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RECONSTRUCTING THE CHALCOLITHIC METALLURGICAL PROCESS AT ABU MATAR, ISRAEL

Aaron N. Shugar

Archaeometallurgy Laboratory, Lehigh University, Bethlehem, PA USA

ABSTRACT

The earliest copper production in the Northern Negev is attributed to the Ghassulian Beersheva culture in the early 5th millennium BCE. The site of Abu Matar is one of the largest Ghassulian settlements in the region and was first excavated in the 1950's. These excavations provided the first evidence for Ghassulian copper production with the majority of metallurgical finds coming from underground structures. Investigations of these materials established a one stage smelting process model for copper production in the region which still stands. Subsequent excavations at Abu Matar in 1990/91 revealed more extensive above ground metallurgical activities on the site. The metallurgical materials recovered include copper ores, hammer stones, furnace fragments, crucible fragments, and slag. The author investigated all these materials using various analytical techniques, including optical microscopy, electron microscopy (EPMA), and inductively coupled plasma spectrometry (ICP-AES). The results support a two stage smelting process model for copper production conducted in a well-established center for craft specialization. The results of this study provide a new understanding of Chalcolithic metallurgy in the Southern Levant.

KEYWORDS

Chalcolithic, Abu Matar, Smelting, Furnace, Crucible, Copper, Electron Microprobe, ICP

INTRODUCTION

The earliest evidence for copper smelting in the Northern Negev comes from the Ghassulian Beersheva culture [1, 2, 3]. The most significant finds come from the 1950 excavations of Abu Matar by Jean Perrot [1] and the more recent 1990/91 excavations by Gilead, Rosen and Fabian [4, 5]. Excavations of other sites in the region expanded knowledge of the metallurgical activities of the Ghassulian culture. Sites including Horvat Beter [6], Bir Safadi [7], Nevy Noy [8], and Shiqmim [9], reveal a well established, geographically restricted, metallurgical tradition operating within the Ghassulian-Beersheva culture. Metallurgical materials found on these sites, including ores, slag, and crucibles provided ample proof for a developed metallurgical industry which has been interpreted by some as representing a village based economy [10].

It was in fact a visit by Tylecote in 1969 to Abu Matar, at which he was shown several refractory ceramics, which established the initial conception of the Ghassulian metallurgical process [11]. His representation is still held today as a reasonable and likely process model [12]. Tylecote's initial interpretations have been extended in recent years by further examination of Abu Matar's metallurgical assemblage and detailed investigation of Shiqmim's metallurgical assemblage as well as extensive investigations of the Feinan mining region [2, 3, 13, 14, 15].

Based on the analysis of metallurgical remains found at Abu Matar and the other contemporary sites in the region, several theoretical process models have been suggested for copper production in the Southern Levant. Of these, the model advocated by Hauptmann, based on crucible smelting, is still widely held today [16, 17, 18]. The terminology Hauptmann has used for describing the crucible smelting process model may be unintentionally deceiving causing confusion and arguments over the functionality of the process. He states in various publications that during the Chalcolithic period in the Southern Levant

metal was "...produced in a one stage smelting process..." [19]. This statement has caused some controversy with the insinuation that smelting occurred in crucibles, producing relatively little slag, and the resulting metal was directly cast, thus a one stage process.

Hauptmann has recently clarified this by stating that smelting occurred in crucibles and the resulting mass was removed and crushed to remove the trapped copper prills [20]. The process is as follows. High grade oxide or carbonate copper ore was mined, partially beneficiated, and transported from Feinan into the region to be further concentrated and smelted. The highest quality beneficiated copper ore (reaching 50 – 60 % copper content) was smelted in crucibles placed in a hearth ground furnace using blowpipes. After smelting, the partially reacted mass was removed from the crucible and crushed to remove the entrapped copper prills. The copper prills were then re-melted for casting into utilitarian objects, which would have been worked and polished on site.

Similar models based on crucible smelting have been proposed for the metallurgical activities at Shiqmim. More recently, Golden *et. al.* [3] proposed a 'proto furnace' design in which the crucible was retained providing increased heat retention during smelting. Lack of evidence for a proper smelting furnace at contemporary sites combination with scattered slag and slagged crucible fragments at these sites has been cited as evidence for maintaining the crucible smelting model.

PRESENT STUDY

In 1990/91 new excavations of Abu Matar were undertaken by Gilead, Rosen and Fabian [4, 5]. These excavations revealed extensive metallurgical activities situated above ground relatively near the underground structures uncovered by Perrot years earlier (Area A, see [1, 4, 5] for more details). The new excavation at Abu Matar revealed the missing evidence of a smelting furnace with well slagged furnace fragments, providing a more complete picture of the metallurgical activities that occurred on site, representing the entire process of the extractive metallurgy of copper.

