The Cave of the Sandal, Ketef Jericho: new evidence from recent Chalcolithic copper finds

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Introduction
In 1993 during ‘Operation Scroll’, two copper tools and one copper mace-head were found at the Cave of the Sandal, Ketef Jericho (Eshel & Zissu 1998; 2000). The ‘utilitarian’ tools represent two different Chalcolithic types: a flat axe and a narrow chisel. The disk-shaped, undecorated mace-head is also a known Chalcolithic metal artefact type, but the disk-shape is not the most common variation (Bar-Adon 1980). Mace-heads probably served foremost as weapons. However, it is possible that mace-heads also encompassed some additional symbolic meanings, as a prestige object, at contemporary sites throughout the wider region. Sufficiently large numbers of the copper and/or copper-alloy artefacts from the Chalcolithic period have been discovered in excavations in the Southern Levant (Ilan & Sebpane 1989; Levy & Shalev 1989; Gonen 1991; Levi 1998) to build a comprehensive typology of metal objects. The technical investigations of these three artefacts from the Cave of the Sandal, requested by the excavators Dr. Hanan Eshel and Boaz Zissu, provide new compositional and metallurgical data against which to compare metal object types from other Chalcolithic sites.

Alloy compositions cannot be evaluated accurately without undertaking quantitative compositional analysis of uncorroded metal remaining in the artefacts, but not all objects are available for sampling. Selected Chalcolithic copper artefacts have already been investigated for composition and metallographic structures; such as the ‘treasure’ of Nahal Mishmar (Key 1986; Potashkin & Bar-Avi 1980; Shalev & Northover 1993; Tadmor et al. 1995) as well as metal artefacts from Nahal Zeelim (Key 1980; Shalev & Northover 1993), Bir Safadi (Tylcoatc, Rothenberg & Lupu 1974), Shigimin (Shalev & Northover 1987), Nahal Makuh, Nahal Qanah and Gilat (Shalev & Northover 1995) and Peqi’in cave (Segal et al. in prep.). Based upon published compositional data, it has been proposed that during the Chalcolithic period two distinct metal ‘industries’ existed to produce copper tools and prestige objects (Levi 1998). Unexpectedly, the utilitarian tools were made of unalloyed copper while the prestige objects, such as crowns and standards, were made of copper alloyed with arsenic and/or antimony. Normally, one would expect tools to be alloyed in order to produce more effective cutting edges, taking advantage of the higher hardness produced by cold-working copper-arsenic alloys, for example. Nevertheless, this is not the case. Rather than hardness, then, other properties, perhaps colour and better casting characteristics, of copper-arsenic or copper-antimony alloys were preferred, and possibly deliberately selected for specific prestige metal objects.

The aim of the current research was to investigate the metal composition, metallography and microhardness of the three excavated artefacts. Are the axe and chisel unalloyed? Is the mace-head also unalloyed? If so, then the mace-head should be classified, on composition alone, perhaps more as a functional ‘tool’ than a prestige object. This technical investigation aims to reconsider briefly the classification of Chalcolithic tools and weapons, and contrast the results with published technical data for prestige metal objects. The production of copper-arsenic alloy objects has been viewed as most probably quite distant, outside the Southern Levant (Levy 1998). Nevertheless, several other options exist for procedures and locations for production of copper-arsenic alloys (Tyolecote 1991). In addition, we tried to assess closer locations of ores possibly utilised for artefact production. Lead isotope ratio determination is very useful for provenance studies, and was used here for this end.

Analytical procedures
Samples for metallography were cut with a jeweler’s saw. The sections were mounted in epoxy resin, ground and polished following usual procedures. The polished sections were etched in aqueous ferric chloride and acidified potassium dichromate solutions. The metallographic structures were observed under a Nikon metallurgical microscope.

The mounted sections were also subjected to Vickers microhardness tests to quantify better the combined effects of cold-working/annealing and alloy compositions. The load used was 300 g. Microhardness values and the estimated degree of cold-working are especially important for evaluating tools of unalloyed copper as well as prestige objects of selected copper alloys.

