at Thermi level I, Küllüoba level IIC and Troy level IIg (Schliemann 1881: 482-83, fig. 599; Lamb 1936: 159, fig. 44-32.20; Efe 2006: 302, fig. 2).

Hammering was probably also employed to thin, flatten and shape a range of artefacts, from diadems to bracelets, from awls/punches to knives, daggers and beads. A particular case is presented by the three gold studs (fig. 5.13) which have close parallels from a large number of other broadly contemporary sites (Duru 1972; Seeher 2000: 63). These were certainly applied as ear decoration, as shown by the remarkable anthropomorphic depiction on a pithos found at Küllüoba, which clearly shows one of these studs inserted into the earlobe (Efe 2009: 270, fig. 8). The ear studs were made by applying an extremely thin gold sheet to a core of organic material, which was further worked with a small punch or a chase (chasing technique) to create small decorative grooves (Seeher 2000: 62-63). Chasing was also employed to trace grooved decorations on bracelets and pins, while repoussé - using a small punch to emboss metal sheets - was employed to decorate diadems. Cold gilding - the application of a gold sheet to another metal medium through hammering - is observed in one single case (S119): a small copper pin with a spheroid head. Comparable examples are documented amongst the gilded silver figurines and vessels from Alacahöyük (Yalçın 2011: 59; Yalçın, Yalçın 2013: 42).

In a few cases, the lost-wax technique was used to produce complex three-dimensional objects like the battleaxe and the three knobbed maceheads. This technique, known in the Near East at least from the mid fourth millennium BC, entails creating a wax model of the desired object, covering it with clay, firing it to harden the clay and eliminate the wax, filling the resulting void with molten metal and breaking the mould to extract the artefact (Hunt 1980; Goren 2008; Davey 2009). It is a complex, lengthy process that excludes the replication of the same object, since the moulds are broken after each cast.

Finally, particularly problematic is the case of the 32 lead bottles. These are closed vessels created in a single piece. Seeher observes that they are completely smooth on the inside as on the outside, and there are no signs of the seam that would have been created if they had been cast with bivalve moulds; nor is there any sign of hammering (Seeher 2000: 51). He also suggests that they may have been manufactured by repeatedly pouring lead onto unbaked clay models, and that the clay core was then washed away. However, experiments conducted by the research team resulted in vessels with varying thickness, something not observed in the archaeological specimens. An alternative theory is that they too may have been manufactured with the lost-wax technique, though there are no known third-millennium BC lead artefacts from Anatolia made with this technique.

What emerges from this brief overview is that, while many of the items found at Demircihüyük may have been relatively easy to create, some were clearly the product of skilled specialists who employed complex techniques requiring substantial amounts of time. Despite extensive exposure of the settlement levels, there is very little evidence for metallurgical activities at the site; this is limited essentially to a stone mould used to produce flat axes that was found in level H (ca 2750 cal. BC: Obladen Kauder 1996: 181). There are, however, no ores, slags, crucibles or tuyères that would represent significant episodes of smelting and casting activities; this absence is all the more relevant since all other excavated Early Bronze Age sites in the region (for example Küllüoba, Keçiçayırı, Seyitömer Höyük, Kureyşler-Höyüktepe, Çiledir Höyük) have yielded substantial evidence for the presence of metallurgical workshops (see below). While it is possible that such activities may have taken place outside the settlement proper or in the unexcavated portion of the site, the small size of Demircihüyük suggests that it may have not hosted a full-time smith. It is thus plausible that many, if not most, of the metal artefacts may have been produced elsewhere and reached the site in their final form.

The following sections try to address the possible origins of both the finished products and the raw materials employed in their manufacture.

#### **Possible metal sources**

Starting in the late 1950s, the Turkish government's General Directorate of Mineral Research (MTA) has sponsored a nationwide programme of geological research aimed at, among other issues, identifying the major metallogenic deposits in Turkey (see Ryan 1960; MTA 1972; de Jesus 1980 for early reports). The results of these efforts have recently been made available online in the form of detailed single-province maps (http://www.mta.gov.tr/ v2.0/default.php?id=maden haritalari), and are presented here in a synthetic form (fig. 8). However, since these geological surveys were carried out with sophisticated technologies and aimed to find profitable deposits in the context of today's global economy, they cannot be taken a priori as an accurate picture of what was available to prehistoric metal prospectors, for several reasons. For instance, small-scale enterprises that are not economically feasible today could have been viable in the Early Bronze Age; deposits exploited in the Bronze Age may have been exhausted since then; small deposits may have been missed by modern prospectors; Early Bronze Age metallurgical technologies could not have extracted metal from particular categories of ores; some deposits may have been too inaccessible to allow linkage with major exchange arteries; and some deposits may have been located in treeless environments, thus preventing large-scale refinement (that required substantial amounts of firewood).