METHODOLOGY

Proper classification of archaeometallurgical materials is one of the most important aspects of the investigative process. Classifying these materials in a detailed manner strengthens the accuracy of statistical sampling and subsequently, the accuracy of the interpretations of technical studies [21]. By combining physical observations, technical studies, and experimental investigations, a clear classification of material types can be made. More specifically, classification allows for the separation of fragmented refractories into furnace fragments and crucible fragments as well as the separation of different slag types. As a result, the subsequent analyses of these two refractories should provide data that will clearly show the metallurgical process employed on the site. The physical characteristics measured include vessel diameter, vessel thickness, and level of porosity. When these features are recorded, clear differences appear in the assemblage showing distinct classes assignable to either furnace refractories or crucible refractories.

Analysis of slag is typically used for determination of the production process directly associated with an artefact. Most Chalcolithic slag is typically a heterogeneous mixture of partially reacted materials, mineral formations, glassy slag, and occasionally charcoal [22, 23, 24, 25]. Therefore, proper classification of refractories is a key element in ensuring accurate results. The slags analysed in this project were all found adhering to refractory ceramics, either furnace fragments or crucible fragments recovered from Abu Matar.

The analysis of slag began with optical microscopy to identify mineralization. Electron microscopy (EPMA) spot analysis was mainly used to analyse the entrapped metallic copper to determine if there were statistical differences between the chemical composition of the furnace and crucible slag which

could indicate which production process the refractory was used for. EPMA spot analysis was also used for confirmation of the minerals detected by optical microscopy. Inductively coupled plasma spectrometry was used to gather bulk chemical data on slag samples to compare with previously published data. The analysis reveals distinct quantitative differences for the two types of refractories found at Abu Matar, and identifies the technological process employed as a two stage activity consisting of smelting and remelting.

SAMPLE PREPARATION AND MACHINE SETUP

A standard method of sample preparation was used for furnace slag and crucible slag. Samples were cut from the original samples and mounted in Buehler Epo-Kwick fast cure epoxy resin. They were then ground and polished with diamond paste to $\frac{1}{4}$ μm . The polished samples were mounted on micro-slides for analysis on a reflected light microscope fitted with 5x to 100x objective lenses and a 10x eyepiece, providing magnification of 50x to 1000x. The microscope was fitted with a rotating stage to allow for the identification of individual minerals by use of polarised light.

The electron microprobe used was a Jeol JXA-8600 superprobe housed at the Institute of Archaeology, UCL. The energy was set at 25 KeV and the crystals used for WDS detection were TAP and LIF. Samples were prepared in the same way as the samples for optical microscopy. In addition, the samples were carbon coated with a standard carbon sputter coater.

The ICP used was an ICP-AES Jobin-Yvon polychromator (JY-48) located at the Israel Geological Service in Jerusalem. The analysis was done by Dr. I. Segal. The samples were crushed and powdered to 200 microns. The samples were then mixed in a zirconium crucible with sodium peroxide in a ratio of 0.5g of sample per 2g of Na_2O_2 . They were then fused for 20-30 minutes in a furnace at 530°C. Then they were taken up in aqueous solution with 20 ml of HNO_3 and up to 100 ml of distilled water along with 5 ppm of Sc, which was used as an internal standard. Blanks were also obtained from the Na_2O_2 matrix [26].

RESULTS

The slag analysed was extremely heterogeneous containing various partially reacted materials, minerals, and metal. Differences in the main properties of the slag confirmed the assignment of fragments into furnace and crucible refractories with adhering slag. The results of the overall analysis of the slag adhering to the refractories indicated that a two stage two refractory process was undertaken for the production of copper at Abu Matar using a proper shaft furnace for smelting and crucibles for remelting/casting. The main characteristics which define the differences between the furnace slag (smelting activity) and the crucible slag (re-melting), based on optical examination are found in the mineralization present in the slag. The main types of minerals found in Chalcolithic slag are silicates, oxides, and occasionally sulphides [25].

SILICATES

Slags are composed primarily of silicates [25: p.13]. Fayalite (Fe_2SiO_4) has been reported as being 'the most common and very often the only mineral in early copper smelting slags...' [22: p.78]. Its formation relies on the presence of sufficient iron and silica in the slag although several other elements may replace iron in the formula such as Zn, Mg and Mn. Pyroxenes ($\text{Fe, Mn, MgCaSi}_2\text{O}_6$) are also quite common in smelting slags [25]. Their formation is likely due to an increase in CaO which probably derives from the fuel ash and the ceramic body [24].