The metal compositions of the three artefacts were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using Jobin Yvon JY-38 mono- and JY-48 poly-chromators at the Geological Survey of Israel. The operating conditions of the ICP-AES have been described earlier (Segal et al. 1994). The limits of detection (LOD) of determined elements are estimated at about 1 ppm for the selected sample size and dilution of the sample solution. In addition, the artefacts were drilled, with the initial corrosion products excluded from the 25 mg samples. The precision, or relative standard deviation (RSD) of method for the analyses is as follows: 1 % for major elements, about 3 % for minor elements and about 10 % for trace elements. The results of the ICP-AES were checked against area analyses under Scanning Electron Microscope (JEOl 840) equipped with an Energy Dispersive System (SEM-EDS) for the metallographic sections. A good accordance was observed between the two analytical techniques. Detailed micro-analytical and metallographic studies were performed on the mounted samples using SEM-EDS and a back-scattered electron detector (BEI). A mounts of oxygen inclusions were estimated under a Nikon metallurgical microscope using polished sections.

Lead isotope determination was carried out using a Perkin-Elmer Sciei Elan 6000 Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The precision of this method for major lead isotopes is about 0.3 % (Halicz, Erel & Veron 1996).

Copper artefacts
Drawings of the three artefacts as well as their sizes and selected sample positions are shown in Fig. 1. The Locus (L)
and Basket (B) numbers designate the excavation location and object find number in the publication of the site. The objects were relatively well-preserved, only copper-oxide and carbonate corrosion layers covered their surface. From the metallographic sections, the penetration of corrosion into the metal is estimated at about 30 microns.

1. Flat axe (L 30, B 165) with convex surfaces and sharp rounded edge. Its weight is 285.5 g, its length is 13.0 cm. A mounted metallographic section was made from the cutting edge (transverse section). No analogs to this axe were found in Bar-Adon (1980).

2. Narrow chisel (L 30, B 171) with widening towards its sharp rounded working edge. It was broken in antiquity, but both parts were found in the excavations. Its weight is 229.5 g, its length 12.1 cm. The chisel was sampled from the cutting edge both in transverse and longitudinal sections. Fifteen chisels found in Nahal Mishmar varied in length from 15 to 30 cm and in weight from 156 to 807 g (Bar-Adon 1980).

3. Disk-shaped mace-head (L 30, B 1101) with convex surfaces and shaft-hole, the rims of which have sharp carinated edges. It weighs 242.5 g and is 8.5 cm in diameter. The mace-head was sampled twice: from the disk edge and from the carinated end of the shaft-hole in transversal sections. Bar-Adon (1980) called this type simply a ‘disk’ and grouped it together with short standards. Eleven ‘disks’ from Nahal Mishmar ranged in length from 15 to 30 cm and in weight from 156 to 807 g (Bar-Adon 1980).

Analytical results
Overall compositional analysis by ICP-AES (Table 1) shows that each artefact is made of unalloyed copper. The two tools are significantly “purer” than the mace-head, they contain less than 0.1% of impurities. Only traces of iron, cobalt, manganese and lead were observed in the tools. The disk-shaped mace-head contains higher concentrations of lead (0.013 %), nickel (0.17 %) and iron (0.015 %). These observations are in correspondence with published results on Nahal M ishmar objects. It is confirmed again that (so far) all the Chalcolithic tool-types were made of unalloyed copper (Shalev & Northover 1993; 1995; Tadmor et al. 1995). In contrast, according to Key (1980) and Tadmor et al. (1995), although most of prestige objects were of alloyed copper, two standards (61-52 and 61-104) were also found to have been made of unalloyed copper. It is possible that Nahal M ishmar artefacts 61-40, 61-58 and 61-426 with arsenic content less than 1.92 % (Key 1980) are also unalloyed, because this value corresponds to the limit of detection of the optical-emission analytical technique used by Key. Now, the disk-shaped mace-head from the Cave of the Sandal is also shown to be unalloyed copper and probably should not be classified together with ‘short standards’ as done by Bar-Adon (1980). Therefore, a proposed distinction between unalloyed tool-types and alloyed prestige objects is not necessarily exclusive. More objects should be investigated to assess the significance of this proposed correlation. Cold-working properties and marginal colour differences are readily apparent for production of sheet metal of copper-arsenic alloys (Letchman 1996). However, intermediate alloy colours and compositions around 1-2 % arsenic in copper may not be very distinctive for larger, cast, partially cold-worked, utilitarian tools. Prestige copper-arsenic alloys with over 2 % arsenic are strikingly different in colour. Furthermore, loss of arsenic is most probable from remelting under oxidising conditions (McKerrell & Tylecote 1972). Thus, some overlap and mixing of alloy compositions and object types should actually be expected. Based upon composition alone, the three artefacts analysed from the Cave of the Sandal could have been smelted from high-grade copper ores, such as the best examples of copper ore from Feinan as well as the Timna region. These variable copper ores can also contain significant concentrations of iron and sulphur. Sometimes nickel is detected in ores. It has been proposed that up to 0.4 % of nickel in A bu Matar and Bir es Safadi axes originated in Feinan ores (Hauptmann 1989) and 0.15 % of nickel in the Timna copper (Rothenberg 1990).