Therefore, when detailed archaeo-metallurgical surveys are not available, it is difficult to assess the potential for Bronze Age exploitation of sources known today. Nonetheless, these modern data can be employed to sketch an impressionistic, general view of how the metallurgical landscapes of third-millennium BC Anatolia could have looked. It is striking, for instance, how copper is relatively common across Anatolia, with the notable exception of southwestern Anatolia and the central plateau. Even though the deposits of the Black Sea mountains (Pontide block) and the Antitaurus mountains (Tauride block) contain ca 98% of the total modern copper reserves of Turkey (MTA 2001a), numerous copper deposits elsewhere were certainly exploited during the Early Bronze Age for local and regional consumption (see Wagner, Öztunalı 2000, among others). On the other hand, silver and gold are much rarer and concentrated in smaller areas, particularly northwestern and western Anatolia, the Bolkardağ mountains (eastern Taurus), the eastern Black Sea range and the Antitaurus mountains (Yener 1983; Bayburtoğlu, Yıldırım 2008; Legeranlı 2008). Limited occurrences of tin minerals (stannite and cassiterite) in the form of veins or placer deposits have also been identified in the eastern Taurus range and the Marmara Sea area (Kaptan 1995; Yener et al. 1989; 2015; Yalçın, Özbal 2009; Yener 2009). In view of the discussion of the chemical composition analysis (see above), it is also important to stress that many of the aforementioned deposits are polymetallic, something that may to some extent explain trace and minor concentrations of secondary metals in many of the identifiable alloys.

In addition to this coarse picture, a more detailed understanding of the metallurgical landscapes around Demircihüyük comes from several archaeo-metallurgical surveys conducted in the early 1980s (Pernicka et al. 1984; Wagner et al. 1984; 1986; Seeliger et al. 1985). These identified several dozen mining and primary smelting facilities across Anatolia, whose exploitation can be attributed with varying degrees of confidence to the Bronze Age; table 8 and figure 9 present the evidence of the mines closest to Demircihüyük. Gümüşköy ('the silver village') is the most important of them, and is today the major supply source of silver in Turkey, representing almost 60% of the country's total silver reserves (fig. 9, no.10; MTA 2001b). The main minerals found are galena (a lead sulphide often associated with trace amounts of silver) and native silver, though small occurrences of oxidic copper ores (including malachite) are visible on the surface and may have been targeted by prehistoric miners (Pernicka et al. 1984: 567–68). Evidence for a continuous and intensive pre-modern exploitation of the mine is found almost everywhere on site, from ceramic sherds, crucible fragments and stone tools embedded in the ore dumps, to Roman, Byzantine and Islamic coins (Kaptan 1984; Kartalkanat 2008: 95). Narrow, irregular shafts have been intercepted by modern mining operations ca 50m below the surface; here, a charcoal sample from a backfill has provided a radiocarbon date of 2287-1922 cal. BC (Wagner, Öztunalı 2000: 38). A structural timber has yielded a date of 2620-2136 cal. BC and, more recently, a radiocarbon sample from within the ore waste was dated at 1941-1772 cal. BC (Kartalkanat 2008: 96; the published calendric dates have been recalibrated with online OxCal 4.2, at 95% confidence). These dates confirm that the mine was active from at least the mid third millennium BC. Lead isotope analysis carried out on metal objects from Beşiktepe, Poliochni and Thermi (dated mostly to the early to mid third millennium BC) further suggests that most of the copper-based artefacts at these sites may have come from Gümüşköy (Begemann et al. 2003). Since it is only 60km away as the crow flies from Demircihüyük, it is plausible that most of the lead and silver, as well as some of the copper, found at the site may have come from this mine; but, of course, provenance analysis is required to confirm this hypothesis.