Fayalite has been found in smelting slags from Abu Matar [14: p.189 fig. 7.26] with similar microstructure to that found in the assemblage examined here, including intergrowth of magnetite and occasional

irregular shaped prills (fig 1). Fayalite is present in most of the furnace slag from Abu Matar but usually occurs in isolated areas. The presence of fayalite in the crucible slag from Abu Matar is less common. It only occurs in one sample and in this particular case, the presence of fayalite is likely not due to the pyrotechnological processes undertaken within the crucible. The area rich in fayalite has a clear barrier between the copper oxide-rich glassy slag of the crucible and the fayalite-rich slag section. This is also the case with a crucible fragment analysed from Miftan (same site as Abu Matar). This fragment clearly shows the angular inclusion of smelting slag into remelting slag (fig 2). The mineral rich smelting slag shows signs of partial reaction with the smelting slag but can be easily identified. Without careful inspection of the sample one might be drawn to the conclusion that this sample represents crucible smelting activities occurring at Abu Matar during the Chalcolithic when in fact, it is more representative of accidental intrusion of smelting slag into the remelting process. It is more likely that this isolated case is due to the inclusion of some smelting slag into the crucible slag. This could result from some stray crushed smelting slag falling into stored charcoal and then being added to the crucible with the charcoal fuel. It is also possible that some smelting slag remained attached to copper prills and entered the crucible slag when the prills were collected for remelting. This accidental addition has been witnessed in experimental smelting and casting of copper alloys at Batan Grande, Peru [27]. It may be possible to identify the presence of smelting slag within remelting slag by spot analysis and comparison of the copper prills entrapped in both slag types (table 1).

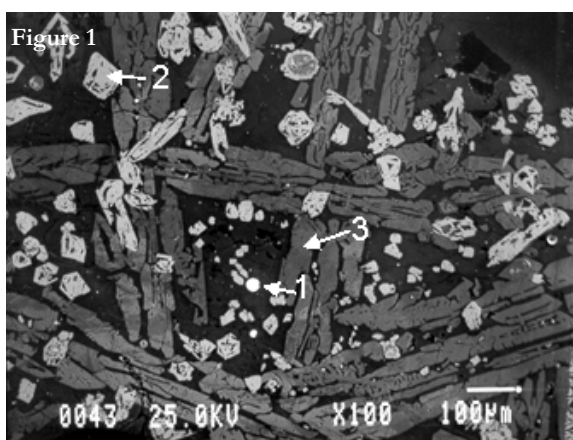


Figure 1 and 2: (fig 1) Sample M-F-05 is a typical furnace slag fragment showing skeletal fayalite (3) with intergrowth of magnetite (2) and some copper prills (1). (fig 2) EPMA micrograph of sample Miftan 1 showing the angular inclusion of smelting slag embedded in the glassy remelting slag. The data are presented in Table 1.

Sample	Spot	Pb	As	P	Ca	S	K	Cu	Fe	Mn	Mg	Co	Ni	Si	Sb	Al	Ti	Zn	Sn	Total
M-F-05	1	n/d	0.573	0.414	0.044	0.004	n/d	95.74	1.67	0.005	n/d	0.001	0.001	n/d	n/d	n/d	0.086	n/d	n/d	98.54
M-F-05	2	0.229	0.132	0.02	0.024	0.013	n/d	0	61.88	0.023	0.077	0.058	0.002	0.283	n/d	1.1	0.182	n/d	n/d	64.03
M-F-05	3	n/d	n/d	0.068	0.516	0.067	n/d	0.08	40.64	0.039	1.06	0.022	0.018	15.42	n/d	0.004	0.013	0.005	0.012	57.96
Miftan	1	n/d	0.02	1.42	0.21	n/d	n/d	95.1	2.1	0.02	n/d	n/d	n/d	n/d	n/d	n/d	0.21	n/d	n/d	99.03
Miftan	2	n/d	0.04	0.91	0.04	0.02	n/d	52.3	0.91	0.01	n/d	n/d	n/d	n/d	n/d	n/d	0.08	n/d	n/d	54.25
Miftan	3	0.03	0.02	0.41	11.1	0.08	0.71	14.7	12.4	0.01	1.98	0.01	0.01	22.8	0.05	2.57	0.19	n/d	n/d	67.05
Miftan	4	n/d	0.03	1.37	n/d	0.02	0.01	98.2	n/d	0.01	n/d	n/d	n/d	n/d	0.01	n/d	0.15	n/d	0.01	99.8
Miftan	5	n/d	0.03	1.49	0.04	0.02	n/d	98.1	0.11	0.02	n/d	n/d	n/d	n/d	n/d	n/d	0.18	n/d	n/d	99.96
Miftan	6	n/d	0.06	0.89	0.05	0.01	n/d	54.2	0.45	n/d	n/d	0.01	n/d	n/d	0.01	0.58	0.13	n/d	n/d	56.35

Table 1: EPMA data from spot analysis of the furnace slag from sample M-F-05 (fig 1). Spot 1 is a copper prill with relatively high iron. Spot 2 is a magnetite formation and spot 3 is of fractured fayalite, and from sample Miftan 1 (fig 2). Analyses 1-3 are from the smelting slag area while analyses 4-6 are from the glassy remelting slag area.