Metallography and microhardness measurements
Unalloyed, annealed copper has a Vickers microhardness of about 40 HV, while cold-worked copper at about 95 % reduction in thickness reaches a microhardness maximum at around 120 HV as kg/mm² (Smith 1982: 95). In practical terms, these differences are readily observed for copper sheet and for edge hardness. One might expect copper ‘utilitarian’ tools to have appreciably hardened cutting edges.

1. Flat axe
Visual examination of the axe revealed ‘stipples’ on both sides of the working edge, suggesting its use for hard materials. The

**Table 1. Chemical composition of copper artefacts from the Cave of the Sandal, in wt %**.

<table>
<thead>
<tr>
<th>Identification</th>
<th>Sn</th>
<th>Zn</th>
<th>As</th>
<th>Sb</th>
<th>Pb</th>
<th>Co</th>
<th>Ni</th>
<th>Fe</th>
<th>Mn</th>
<th>Ag</th>
<th>Au</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ax e</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>0.035</td>
<td>0.005</td>
<td>0.0001</td>
<td>0.015</td>
<td>nd</td>
<td>99.2</td>
</tr>
<tr>
<td>Chisel</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>0.009</td>
<td>0.001</td>
<td>0.045</td>
<td>0.006</td>
<td>0.0003</td>
<td>0.006</td>
<td>nd</td>
<td>98.9</td>
</tr>
<tr>
<td>Disk-shaped</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>0.013</td>
<td>0.001</td>
<td>0.17</td>
<td>0.015</td>
<td>0.0003</td>
<td>0.015</td>
<td>0.001</td>
<td>99.1</td>
</tr>
</tbody>
</table>
mace-head    |

Note: nd - not detected.
polished section revealed tiny copper sulfide inclusions located at the boundaries of the primary casting grains. They range in size from 0.09 to 0.15 mm. The copper contains less than 0.03 % of oxygen. Clear structure appears after etching (Fig. 2). The etched sample showed a similar structure in both sections: slightly deformed recrystallised polygonal grains (size 0.02-0.04 mm) superimposed on compressed original grains (Fig. 5). The compression degree increases towards the blade from 20-40 % up to 50-60 %. The structure is not fully recrystallised.

The chisel was cast in a one-piece mould, then probably hot-worked at 400-550 °C, forging was finished on cooled metal. Microhardness was measured at 100 HV and 108 HV for the blade edge. A gain, the working edge was work-hardened. This narrow chisel could serve as a suitably utilitarian tool.

3. Disk-shaped mace-head

Visual observation of the surface defects indicated that a two-piece closed mould was used for casting. This mace-head does not contain a cavity inside; it is a solid casting. Both polished sections revealed the presence of copper sulfide and Cu-Cu₂O inclusions around the casting grains. The sample from the shaft-hole edge contains less than 0.01 % of oxygen and the second one 0.05-0.07 %. In both the etched sections partly recrystallised, undeformed, small grains superimposed on deformed elongated cast grains were observed (Fig. 6). Their compression is estimated at about 40 %.

The disk was cast and subsequently hot-forged at ca. 400 °C to remove casting defects. The shaft-hole edge was slightly cold-worked. The microhardness of the disk edge was 95 HV and near the shaft, 98 HV. These microhardness values most likely represent surface ‘finishing’ of the disk possibly as well as deliberate work-hardening of the edge and around the shaft-hole. Due to the limited section size and depth into the object, the center microhardness could not be measured for better comparison.