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| Мар           | Locality                |      | Туре          |        | Target metals                                | Bro           | onze Age         | dating evid       | dence            | Other periods                 | Bibliography  |
|---------------|-------------------------|------|---------------|--------|--|---------------|------------------|-------------------|------------------|-------------------------------|---|
| no.           |                         | Mine | Smelt<br>site | Placer |  | Shaft<br>type | Radio-<br>carbon | Arch.<br>material | Prov.<br>objects |                               |   |
| 1             | Dereköy                 | х    | x             |        | Copper                                       | 1             |                  |                   |                  | Rom, Ott                      | Wagner et al. 1986: 730-31  |
| 2             | İkiztepe                | х    | x             |        | Copper                                       | 1             |                  |                   |                  | Rom, Ott                      | Wagner et al. 1986: 728–29  |
| 3             | Doğancılar              | х    | x             |        | Copper                                       | 2             |                  |                   | Yes              |                               | Pernicka et al. 1984: 557–58  |
| 4             | Yuvalar                 | х    | X             |        | Copper                                       |               | MBA,<br>LBA      | 2                 |                  | Rom, Byz                      | Pernicka et al. 1984: 559;<br>Wagner et al. 1986: 725–26                                      |
| 5             | Kartalkaya<br>(Astyra)  | Х    |               |        | Gold   | 1             |                  | 1                 |                  | Iron Age, Class,<br>Hell, Byz | Pernicka et al. 1984: 553–57  |
| 6             | Balya                   | Х    | x             |        | Copper, lead,<br>silver, gold,<br>arsenic(?) | 2             |                  | 3                 | Yes              | Archaic, Hell,<br>Byz, Ott    | Pernicka et al. 1984: 540–49  |
| 7             | Serceörenköy            | Х    | x             |        | Copper,<br>silver, lead                      | 2             |                  | 2                 | Yes              | Hell, Byz, Ott                | Wagner et al. 1986: 734–35  |
| 8             | Tahtaköprü              | Х    | х             |        | Copper                                       | 1             |                  |                   | Yes              | Rom                           | Pernicka et al. 1984: 568–69;<br>Wagner, Öztunalı 2000: 39                                    |
| 9             | Emet/Tepecik            |      | x             |        | Copper                                       |               |                  | 3                 |                  |                               | Efe 2002: 53–54   |
| 10            | Gümüşköy                | Х    | x             |        | Copper,<br>silver, lead,<br>arsenic(?)       | 2             | EBA +<br>MBA     | 2                 | Yes              | Rom, Byz, Ott                 | Demirok 1982; Pernicka et al.<br>1984: 567–68; Wagner, Öztunalı<br>2000: 38; Kartalkanat 2008 |
| 11            | Kureyşler-<br>Höyüktepe |      | X             |        | Copper                                       |               |                  | 3                 |                  |                               | Fidan et al. 2017   |
| 12            | Sardis                  |      |               | x      | Gold   |               |                  |                   | Yes              | Iron Age,<br>Class, Hell      | Young 1972; Meeks 2000;<br>Bayburtoğlu, Yıldırım 2008: 8                                      |
| 13            | Arap Dağı               | х    | x             |        | Gold, Silver                                 | 2             |                  |                   |                  | Byz, Ott                      | Wagner et al. 1986: 731-32  |
| Not on<br>map | Hisarcık                | Х    |               |        | Tin  | 2             |                  | 3                 | Yes              | Iron Age                      | Yalçın, Özbal 2009; Yener et al.<br>2015; Yalçın 2016   |
| Not on<br>map | Kestel-<br>Göltepe      | х    | х             | (x)*   | Tin, gold(?)                                 | 2             | LCh +<br>EBA     | 3                 |                  |                               | Yener et al. 1989; Yener 2000   |

Table 8. Synoptic table of western Anatolian mines and smelting sites with evidence for Bronze Age exploitation. The fields listed under the 'Bronze Age dating evidence' heading assess which sorts of evidence have been gathered to support a dating of the site to the Bronze Age or, more specifically, the Early Bronze Age (1 = possibly Bronze Age; 2 = very likely Bronze Age; 3 = definitely Early Bronze Age). The 'Shaft type' column notes dating based on the sizes and shapes of the mine shafts (narrow, irregular adits suggest a prehistoric exploitation); the 'Radiocarbon' column indicates the date of radiocarbon samples collected; the 'Arch. material' column records the presence of dateable ceramics on site; 'Prov. objects' indicates whether Early Bronze Age metal artefacts have been correlated with the mine site through provenance analysis. \*Tin placers are also known in the immediate proximity of Kestel at Kilavuz, Cellaler and Eynelli (Yener, Özbal 1987; Yener et al. 1989).