OXIDES

Other than silicates, oxides are the most common formations in slags, and nearly all of them are some form of iron oxide [25]. Magnetite (Fe_3O_4) is present in almost all metallurgical slag which contains medium to high levels of total iron. The mineral can be found in the silicate matrix either in the form of small rhomboid crystals or grains, as dendritic crystals, or as idiomorphous crystals.

The presence of magnetite in furnace slag is very typical for early slag and can be linked to the higher levels of iron found in some of the copper ores in conjunction with the use of haematite as a fluxing agent. As seen in figure 1, magnetite can be found in furnace slag in association with fayalite but the presence of magnetite is not localized to only these areas. Magnetite is typically also found in conjunction with metallic copper seen here as irregular shaped prills (bright spots).

Delafossite (CuFeO_2) is occasionally found in all metallurgical slag. It is more typically found in remelting slag (crucibles) but it can form in smelting slag as well [25]. Delafossite has a platy crystal morphology, sometimes curved or wavy, and can also be surrounded by magnetite crystals (fig 3). Delafossite is sometime found with intergrowth of cuprite (Cu_2O) in Chalcolithic slag. The presence of delafossite indicates a less reducing to partially oxidizing atmosphere during the smelting process combined with insufficient silica to form fayalite.

Delafossite is regularly present in the Abu Matar furnace slags. It tends to occur in wavy bands with occasional intergrowth of magnetite alongside irregular shaped metallic copper. There is occasional cuprite growth between delafossite crystals as well as some fayalite formations. The presence of delafossite in the crucible slag is always associated with an intergrowth of cuprite. As in the furnace slag, the presence of magnetite is also common, but delafossite does not form wavy crystals in the crucible slag, and is found as straight lathes only.

Cuprite is another oxide that usually forms under partially oxidising conditions and is therefore typically found in remelting, or crucible slag. It has strong dark red/orange internal reflections when viewed under crossed polarisers. It typically is found at the rim of crucible slag where the highest levels of oxidation occur (fig 4). Cuprite is less commonly present in furnace slag. Cuprite appears mainly on the surface of smelting slag and is likely due to the oxidation of the furnace slag after charcoal is no longer added to the smelt or during cooling while oxidising air is allowed to penetrate the furnace. Cuprite usually forms streaks and striations in the glassy matrix creating increases in the intensity of the colour. The presence of cuprite in such abundance can safely be related to the oxidising nature of remelting copper prills in crucibles using forced air from blowpipes.

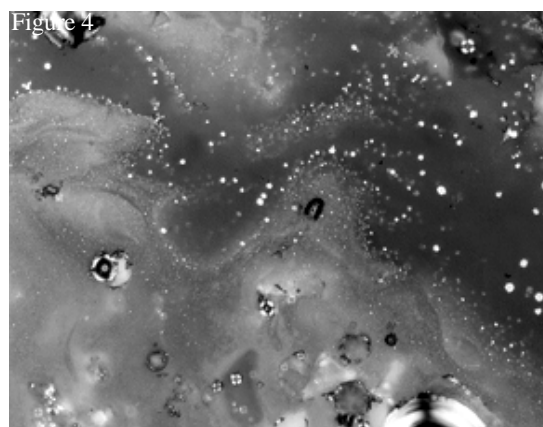
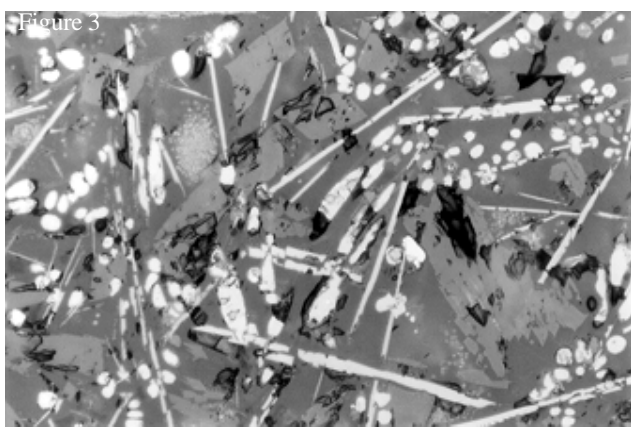


Figure 3 + 4: (fig 3) Photo of cuprite formations in the crucible slag of sample M-C-38 under crossed polarisers (width = 0.31 mm). The streaks and striations of the cuprite are clear. Small copper prills are also present (bright prills). Sample M-F-07 under normal polarised light (width = 0.2 mm). (fig 4) Photo shows the complexity and heterogeneity of the furnace slag with delafossite (white straight lathes) intermixed with some magnetite, fayalite (light grey) and some metallic copper (bright prills).

