

## MICROPROBE ANALYSIS OF EARLY COPPER ARTIFACTS FROM THE NORTHERN SINAI AND THE JUDEAN CAVES

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A number of significant archaeological finds have been made in Israel related to the development of early copper metallurgy and smelting practice, and dates as early as the 3rd/4th millennium B.C. Among them are the mining and smelting finds made at Timna;<sup>1</sup> the casting enclave at Abu Matar;<sup>2</sup> and the large hoard of cast copper objects found at the caves in Nachal Mishmar<sup>3,4</sup> and smaller finds at Nachal Badir,<sup>5</sup> both locations in the Judean Desert. Controversy exists as to the cultural origins or possible commonality of these finds.<sup>6</sup> The use of metallographic and microanalytical techniques to study metal objects found at some of these sites might shed light on this problem.

Previous analyses exist for the ores found at Timna<sup>7</sup> and Abu Matar.<sup>8</sup> Timna ores are mainly nodular chalcocite and malachite,<sup>7</sup> whereas the ore found at Abu Matar is mainly malachite and cuprite with some chalcocite.<sup>8</sup> In both cases they are free of arsenic, and therefore pose a dilemma with respect to the high bulk arsenic levels reported for maceheads from both Abu Matar and Nachal Mishmar.<sup>4</sup> The copper metal finds at Timna are consistent with smelting from the in situ ores.<sup>9</sup> We have therefore obtained a number of metal objects from Abu Matar and the Judean Desert in order to compare the results with each other and against the reported ore analyses.

### *Copper Piece from Abu Matar*

The first sample examined was a small piece of copper from Abu Matar that was found together with pieces of ore and crucibles, and is possibly a splashing from the casting of a large piece. Examination by scanning electron microscopy (Fig. 1) indicated the structure to be typical of cast crude copper and to contain many blowholes due to gas evolution and a large number of second-phase spherical inclusions. EDS analysis of the metal matrix indicated only copper to be present, and the inclusions to be copper sulfide.

### *Axehead from Safadi (loc. 307) near Abu Matar*

This piece has been the focus of previous study by optical metallography.<sup>8</sup> Initial examination in the SEM reconfirmed the previous findings that the piece has a cast-and-worked structure. Again, EDS analyses of the metal matrix detected only copper. However, three distinct types of inclusions were found. First, there is a copper oxide second phase with morphology typical of the copper-copper oxide eutectic (Fig. 2). There are numerous inclusions that contain mostly nickel, copper, and sulfur; Fig. 3 shows one of these inclusions with the x-ray line scan for Ni superimposed. The inclusion thus appears to be nickel-copper sulfide, and is therefore problematic since nickel has not been reported to be present in any of the ore analyses.<sup>1</sup> The Abu Matar metal analysis given by Dayton<sup>6</sup> (quoted from Key<sup>4</sup>) and indicating the presence of Ni is erroneous and the object should be properly identified as coming from Nachal Mishmar. Although the presence of Ni in the axehead from Safadi warrants further study, the lack of detectable arsenic in the copper matrix still points to consistency with fabrication from local ore source.

A third type of inclusion (Fig. 4) is found only near the surface of the axehead and is found to contain only silica. It is believed that these are probably quartz grains included in the piece during casting and originating from either the casting crucible or mold material.

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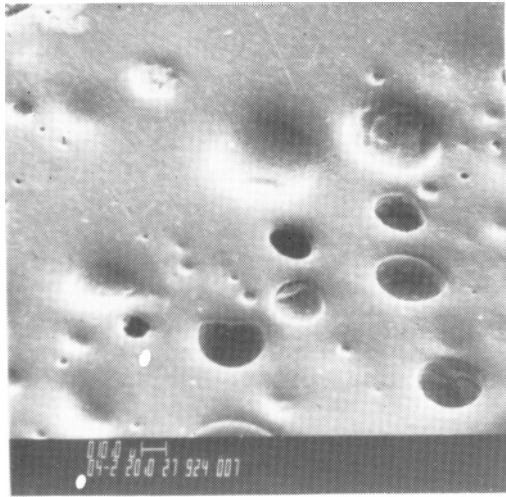


FIG. 1.--Copper object from Abu Matar. Secondary-electron image (SEM) showing blowholes and sulfide inclusions.

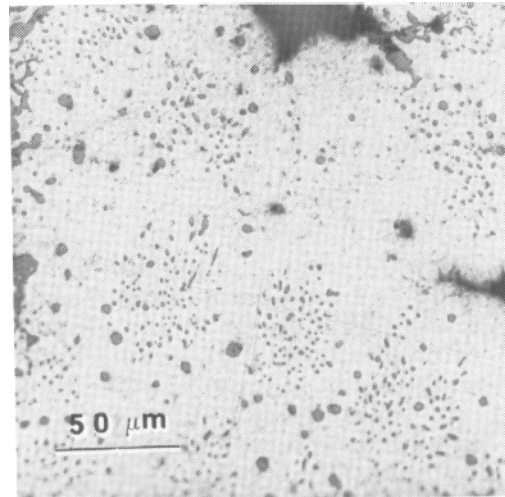


FIG. 2.--Axehead from Safadi-Abu Matar. Optical photomicrograph showing copper-copper oxide eutectic.