Another probable source for Demircihüyük's copper is Tahtaköprü (fig. 9, no. 8): a deposit of sulphidic and oxidic copper ores ca 60km west of the site. Here, limited evidence of pre-Classical mining is represented by narrow, irregular shafts targeting the cupriferous veinlets (Wagner, Öztunalı 2000: 39). At least two early third-millennium BC objects found at Beşiktepe may have originated here (Begemann et al. 2003: 196). Tepecik (80km away) is a small mound whose outskirts have been damaged by road construction, revealing appreciable quantities of copper ore and slag associated with early third-millennium BC pottery (fig. 9, no. 9; Efe 2002: 54). The mound is located 5–6km from a small copper deposit (Emet 3), and the context thus suggests that Tepecik may have been a copper smelting site. Bakırtepe, an open-air copper mine exploited until a few decades ago, was also probably used during the Early Bronze Age, given that the nearby Kureyşler-Höyüktepe (a site with early third-millennium BC occupation) shows evidence of on-site smelting and casting activities (fig. 9, no. 11; Fidan et al. 2017).

Furthermore, so far all other excavated third-millennium settlements in Kütahya and Eskişehir have yielded some evidence for the later stages of metalworking connected with the production of metal objects from already smelted copper. For instance, moulds and *tuyères* are reported from Seyitömer Höyük, Çiledir Höyük, Kureyşler-Höyüktepe and Keçiçayırı, while at Küllüoba at least six simple moulds and two bivalve moulds have been found (Çakalgöz 2000: 51, pl. 46.157; Efe 2006; Fidan 2013b; 2016: 94; Bilgen 2014: 202, fig. 29; Türktüzün et

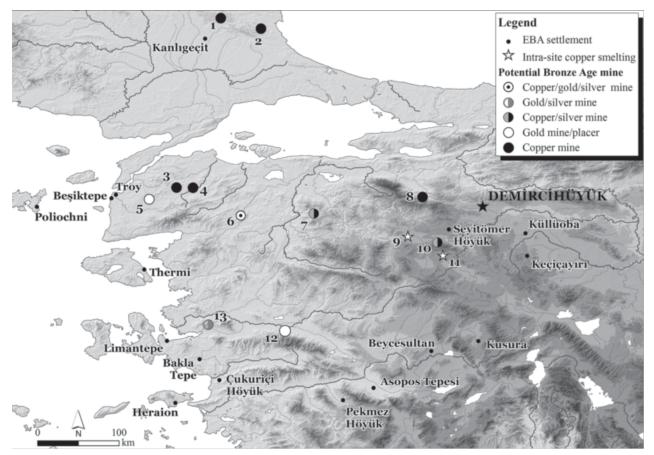


Fig. 9. Location of mines and smelting sites in western Anatolia with evidence for Bronze Age exploitation. Numbers refer to the sites listed in table 8.

al. 2014: 66, figs 40, 41; Fidan et al. 2017). Considered together, they indicate that the highlands between Kütahya and Eskişehir were an important metallurgical district and that metalworking might have been an important socioeconomic strategy for the local communities.

There are at least two copper smelting sites (Tepecik and Kureyşler-Höyüktepe) contemporary with Demircihüyük, plus several copper mines that have at least some evidence of Early Bronze Age exploitation, all within an 80km radius. In addition, while the radiocarbon evidence places the earliest exploitation of Gümüşköy a few centuries later than the occupation span at Demircihüyük, it is still possible that it might have been mined at an even earlier date, although direct archaeological evidence is missing. The different strands of evidence make us hypothesise that the majority of the copper-based objects, and possibly also of the leadand silver-based artefacts, might have reached the site through local exchange networks. This working hypothesis will need to be tested with lead isotope analysis.