PARTIALLY REACTED MATERIAL

The furnace slag includes partially reacted ore fragments, recognizable either by their similarity in texture and composition to copper ore fragments or by their rough edges which have partially decomposed and have been absorbed into the slag at their edges. Evidence of partial reaction is also seen in the cracking of some quartz grains. Cracking due to high temperatures occurs in various directions and is not associated with the cracking caused by tectonic movements.

Merkel and Rothenberg [24] emphasise the importance of finding partially reacted ore fragments in slag. Their presence provides a clear indication of the initial furnace charge and as such, a clear indicator of the ores chosen in producing metal. The partially reacted ore fragments found in the furnace slag in this study indicate that the initial charge included both copper carbonate ore, and sulphide-rich copper ore (figs 5 and 6). The partially reacted ore includes silicate based carbonate ore fragments with partial reaction of the quartz grains with an iron-rich copper matrix and pure copper sulphidic ore, mainly chalcocite, with occasional covellite [28] (table 2).

The furnace slag contains numerous partially reacted and slightly fractured quartz grains. There tends to be some reaction at the edges of the grains which is indicative of them starting to react with the glassy slag matrix. The partially reacted quartz grains show random cracking, not exclusively in one direction due to the unstable temperatures in the furnace. It is more likely associated with the cyslobolite phase changes of SiO_2 . The presence of fractured quartz in the crucible slag is infrequent and not as common as in furnace slag. On the odd occasion when silica is found, the grains are usually small and rounded.

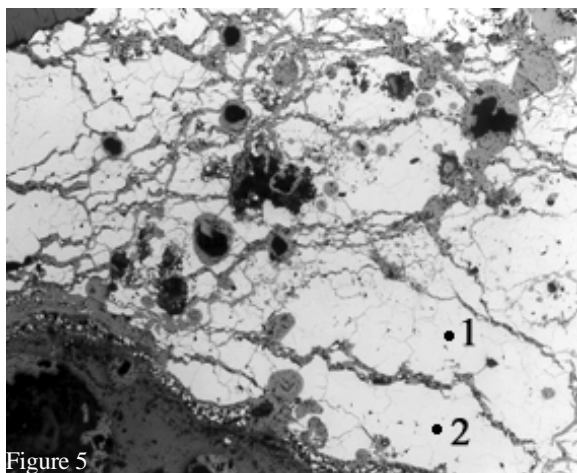


Figure 5

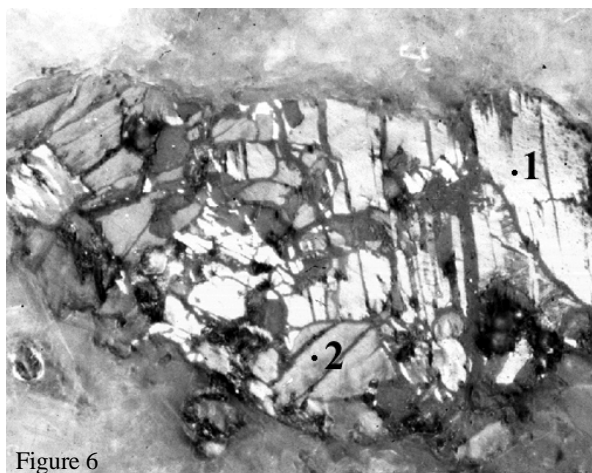


Figure 6

Figures 5 + 6: (fig 5) Sample A-F-12 under normal polarised light (width = 1.29 mm). Chalcocite ore fragment adhering to a furnace wall. The fragment is beginning to crack and interact with the existing slag. Photo of sample A-F-23 under crossed polarisers (width = 0.12 mm). (fig 6) A partially reacted copper sulphide ore fragment found in the furnace slag. The fragment consists mainly of covellite (1 + 2). EPMA data is presented in table 2.