FIG. 3.--Axehead from Safadi-Abu Matar. Secondary-electron image (SEM) of inclusion with Ni Ka linescan superimposed.

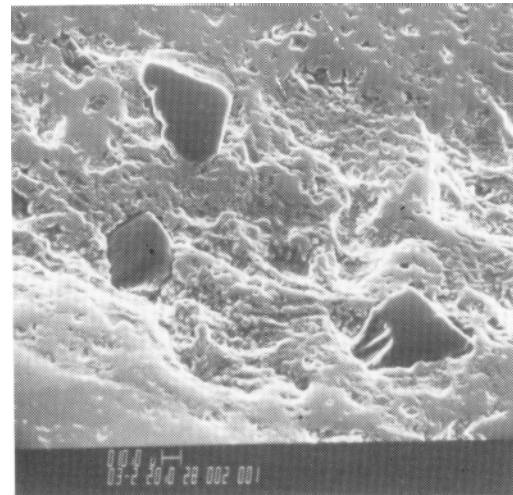


FIG. 4.--Axehead from Safadi-Abu Matar. Secondary-electron image (SEM) of silica inclusions near surface.

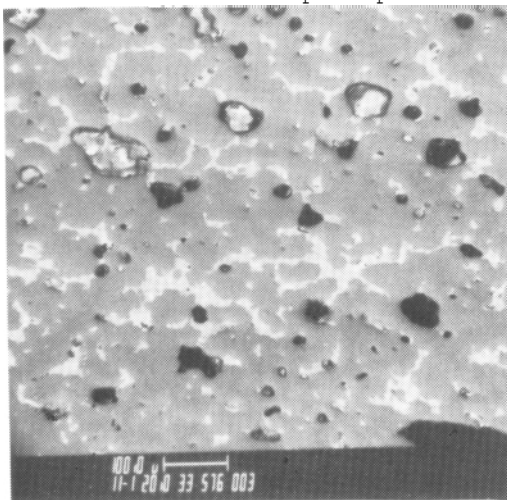


FIG. 5.--Macehead from Judean Desert. Back-scattered electron image (microprobe) indicating two-phase matrix and inclusions.

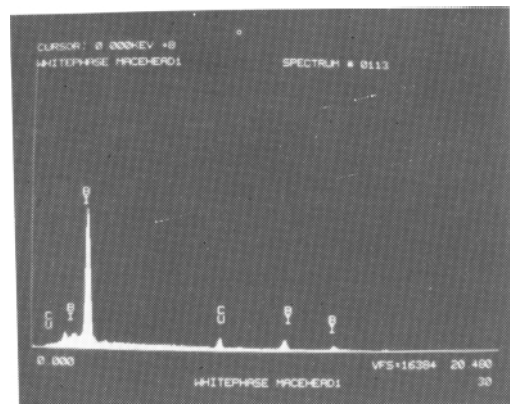


FIG. 6.--Macehead from Judean Desert. EDS x-ray spectra showing high Bi content in inclusions.

Macehead from Judean Desert (Aharoni 52-01-82-F, 46938)

This macehead is of a shape similar in form to those shown on p. 119 of the work by BarAdon;<sup>3</sup> the inside of the shaft hole still contained the clay center around which the head had been cast. The clay is not completely enclosed in cast metal, as is shown on p. 235 of Bar-Adon.<sup>3</sup> Microprobe examination of a polished metallographic section (Fig. 5) indicated the majority of the structure to be a two-phase material. The major phase, occupying about 90% of the cross-sectional area, is a Cu-Sb-As alloy giving the following approximate analysis: 95.3 Cu-2.4 Sb-2.4 As (wt.%). The minor phase appears to be a complex intermetallic sulfide with approximate composition 61.3 Cu-25.3 Sb-7.8 As-bal. S (wt.%). In addition to these phases there are at least two other types of inclusions found in much smaller amounts--copper sulfide with a small amount of Sb and As, and a copper-bismuth phase with small amounts of Sb and S (Fig. 6). The overall alloy composition appears to have a combined Sb + As analysis of  $9. \pm 0.6$  (wt.%).

It appears that this macehead has been smelted and cast from a "gray ore" or fahlerz containing tetrahedrite ( $\text{Cu}_3\text{SbS}_3$ ) and chalcocite ( $\text{Cu}_2\text{S}$ ). These types of ore may have an appreciable portion of the Sb replaced by As, and Bi concentrations typically run quite high. This ore is distinctly different from those found at Timna<sup>7</sup> and Abu Matar,<sup>8</sup> but it also appears to be different from the maceheads found at Nachal Mishmar, Nachal Seelim, and Abu Matar, all of which have little Sb content.<sup>3</sup> It thus appears that considerably more detailed and updated microanalysis is warranted on these maceheads as a group.

#### References

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