Abstract: The following contribution presents the results from the portable X-Ray fluorescence (p-XRF) analysis of the Early Bronze Age metal dagger from Karaburun, found in 2015 and first published in 2018. The non-destructive analysis revealed the dagger’s chemical composition as arsenical (1.10%) copper (98.22%), an alloy used since the reinvigoration of Anatolian metalwork in the mid IVth millennium B.C. A review of current excavations and geology-based surveys in the region confirms the impression that our dagger might well have been produced by a local workshop in the vicinity of modern İzmir, or even on the Karaburun peninsula itself.

Keywords: Anatolia • Western Anatolia • Early Bronze Age • Daggers • Archaeometry • pXRF-analysis


Anahtar Kelimeler: Anadolu • Batı Anadolu • Erken Tunç Çağı • Hançerler • Arkeometri • pXRF-analiz

Prologue

Traditional field surveying, a method of spatial reconnaissance as old as curiosity in archaeological features itself, continues to deliver important insights into the archaeology of defined area, despite its comparatively simple methodology and rather antiquarian flavour. A good example to support this observation is the discovery of a metal dagger in the course of the Karaburun peninsula survey, initiated by Çiler Çiligiroğlu, Ahmet Uhri, Berkay Dinçer and other specialists from Turkish and international universities to highlight the waning and waxing through the ages of human impact on
The dagger was found during the Karaburun survey season in 2015 in the southeastern part of the peninsula, known as Manal Bay, a part of the communal district of Çatalkaya Mahallesi. The overall archaeological harvest from this area was quite remarkable: Spread over roughly 1.6 hectares, together with flint and obsidian tools and production debris, considerable quantities of Ottoman, Byzantine, Roman and especially Early Bronze Age pottery was recorded, which proves the presence of human communities in this particular part of Western Anatolia in the IIIrd millennium B.C.

The actual pièce de résistance, however, is the above mentioned tanged and riveted dagger, since metal objects, although occasionally retrieved, are certainly not a frequent discovery during archaeological field surveying. The tiny stabbing weapon, published by Sinan Ünlüsoy in 2018 represents -until further notice- the first Early Bronze Age metal item discovered in this region. Its typological autopsy showed close parallels with copper-based Central and Western Anatolian daggers from domestic and funeral contexts, attested at sites such as: Ahlatlıbel, Demircihöyük-Sariket, Bademağacı and Beycesultan, together with numerous unstratified examples from the notorious Yortan cemetery near Bayındırköy, that match the general design of the Karaburun specimen. That said, dagger blades with a single rivet to originally secure the halves of a wooden or bone handle are likewise known from even earlier, Late Chalcolithic contexts: The cemetery at İlpinar, securely dated to the mid IVth millennium B.C., provided prominent examples of such riveted daggers with triangular or rhombic blades. However, its shape and execution enable it to be described as an item dating from the Anatolian Early Bronze Age.

Non-destructive portable X-Ray fluorescence (pXRF) analysis

For a more comprehensive appraisal, the bulk analysis of the dagger’s chemical composition is without question an indispensable requirement, as already indicated in S. Ünlüsoy in his initial presentation of the object - the proverbial ”missing jigsaw piece” referred to in the title of this article. This could finally be realized in September 2019 in collaboration with the Sarayköy Nuclear Research and Training Centre (SANAEM), which provided the necessary equipment to carry out surface bulk analysis to determine the elements forming the object’s composition. Non-destructive bulk analysis using a portable X-Ray fluorescence device (henceforth abbreviated as pXRF) has risen from its roots in geochemistry and is of considerable prominence as a comparably easy-to-handle spectrographic assessment method in archaeological research in particular over the course of the past two decades. With simply pinpointing of the surface of a solid object, the energy response of
the backscattered X-Ray beam shot at the item coincides with the chemical elements the specimen is made from. Depending on the object’s consistency, different analytical settings tailored for lighter elements expected in soils or heavier ones associated with metals allow for revealing the weight percentages of the different elements employed. As a result, an ever-growing number of studies either centering on descriptive bulk analysis of metal objects or the characterization of obsidian in the scope of provenance studies has been produced over the past few years. Since no physical harm to the object is involved, permits to conduct pXRF-based artefact autopsy are issued by the relevant authorities much more willingly than if sampling – and the necessity of damage, no matter how small- to the item would have been involved.