Sample	Spot	Pb	As	P	Ca	S	K	Cu	Fe	Mn	Mg	Co	Ni	Si	Sb	Al	Ti	Zn	Sn	Total
A-F-23	1	n/d	n/d	0.739	0.051	29.22	n/d	65.59	0.354	n/d	n/d	0.006	n/d	0.319	n/d	n/d	0.038	n/d	n/d	96.32
A-F-23	2	n/d	n/d	0.44	0.109	30	n/d	67	0.458	0.005	n/d	n/d	n/d	n/d	n/d	0.006	0.069	n/d	n/d	98.09
A-F-12	1	n/d	0.042	0.97	0.145	21.72	n/d	74.82	0.004	n/d	n/d	n/d	n/d	n/d	0.028	n/d	0.034	n/d	n/d	97.75
A-F-12	2	n/d	0.019	0.909	0.009	21.81	n/d	76	0.044	0.011	n/d	0.004	n/d	n/d	n/d	n/d	0.03	n/d	n/d	98.83

Table 2: EPMA data from sample A-F-23 (figure 5). The composition indicates the ore fragments mainly consist of covellite (CuS). EPMA spot analysis data for partially reacted ore fragments found in furnace slag (sample A-F-12). Data refers to the spots indicated in figures 5 and 6 respectively (n/d indicates not detected).

PRESENCE OF SULPHIDES

The presence of sulphides in copper slag usually indicates the use of sulphide-rich copper ore during the smelting process. Matte, the sulphidic component of the ore partially melted to a sulphide or sulphide/oxide mixture, is a typical product of smelting sulphidic ores. Since sulphides do not mix well with metallic copper, they tend to form separate phases within the slag. The exact composition of matte depends on the bulk chemistry of the ore, and the redox conditions in the slag. In the slags from Abu Matar, matte consists mainly of covellite (CuS) and chalcocite (Cu₂S) although bornite (Cu₅FeS₄), chalcopyrite (CuFeS₂), and cubanite (CuFe₂S₃) are also commonly found [25: p.16]. Until recently, it has generally been accepted that in the Ghassulian culture, smelting proceeded with mainly copper carbonate ores and no sulphide-rich copper ores, or copper sulphide ores were used. Experimental research has shown that a charge containing 18.5% sulphur will produce matte. Charges with 5.5% sulphur produce copper with sulphide inclusions and bulk sulphur concentrations reaching 0.7% [27: p.221]. The average sulphur content in the ores analysed by ICP for bulk composition (excluding the flux) is 5.4% which has resulted in various sulphide inclusions in the smelting slag with minimal matte production.

The level of sulphide present in the majority of furnace slag as well as the presence of partially reacted sulphidic ores adhering to the slag surfaces, or within the formed slag itself are clear indications that sulphur-rich copper ore was used along with oxide/carbonate copper ore in the smelting process undertaken at Abu Matar. Additional evidence is the presence of partially reacted sulphidic ore fragments adhering to the slag. Partially reacted sulphidic ores are also found within the slag (figs. 5 and 6).

CHEMICAL ANALYSIS BY EPMA AND ICP

EPMA ANALYSIS

During furnace smelting iron can appear in metallic copper as a major impurity [29: p.45]. Based on the copper-iron phase diagram, approximately 3% of iron is soluble in liquid copper at 1100°C. With increased temperature there is better separation of iron from the copper into the slag but there is also a higher solubility of iron in copper [30].

<i>Technology</i>		Cu	Fe	As	S	Ca	Sb	Ni	Pb	P	Si	Al	Ti	Co	K	Mn	Mg	Zn	Sn	
<i>Furnace</i>	<i>N</i>	75	70	33	55	64	12	9	33	75	7	6	75	18	15	43	13		13	
	<i>Mean</i>	96.96	0.96	0.49	0.11	0.11	0.02	0.01	0.09	1.05	0.63	0.2	0.11	0.01	0.03	0.01	0.19		0.02	
	<i>Std.</i>																			
	<i>Deviation</i>	1.7	0.93	0.46	0.27	0.13	0.02	0.01	0.09	0.47	0.69	0.28	0.07	0.01	0.02	0	0.26		0.01	
	<i>Minimum</i>	92.77	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.14	0.09	0.01	0.01	0.01	0.01	0.01	0.01		0.01	
	<i>Maximum</i>	100.84	4.12	1.95	1.87	0.77	0.05	0.03	0.46	1.88	1.68	0.68	0.48	0.02	0.07	0.02	0.94		0.04	
	<i>Skewness</i>	-0.34	1.35	1.23	5.33	3.13	1.6	1.18	2.55	0.19	1.11	1.37	2.24	0.88	0.81	0.7	2.31		1.49	
<i>Crucible</i>	<i>N</i>	77	73	47	58	65	21	9	25	77	5	5	77	19	24	37	6	1	20	
	<i>Mean</i>	95.89	0.33	0.54	0.12	0.12	0.02	0.02	0.1	1.11	0.79	0.25	0.12	0.01	0.04	0.02	0.25	0.03	0.02	
	<i>Std.</i>																			
	<i>Deviation</i>	1.81	0.58	0.56	0.24	0.3	0.01	0.04	0.17	0.7	1.5	0.31	0.19	0	0.12	0.01	0.43		0.01	

Table 3: Means from EPMA data for the analysis of the copper prills (in wt%) separated by furnace slag and crucible slag. Note the higher concentration of Fe found in the prills from the furnace.