Provenance study

For provenance elucidation of the three studied objects, lead isotope ratios were measured. \( \frac{208\text{Pb}}{206\text{Pb}} \) and \( \frac{207\text{Pb}}{206\text{Pb}} \) ratios are shown in Table 2 and Fig. 7. For comparison of our data with the relevant ores, results of lead isotope ratios in Feinan (Hauptmann et al. 1992) and Timna (Gale et al. 1990) ores are also plotted. Values for Feinan ores are indistinguishable from Timna ores. As was concluded by Hauptmann et al. (1992) two types of copper ores, Middle Brown Sandstones (MBS) and Dolomite Limestone Shales (DLS), were used for ancient smelting at Feinan. MBS plot in the lower left area of the isotope graph, values of DLS are significantly higher. The isotope ratios of Chalcolithic objects from Feinan fall into a wide range showing that both types of ore were used in the Chalcolithic period. Later - from EB II - only DLS were utilised. Timna copper ores, having mainly higher lead isotope ratios (Gale et al. 1990), cover only the Feinan DLS range. A comparison of lead isotope ratios for our objects with published Chalcolithic and early stage EB I copper artefacts from Levant is shown in Fig. 8. The data used

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\begin{array}{l|ll}
\text{Identification} & \frac{207\text{Pb}}{206\text{Pb}} & \frac{208\text{Pb}}{206\text{Pb}} \\
\hline
\text{Axe} & 0.8424 & 2.0819 \\
\text{Chisel} & 0.8383 & 2.0815 \\
\text{Disk-shaped mace-head} & 0.8613 & 2.1059 \\
\end{array}
\]
in the Feinan region. Therefore, it can be concluded that their ore source is Mishmar, Arad, Ashqelon and Feinan ores and copper samples correspond well with pure copper objects from Nahal sigma uncertainty is shown in Fig. 7), isotope ratios for our Taking into consideration the precision of our method (the 2 per artefacts remains unidentified. It seems more important alloying concentrations of arsenic and/or antimony in the cop- produced such unalloyed copper. However, a source for the alloying of metals and object typology as well as alloy selection in the Chalcolithic period.

Acknowledgements
We would like to thank the excavators, Dr. Hanan Eshel and Boaz Zissu for the opportunity to analyse these interesting artefacts. The structures of the metallographic samples were interpreted on the basis of copper standard samples prepared, hot-worked and investigated in the laboratory of Prof. N. R yindia at Moscow University.

References


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were: Nahal Mishmar (Tadmor et al. 1995) pure copper objects, Wadi Fidan 4 (Hauptmann et al. 1992), EB I Arad (Hauptmann, Begemann & Schmitt-Strecker 1999) and EB IA Ashqelon (Segal, Halicz & Kamenski, in press). As was considered in the mentioned papers, pure copper objects are consistent with Feinan ores, prills and slags.

Taking into consideration the precision of our method (the 2 sigma uncertainty is shown in Fig. 7), isotope ratios for our samples correspond well with pure copper objects from Nahal Mishmar, Arad, Ashqelon and Feinan ores and copper objects. Therefore, it can be concluded that their ore source is in the Feinan region.

Conclusions
The three analysed objects are made of unalloyed copper. The two tools are relatively ‘purer’ than the disk-shaped macehead, based upon the sums of the measured impurities. The question if the ancient smiths appreciated and manipulated or deliberately selected different alloy compositions for tools as opposed to prestige objects is unresolved based upon available technical evidence. Two types of casting moulds apparently were used - two-piece closed and one-piece open moulds. The tools were produced by casting and forging in order to achieve necessary technical properties as well as final form and desired appearance. Two technological schemes of forging were applied: cold-working with annealing and hot-working. Such steps in manufacturing were apparently known in the Chalcolithic period of the Southern Levant. Current research strongly suggests the use of Feinan ore as a source. High-grade copper ores from this mining region could have produced such unalloyed copper. However, a source for the alloying concentrations of arsenic and/or antimony in the copper artefacts remains unidentified. It seems more important to emphasise the existence of local metalworking and object typology as well as alloy selection in the Chalcolithic period.

Fig. 7. Lead isotope ratios in studied objects compared with Timna and Feinan ores and slags.

Fig. 8. Lead isotope ratios in studied objects compared with the Chalcolithic and EB I pure copper artefacts from Nahal Mishmar, Wadi Fidan 4, Ashqelon and EB I Arad.