This processual advantage, however, is simultaneously a potential obstruction, since a precise analysis of the elementary composition could only be achieved through core sampling, and not from only with scanning random points on the surface of an object - an issue thematised in a number of the more recent contributions\(^\text{10}\). That said, we are very well aware of the fact that a simple non-destructive surface analysis of one single dagger found during an archaeological field survey will not overturn accumulated archaeometrical certainties related to Anatolian metal objects at large. However, we are convinced that this initial, basic spectrographic evaluation casts some valuable light upon archaeological questions related to metal production and consumption in the Early Bronze Age of Western Anatolia, which are subject to debate in the final part of this paper.

**pXRF analysis of the Karaburun dagger - procedure and results**

For this particular study, an OLYMPUS brand VANTA model pXRF device (4 W powered, max. 40 kV, SDD detector 140 eV/5.9 Mn Kalfa, Rh anot) was used, which allows for non-destructive bulk analysis of the chosen object.

For the measurements to be taken, the Alloy Plus mode was activated, with the elements range set between Al and U. The detection limits range from 200 ppm to a few ppm. The limits for especially Fe, Cu, As, Pb are between 5 ppm and 20 ppm. Calibration is imperative to ensure reliable readouts for the object’s elementary composition. In order to confirm the accuracy of our XRF measurements, some reference materials were analyzed. The measured concentrations are listed in the following chart (Fig. 2).

30 seconds per scan was considered sufficient to receive a secure readout of the elements involved. Since historical metal objects are not industrially produced, but in its very sense manufactured, they generally display a rather heterogenous casting structure that, depending on the size and condition of the investigated piece, requires several analysis runs to obtain a statistically safe and sound impression of the chemical composition of the artefact. That aside, the corrosion processes, casting-related phenomena such as plating or an inverse segregation of alloy phases and -last but not least- conservation treatments can further jeopardize the accuracy of the readouts\(^\text{11}\). To minimize the risk of erroneous measurements, a total of 11 analysis runs targeting both the front and back of the blade were carried out, specifically pinpointing those areas where there was little or no evidence of corrosion (Fig. 1).

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10 Feretti – Moidi 1998; Liritzis – Zacharias 2011; Shackley 2012. - There certainly are a variety of alternative (however generally destructive) methods of analysis, such as: PIXE, ESM-EDX and NAA that would provide measurement results with a considerable higher precision.

11 For a concise account of current pXRF possibilities and limitations with special reference to metal analysis see Lehner 2014; Massa et al. 2017, 56-59.
**Fig. 1** Dagger from Karaburun-Çatalkaya, with the p-XRF measurement points indicated (after Ünlüsoy 2018, with additions)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (%)</th>
<th>Au (%)</th>
<th>Ag (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSBL</td>
<td>5.37 ± 0.02</td>
<td>4.72 ± 0.08</td>
<td>89.98 ± 0.03</td>
</tr>
<tr>
<td>ABKMF</td>
<td>12.46 ± 0.02</td>
<td>12.1 ± 0.12</td>
<td>58.57 ± 0.04</td>
</tr>
</tbody>
</table>

*Compositional analysis of certified reference gold alloys, C: Certified, M: Measured*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (%)</th>
<th>Pb (%)</th>
<th>Ag (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNR141</td>
<td>7.66</td>
<td>8.9 ± 0.1</td>
<td>-</td>
</tr>
<tr>
<td>CNR91</td>
<td>1.51</td>
<td>1.57 ± 0.04</td>
<td>1.24</td>
</tr>
</tbody>
</table>