Conversely, both gold and tin must have reached the site from areas much further afield. The closest possible source of gold is Balya Maden (230km away), a recently abandoned mine that taps into veins of silver, gold and oxidic copper minerals (fig. 9, no. 6; Pernicka et al. 1984:

540-49). Its importance, particularly for silver, is suggested by the fact that it yields ca 15% of the total reserves of Turkish silver (MTA 2001b). Its surrounds are dotted with impressive numbers of open-air pits, shafts, ore waste and slag; pre-Classical shafts have been intercepted by modern adits ca 50m below the surface and some diagnostic Early Bronze Age handmade sherds have been found on the surface. Balya may also be the origin of some of the silver and lead objects from Poliochni and Thermi (Pernicka et al. 1990: 279-80; Begemann et al. 1992: fig. 5). The two gold mines of Kartalkaya and Arap Dağı (fig. 9, nos 5, 13) also have limited evidence of Early Bronze Age exploitation (Pernicka et al. 1984: 553-57; Wagner et al. 1986: 731-32). Another possible gold source is the Sardis placer, situated ca 240km away from Demircihüyük in the vicinity of Mount Bozdağ (fig. 9, no. 12; Meeks 2000; Bayburtoğlu, Yıldırım 2008: 8). Since the gold extraction here did not require mining or smelting, direct evidence for its prehistoric exploitation is lacking. While gold is in general difficult to provenance, an early study (based on proportions of platinum-iridium) on Egyptian and Mesopotamian finished products suggests that the placer could have been active already by the mid third millennium BC (Young 1972).

With regards to tin sources, over the last three decades there has been much debate as to whether the Early Bronze Age mining complex of Kestel/Göltepe (Taurus mountains) could have been exploited to extract and refine tin minerals or not (cf. Hall, Steadman 1991; Muhly et al. 1991; Muhly 1993 for examples of critical reception). However, the recent discovery of another Early Bronze Age tin mine at Hisarcık near Kayseri (Yalçın, Özbal 2009; Yener et al. 2015) seems to have brought this debate to rest. Its exploitation is not only corroborated by ceramics at the site, but also by the results of lead isotope analysis of a tin ingot from Alacahöyük that show good agreement with the Hisarcık mine samples (Yalçın 2016: 72, fig. 4). While this, of course, does not exclude that further Iranian or Central Asian tin (cf. Muhly 1973; Nezafati et al. 2008; Nezafati, Pernicka 2012) may also have reached Anatolia during the third millennium BC, it is plausible that a large portion of the tin consumed in northwestern Anatolia originated in the Taurus mountains (ca 450-500km away from Demircihüyük as the crow flies). Although the archaeometallurgical evidence is certainly patchy and fragmentary, it suggests that, for the Demircihüyük community, gold and tin sources were more distant than copper, lead and silver ones, and their procurement would have likely entailed the participation in interregional exchanges. In order to add to this evidence, the next section aims to plot the spatial distribution of specific artefact types and, consequently, to sketch possible metallurgical networks active in Early Bronze Age western and central Anatolia.

## The circulation of metal products

The Demircihüyük arsenical copper crescentic axe from G.100 (S046; fig. 3.1) has its closest typological parallels in the pieces from Polatlı-Beştepeler and Horoztepe, but shares similarities with specimens found further west at Ovabayındır and Ballıca, and further to the southeast at Soloi (Bittel 1940: 192–94, pl. IV.3397–98; Tezcan 1960: 38, pl. 20.2–4; Müller-Karpe 1994: pl. 90.A13; Takaoğlu

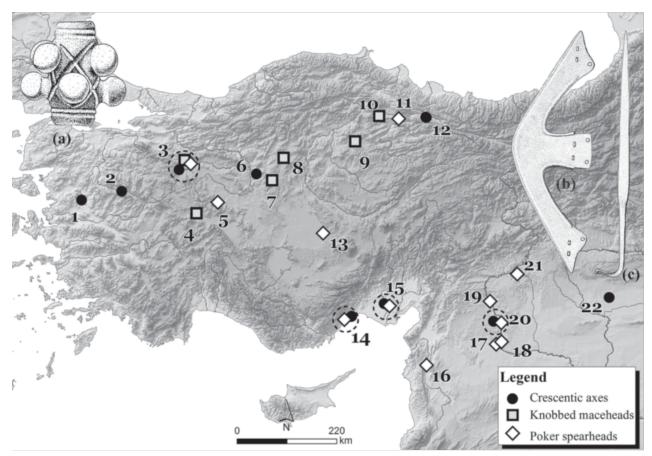


Fig. 10. Spatial distribution of Early Bronze Age artefact types that show links with areas east of Demircihüyük (central Anatolian plateau and beyond; see text for references). Examples of these types are also provided in the figure: (a) knobbed macehead; (b) crescentic axe; (c) poker spearhead. Sites: (1) Ballıca; (2) Bayındırköy; (3) Demircihüyük; (4) vicinity of Afyon; (5) Emirdağ; (6) Polatlı-Beştepeler; (7) Haymana/Oyaca; (8) vicinity of Ankara; (9) Alacahöyük; (10) Göller/Oymaağaç; (11) vicinity of Amasya; (12) Horoztepe; (13) Acemhöyük; (14) Soloi Pompeiopolis; (15) vicinity of Adana; (16) Tell Qarqur; (17) Tell Selenkahiye; (18) Halawa; (19) Jerablus Tahtani; (20) Til Barsip; (21) Titriş Höyük; (22) Chagar Bazar.