Tylecote and Boydell [29] have shown that the iron levels in copper can be significantly reduced if the metal is refined by crucible remelting. Merkel [31] was able to reduce iron content in copper to only 0.014% by subjecting molten copper contained in a crucible to an air blast. Although intentional refining of copper was probably not undertaken in the Chalcolithic, the process of remelting copper prills in crucibles using blowpipes would have had the added side effect of partially refining the metal and decreasing the iron content in the copper held within the crucible. Because of this partial refinement, it may well be possible to differentiate between slag formed from smelting and from remelting deriving

from a single production site based on the comparable iron contents within the resulting metallic copper prills.

There are differences in the amount of iron found in the metallic copper prills entrapped in the furnace slag and in the crucible slag. The prills entrapped in the furnace slag have a substantially higher concentration of iron. In the furnace slag, 70 prills analysed averaged 0.97% iron (range 0.01 to 4.12%) while in the crucible slag, 73 prills analysed averaged 0.33% iron (range 0.01 to 2.84%) (see Table 3 for means).

ICP BULK CHEMICAL ANALYSIS

ICP analysis was performed only on slag samples that were large enough to be removed from their respective refractory without fear of contamination. As such there are relatively few analyses performed but ICP was deemed necessary for comparison with published data. A total of 7 furnace slags and 5 crucible slags was analysed (Table 4). Sample A-C-55 has been separated from the rest of the crucible samples as it has uncommon qualities and is considered an outlier when compared to the rest of the samples. Nevertheless, the average values of the ICP data for the crucible samples has been given for both the samples including and excluding sample A-C-55.

The most interesting findings that derive from the ICP data are the levels of calcium and iron. Calcium is present in the furnace slag averaging 13.3% and in the crucible slag (excluding sample A-C-55) averaging 10.6%. In contrast to the level of Ca in the ores, the levels of Ca in the slag are relatively high and probably derive from the ceramic body of the refractory and the fuel ash [32]. The increased level of Fe in the furnace slag that was recorded from the prill analysis was also seen in the ICP results. The furnace slag contained an average 8% Fe while the crucible slag contained an average of 5.8%. The sulphur content is fairly similar in both the furnace slag and the crucible slag except for two outliers in the furnace slag. Samples A-F-04 and A-F-12 have high levels of S at 1.0% and 1.7% respectively. It is not surprising that these two samples show higher overall sulphur content since under optical microscopy, these two samples showed higher levels of copper sulphides than the others.

Sample	Wt %									PPM																			
	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	TiO ₂	Cu	P ₂ O ₅	S	Mo	Zn	Pb	Co	Ni	Ba	Mn	Cr	V	La	Y	Eu	Sr	Ce	As	Ag	Sb	Th	U	
Slag adhering to Furnace																													
A-F-04	41.9	8.1	11.6	1.1	16.2	0.74	10.1	0.6	0.4	9	186	223	21	63	666	473	110	192	20	20	0.95	413	36	4	2	1.4	6.6	4.9	
A-F-10	51.4	11.8	15.9	1.6	7	1.14	0.51	0.2	0.1	2	107	15	29	63	537	725	120	131	30	28	1.59	550	61	6	1		7.4	2.4	
A-F-12	48.8	10.7	12.8	1.3	6.2	1.04	7.03	0.3	0.7	2	109	25	23	48	438	645	103	130	21	26	1.26	438	50	4	9	0.2	7	2.7	
A-F-16	55	12.2	19.5	1.8	6	1.12	0.52	0.9	0.1	2	105	7	32	62	667	752	132	156	29	34	1.16	530	48	24		0.6	1.4	1.9	
M-F-01	49.9	11.3	12.1	1.1	8.1	1.06	4.51	0.4	0.1	6	135	45	30	55	1143	683	112	150	26	26	1.54	489	53	5	13	4	6.7	3.5	
M-F-04	61.6	11.1	11	0.9	6.1	1.24	0.57	0.3	0.1	2	86	10	27	54	452	802	125	118	31	31	1.5	340	64	22		0.3	8.4	2	
M-F-05	61.2	11.2	10.1	1	6.1	1.05	0.5	0.3	0.1	2	112	11	26	50	435	824	109	115	30	28	1.48	319	60	6	4	0.2	7.1	1.8	
Average	52.8	10.9	13.3	1.3	8	1.1	3.4	0.4	0.2	4	120	48	27	56	620	700	116	142	27	27	1	440	53	10	4	1	6	3	
Slag adhering to Crucible																													
M-C-01	58.5	11.1	9.8	1.7	5.2	0.97	2.79	0.5	0.1	2	102	15	21	46	409	674	98	97	25	26	1.4	364	56	6		0.3	5.7	2.1	
M-C-03	56.5	10.5	12.2	2.1	5.3	0.91	2.49	0.5	0.2	2	94	10	50	62	435	667	98	96	25	25	1.3	408	51	6	14		8.1	1.9	
M-C-05	59.5	9.7	9.6	1.5	5.9	0.97	8.02	0.4	0.2	3	138	54	26	56	444	741	100	123	25	26	1.2	372	51	60	1	1.2	7.5	2.4	
A-C-05	54.2	12.8	14.2	2	6.9	1.17	2.45	0.5	0.2	2	70	5	28	49	586	735	118	139	28	29	1.6	478	60	3	3	0.3	7.4	2.7	
Average without A-C-55	57.2	11	11.4	1.8	5.8	1	3.9	0.5	0.2	2	101	21	31	53	469	704	103	114	26	27	1	406	55	19	5	0.4	7	2	
A-C-55	40.5	7.4	10.6	1.2	15	0.72	12.1	0.4	0.2	19	230	138	27	65	820	459	98	337	18	19	0.95	460	34	7	2	1.9	5.7	7.6	
Average with A-C-55	53.8	10.3	11.3	1.7	7.7	1	5.6	0.5	0.2	5	127	44	31	56	539	655	102	159	24	25	1	416	50	16	4	1	7	3	