*Compositional analysis of reference silver alloys, R: Reference, M: Measured*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pb (%)</th>
<th>Sn (%)</th>
<th>Zn (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNR691</td>
<td>C</td>
<td>M</td>
<td>C</td>
</tr>
<tr>
<td>A</td>
<td>7.9 ± 0.7</td>
<td>8.6 ± 0.2</td>
<td>7.16 ± 0.21</td>
</tr>
<tr>
<td>D</td>
<td>9.2 ± 1.7</td>
<td>9.8 ± 0.2</td>
<td>10.1 ± 0.8</td>
</tr>
</tbody>
</table>

*Compositional analysis of certified reference copper alloys BR691 C: Certified, M: Measured*

**Fig. 2** Compositional analysis of certified reference gold alloys, C: Certified, M: Measured. Note the very good agreement with the certified values for most elements

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu % (Average)*</th>
<th>As % (Average)</th>
<th>Pb % (Average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dagger (Karaburun-Çatalkaya)</td>
<td>98.22</td>
<td>1.10</td>
<td>0.62</td>
</tr>
</tbody>
</table>

*Includes 11 different point measurements*

**Fig. 3** p-XRF analysis results for the Karaburun-Çatalkaya dagger
The rectified results given in the table below testify to a typical copper-arsenic Cu-As alloy, with the Arsenic content a notch above the threshold to classify it as an alloy (Fig. 2-3).\(^\text{12}\)

That said, whether Arsenical Copper, or occasionally even “real” Bronze was intentionally alloyed or was simply the result of smelting “dirty copper” containing a larger quantity of naturally occurring alloying agents like tin (Sn), antimony (Sb) or arsenic (As) is still the subject to controversial debate\(^\text{13}\). Anatolia’s high mineralization and the frequency of polymetallic deposits certainly enhances the possibility of accidental co-smelting of arsenic or tin-rich copper ores, especially considering the hazardous side effects of manufacturing larger amounts of highly toxic arsenic-rich materials that should have been realized in the process at one point\(^\text{14}\). However, the discovery of huge amounts of speiss smelted from arsenopyrite-rich ores to produce arsenic copper, as attested at Arisman in Iran, and arsenic residues in crucibles respectively related metalworking equipment from Çukuriçi Höyük (see below) highlight the frequent utilization of substantial amounts of arsenic-rich minerals, despite the looming threat of being gradually poisoned\(^\text{15}\).

The Karaburun dagger within the context of Western Anatolian/ Eastern Aegean Early Bronze Age metal production and consumption

The use of arsenical copper as the predominant working material in the later IV\(^\text{th}\) millennium B.C. coincides with a reinvigorated Anatolian metallurgy, idle since its inception around 5.000 B.C.\(^\text{16}\). From about 3.500 B.C. onwards, metal production resumes in a variety of places, however exclusively using unalloyed or arsenical copper, respectively exotic alloys like copper-silver as attested from Late Chalcolithic Arslantepe\(^\text{17}\). A review of metal production and consumption in Early Bronze Age Anatolia, and specifically the metalwork along the Central Aegean coast with its hinterland shows that, especially in the first half of the III\(^\text{rd}\) millennium B.C., arsenical copper is still the most prominent alloy applied to a variety of objects, including double-edged stabbing weapons. Recent comprehensive analyses of metal objects from Early Bronze Age Demircihöyük and its Sarıket necropolis, two of the most meticulously excavated and published sites in northwestern Turkey, confirm a majority of arsenical copper items (39%), followed by objects made from unalloyed copper (34%). Artefacts made from Bronze only add up to a rather modest 14% for both domestic and funeral assemblages\(^\text{18}\). The preponderance of arsenic is even more explicit along the Black Sea and its hinterland, where arsenical copper is used throughout the III\(^\text{rd}\) millennium B.C.\(^\text{19}\). This is sharply

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\(^{12}\) There is no general agreement on what weight percentage of alloying agents promotes an unalloyed copper object to Bronze or other copper-based alloys, since definitions of what to consider an (intentional) alloy range from a tiny 0.5 to a substantial 3% (Massa et al. 2017, 66; see also below). We however concur with J. Lehner’s observation (Lehner 2014, 132) and set the demarcation line at 1%.