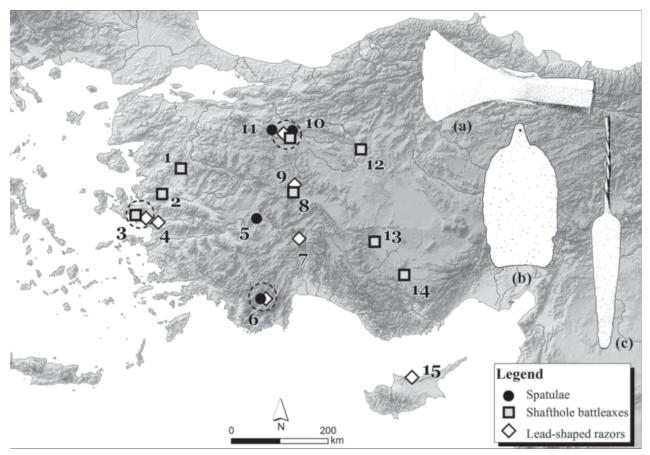


Fig. 11. Spatial distribution of Early Bronze Age artefact types that show links with areas west of Demircihüyük (western Anatolian highlands). Examples of these types are also provided in the figure: (a) shafthole battleaxe; (b) leaf-shaped razor; (c) spatula. Sites: (1) Yortan; (2) vicinity of Manisa; (3) Bakla Tepe; (4) Değirmendere; (5) Beycesultan; (6) Karataş; (7) Harmanören-Göndürle; (8) vicinity of Afyon; (9) Kaklık Mevkii; (10) Demircihüyük; (11) Küçükhöyük; (12) Polatlı-Beştepeler; (13) vicinity of Konya; (14) vicinity of Karaman; (15) Bellapais.

2004: 66). Another unpublished example is said to come from Adana (Tezcan 1960: 38). The detailed work of Guillaume Gernez on Early and Middle Bronze Age Near Eastern weaponry suggests that the origin of crescentic axes can be dated to late Early Dynastic I–II (ca 2800–2600 BC) northern Syria and also that the Anatolian specimens represent a derivative, albeit separate, typological group (Gernez 2008: 177–82). The Demircihüyük example, dated to approximately 2700 BC thanks to its association with a ceramic vessel belonging to settlement levels H-I-K (table 2), is one of the earliest in the Near East. Its presence at the site indicates links with regions further to the east/southeast (fig. 10) already by the early phase of the cemetery, in terms of either the exchange of finished products or the transfer of technological know-how.

Another fossil type is represented by the leaded tinbronze poker spearhead from G.243 (S093; fig. 3.2), which is the westernmost example of a type that has been found spread across the area between northern Syria and central Anatolia (fig. 10; Gernez 2008: 288–89, map 42). According to Gernez, similar spears (without tangs) appeared already around 2800-2700 BC at Carchemish and Tell Razuk, but tanged pieces like that from Demircihüyük did not appear in Syria until after 2450 BC (Gernez 2008: 295). Thus, both the Demircihüyük specimen (from the cemetery, ca 2700-2500 BC) and the Acemhöyük level XI piece (ca 2500 BC; Öztan, Arbuckle 2013: 280, fig. 8) seem to be earlier than the earliest Syrian examples. It is possible that the tanged version may have been elaborated in central Anatolia and later spread to the south. At Demircihüyük, the poker spear is most likely an import from further east, both on typological grounds and based on the chemical composition (as already mentioned, leaded tin bronzes are most common between Cilicia and the Kızılırmak bend). Yet another connection with the eastern part of the central Anatolian plateau is represented by the well-investigated knobbed maceheads (figs 3.7-9), which are mainly distributed in the northern part of the Anatolian plateau (fig. 10; Zimmermann 2006; 2008); the three pieces from Demircihüyük represent - at the moment - the westernmost finds.