Table 4: ICP data of slag adhering to furnace walls and crucible walls. The limited number of samples is due to the lack of a sufficient amount of slag adhering to the refractory surface to ensure that once removed, there would be no contamination.

The levels of the other major compounds (SiO_2 , Al_2O_3 , MgO , TiO_2 , and P_2O_5) are all fairly comparable. What may be surprising are the very low levels of arsenic recorded in bulk chemical analysis, of furnace and crucible slag 10.1 ppm and 18.7 ppm respectively. With individual prills reaching up to 2.5% in the metallic prills and 6.7% in the corroded prills, one might expect higher levels in slag [33] (see table 3).

DISCUSSION AND CONCLUSION

Based on the results presented, it can be established that pyrotechnological processes at Abu Matar occurred above ground in a two refractory, two stage process in which a proper shaft furnace was used for co-smelting copper ores (both carbonate/oxide and sulphide-rich) and crucibles were used for remelting selected copper prills. Their general design is a shaft furnace with a diameter of approximately 22 – 30 cm. The walls of the furnace were thick (approximately 3 cm thick) and porous. Large fragments found indicate that the height of the shaft furnace walls would have been between 15 and 30 cm and they were curved slightly inward creating an ovaloid shape. A combination of copper oxide/carbonate ores and sulphide-rich copper ores from Feinan and from at least one alternative ore source were co-smelted. The presence of both copper oxide ores and copper sulphide ores adhering to the inner surface of the furnace refractory and to the surface of the furnace slag are clear indications of co-smelting of these two ore types. The furnace was charged with the different ore types as well as the fuel (charcoal). If this were done in alternating layers, the heat created at the lower levels of the furnace would be enough to start an exothermic reaction in the sulphide-rich copper ores, partially roasting them within the furnace itself. The result of smelting would be a heterogeneous mass at the bottom of the furnace which would have to be removed for and crushed to remove the entrapped copper prills.

The copper prills were placed in crucibles for remelting. These crucibles were then placed in a bowl hearth of approximately the same dimensions as the smelting furnace (20-30 cm in diameter). It is possible that the small 'proto furnace' described by Golden *et. al.* [3] was used to retain heat. Either blowpipes or bellows could have been used to remelt the prills in preparation for casting. The reduction of iron to an average of 0.33% in copper prills in the remelting slag from approximately 1% in prills from the smelting slag indicates some level of refining.

By properly classifying archaeometallurgical refractories, the ensuing technical studies can provide more accurate data for pinpointing the metallurgical activities that occurred within each refractory. The observations made of the mineralisation present in both the furnace and crucible slag clearly show the different activities associated with them. EPMA analysis of the entrapped copper prills also confirms this distinction through the identification of the refining of copper.

The results of these studies provided a new understanding of Chalcolithic metallurgy in the Southern Levant. In addition to the known metallurgical processes that occurred underground at Abu Matar, it was established that pyrotechnological processes occurred above ground in a two refractory, two stage process in which a proper shaft furnace was used for smelting and crucibles were used for remelting selected copper prills.

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