\(^{13}\) Lechtman 1996; Lehner 2014, 132; Massa 2017, 66.

\(^{14}\) Harper 1987; Ratnaike 2003.

\(^{15}\) Rehren 2012; Mehofer 2016.


\(^{17}\) Palmieri 2002; Zimmermann 2016.

\(^{18}\) Massa 2017, 68.

\(^{19}\) Özbal 2002; Zimmermann 2010.
contrasted with the occurrence of the tin-copper alloy "belt" at the very beginning of the Early Bronze Age around 3.000 B.C., extending roughly from the Northern Aegean islands and northwest Turkey with Troy as an early center of Bronze manufacturing, across the central Anatolian steppe region, as far as Susa in the Iranian highlands. Nevertheless, arsenical copper, a potentially more hazardous material, was still widely processed in the advanced Early Bronze Age of central Anatolia, where it partially equals Bronze as the common material for creating tools, weapons and jewellery.

The dagger from Karaburun, however, retains the traditional chemical fingerprint typical of copper-based objects from the vicinity of modern Izmir; Çukuriçi Höyük (Selçuk, Ephesus), located about 145 km southbound from the Karaburun peninsula and a possible regional production center for metal objects in the early 3rd millennium B.C., yielded considerable amounts of debris associated with the production of arsenic-rich copper. Ore processing prior to smelting together with other evidence for pyrotechnical activities was likewise attested at Liman Tepe, another major Early Bronze Age site in the district of Izmir. However, arsenic was not amongst the trace elements detected in the associated atacamite fragments, an oxidized copper mineral likely to have been used for further metallurgical activities. What remains is a hypothetical but reasonable possibility that the dagger was produced at Karaburun itself. Examples like Çamlıbel Tarlası, a small Chalcolithic ham-

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20 Pernicka 2003, 145-146.
21 Geniş 2014.
22 Mehofer 2016.
23 Mehofer 2014, 466-467; 2016.
24 Kaptan 2008.
The Missing Jigsaw Piece – pXRF Bulk Analysis of the Karaburun Dagger

let in the vicinity of Hattusha/ Boğazkale, well illustrate that very small rural communities could produce metal objects autochthonously, benefitting from local metal and mineral outcrops. As noted above, the collected potsherds and lithic assemblages at Karaburun-Manal Bay do indeed testify to the presence of a sedentary human community in the IIIrd millennium B.C.

Finally, there is ample evidence for potential raw material resources that could have been explored and exploited to supply local workshops in the Izmir catchment area: in addition to the well-known copper mines much further to the north and northwest, with at least some of them definitely also active in prehistoric times, there are several metallic deposits located along the Karaburun peninsula itself. Their majority might be rich in mercury, however some of them, like the Karaburun- Eğriliman outcrop, seem to contain copper in at least modest amounts. The most promising evidence, however, comes from recent surveys conducted in the vicinity of Çukurici Höyük: In the vicinity of about 70 kms, over 50 previously unrecorded metallic repositories could be mapped, with some of them being close to the surface and therefore easily accessible. Hence it seems possible that we are just beginning to comprehend the actual mineralogical potential of the central Aegean catchment.

Be that as it may, the Early Bronze Age community who produced, used, and finally discarded our arsenical copper dagger from Karaburun certainly benefitted from the abundance of metal resources in Anatolia, and its westernmost provinces in particular – the commodity for interregional trade and exchange ever since the advent of extractive metallurgy.

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26 Schoop 2011.
27 Ünlüsoy 2018, 223-224; 226.
30 Wolf 2012, 143.
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