Conversely, the arsenical copper battleaxe from G.494 (S181; fig. 3.3), associated with a jug belonging to the latest phases of the settlement (P-'Q'; table 2), seems to point to western connections (fig. 11); the closest parallels come from Yortan and Bakla Tepe, with another piece from Polatlı Beştepeler displaying a similar but not exactly matching shape (Lloyd, Gökçe 1951: 60, fig. 14.13; Keskin 2009: 48, pl. 4.26). Unpublished battleaxes with apparently comparable shapes are also found in the museum collections of Konya, Karaman, Manisa and Afyon (non vidi; Seeher 2000: 54). Arsenical copper leafshaped razors from G.350 and G.421 (S141, S157; fig. 4.12-13) also have their best parallels with finds from western Anatolian sites like Bakla Tepe, Değirmendere, Kaklık Mevkii and Karataş (fig. 11; Petrie 1927: 22, pl. 23.9; Mellink 1967: 255, pl. 77.16-17; 1969: 325, pl. 74.19; Topbaş et al. 1998: figs 51.120, 57.152; Keskin 2009: 169–70, pl. 6.37–39). It is interesting to note that a razor with a very similar shape to the Karatas and Kaklık Mevkii pieces was found at Bellapais (northern coast of Cyprus) in Early Cycladic III contexts (ca 2100–2000 BC), and thus suggests contacts between the two regions (Webb et al. 2006: 273, fig. 1.16). The razor from Demircihüyük G.350 is associated with two jugs belonging to phase 'Q' (ca 2550-2500 BC; table 2), roughly contemporary with the Kaklık Mevkii and Karataş pieces. Yet another indicator of contacts with western Anatolia is represented by a thin blade with a twisted tang from G.213 (S078; fig. 4.6), associated with two jugs from the latest phases of the settlement (table 2). While its shape might suggest a razor, it was found in a child burial (Seeher 2000: 57), and this hints at an alternative function, probably as a spatula. Very similar examples have been found at Küçükhöyük, Karataş and Beycesultan level XIII (fig. 11; Lloyd, Mellaart 1962: 285-86, fig. F9.6; Gürkan, Seeher 1991: fig. 23.2; Warner 1994: 21, pl. 187g).

#### **Discussion of the results**

The analyses carried out indicate that the small hamlet of Demircihüyük (0.3ha; ca 100–130 inhabitants) was involved in a complex network of exchanges at the regional and supra-regional levels, to an extent not seen at any other contemporary site of comparable size. Even though most of the evidence comes from its funerary contexts, comparison with other excavated cemeteries like those of Hacılartepe, Bakla Tepe, Iasos, Karataş, Kaklık Mevkii, Harmanören-Göndürle, Küçükhöyük, Kusura and Yortan clearly demonstrates the richness and variety of Demircihüyük's metal assemblages (Lamb 1937: 54–64; Mellink 1964; 1965; 1967; 1969; Mellink, Angel 1968; 1970; Alpers-Bordaz 1978; Kamil 1982; Pecorella 1984; Gürkan, Seeher 1991; Topbaş et al. 1998; Roodenberg 2008; Şahoğlu 2016). Arguably, this is due to its location

on a major trunk route connecting the north-central plateau with the Marmara Sea and the Troad (Korfmann 1983: 1–2; Massa 2014: 74; cf. also Şahoğlu 2005; Efe 2007).

The lack of significant evidence for on-site metallurgical activities (essentially limited to a stone mould for flat axes) suggests that most of the metalwork may have reached the hamlet in finished form. Even in the absence of provenance analysis, the reconstruction of the metallurgical landscape around Demircihüyük suggests that local exchange networks (between Bursa and Kütahya) might have been responsible for the circulation of several of the copper-, silver- and lead-based objects found at the site. This, of course, leaves open the possibility that many of the copper-based artefacts may have come to site from further away. An indication of this is, for instance, provided by the examples of native copper and some rarer alloys which suggest that some copper-based items may have travelled further than this, likely as finished products. Conversely, the sources of gold (Troad and/or the Izmir region?) and tin (the Taurus mountains?) seem have been substantially further away, between 230km and 500km from the site.

The Anatolia-wide spatial and chronological distribution of a range of artefacts and alloy types further shows that Demircihüyük stood at the interface between two distinct metallurgical networks: one centred on the western Anatolian highlands, the other on the central Anatolian plateau. It is worth noting that similar conclusions have been reached following the analysis of the funerary customs represented in the necropolis; the burials include traits shared by groups both to the west and to the east of Demircihüyük (Massa 2014: 87-89). As argued in the analytical section above, the occurrence of tin bronzes, as well as leaded tin-bronze objects, native copper artefact(s) and knobbed maces, points to contacts with the eastern/southeastern part of the central plateau from at least the cemetery's early phase, i.e. ca 2700-2600 BC (the Kızılırmak bend, Cappadocia, the eastern Taurus mountains). Exchange with the western and southwestern Anatolian highlands (particularly the Afyon region, the Büyük Menderes valley and the western Taurus mountains) is witnessed by the shaft-hole battleaxe, the leaf-shaped razors and the spatula, all occurring during only the later phase of the settlement (ca 2600-2500 BC). Gold, the closest sources of which are to be found in western Anatolia (the Troad and the Izmir region), is also much more common in the late phase: nine out of ten dateable gold artefacts belong to the late phase (in G.37, G.58, G.83, G.88, G.95, G.305, G.350 and G.367). Further confirmation comes from the appearance of marble spade-shaped figurines, which are a typical product of inland western Anatolia (Massa 2016b: 200-04, fig. 7.5), again during the necropolis' late phase only (in G.107 and G.213).

Lastly, Demircihüyük appears to have been involved to some extent in a long-distance exchange network that reached from northern Syria to central and western Anatolia. The beginnings of this network are traditionally dated to ca 2500 BC (cf. the 'Great Caravan Route' of Efe 2007 and the 'Anatolian Trade Network' of Sahoğlu 2005); however, the evidence collected here indicates a much earlier date. This is witnessed by the appearance at Demircihüyük of several metal types with clear parallels in Cilicia and northern Syria, including the crescentic axe, the poker spear and the large numbers of toggle pins, all of which are present from the early phase of the necropolis (ca 2700-2600 BC). In addition to the metal evidence, a unique Mesopotamian bulla, found in a secure stratigraphic context in the courtyard of the settlement (in level F2: Obladen Kauder 1996: 286, pl. 136.5), pushes further back the date for the first direct contacts between the Eskişehir region and Syria to ca 2800 cal. BC. If we include tin as a potential marker of this long-distance exchange network, its occurrence at northeastern Aegean sites like Thermi and Beşiktepe by 3000-2750 BC corroborates this hypothesis. Therefore, the horizon previously described by others as the 'Anatolian Trade Network' or 'Great Caravan Route' seems to relate only to the mature phase of a process that started much earlier.

## Conclusions

This work has brought together different aspects of archaeometallurgy (artefact typology, analysis of manufacturing techniques, metal compositional analysis, GIS-led spatial distribution of artefacts) that are rarely discussed together in the literature on prehistoric Anatolia. This approach seems to have been successful in sketching broad patterns of metal manufacture and exchange in northwestern Anatolia through the lens of the small but well-connected Demircihüyük community. The discovery of direct contacts between the central plateau and northern Mesopotamia already by ca 2800 cal. BC, as well as the identification of distinct metallurgical networks active in Anatolia during the early Early Bronze Age, is of particular importance for studies on prehistoric Anatolia. This paper is the first preliminary report of an ongoing project entitled 'From mines to graves: metallurgy and metal exchange in northwestern Anatolia, ca 3700–1500 BC' (see Massa 2016a for a brief description). We hope in the near future to carry out provenance analysis on both the finished products and metalworking debris found at various sites in the region, and to conduct microscopic investigations in order to understand better the technological choices made in metalworking.

## Acknowledgements

We are grateful to Bruker Nanoanalytics for providing a pXRF spectrometer on loan, free of charge, and, in particular, to Lee Drake and Mike Dobby for their assistance. Many thanks also go to Asuman Arslan, Director of the Eskişehir Archaeology Museum, and to museum staff members Gülsüm Baykal-Okta and Baykal Aydınbek for their assistance in the analysis. We thank Stefano Spagni for his valuable comments on the analytical results. We would further like to thank the Turkish General Directorate of Monuments and Museums for granting permission to study the Demircihüyük metal assemblage. We are also extremely grateful to Joseph (Seppi) Lehner for commenting upon an early draft of this paper; any mistakes and imprecisions are, of course, our own. Lastly, 'From mines to graves: metallurgy and metal exchange in northwestern Anatolia, ca 3700-1500 BC' was sponsored by a British Institute at Ankara study grant (2016).

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