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Chalcolithic Copper Smelting

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Editor
Professor Beno Rothenberg

Institute for Archaeo-Metallurgical Studies
London

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Excavations at Timna Site 39

by

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Experiments on Copper Smelting

by

R. F. Tylecote

P. J. Boydell

with Appendices by

A. Bercovici

H.-G. Bachmann

J. R. Trayler

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Institute for Archaeo-Metallurgical Studies

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Excavations

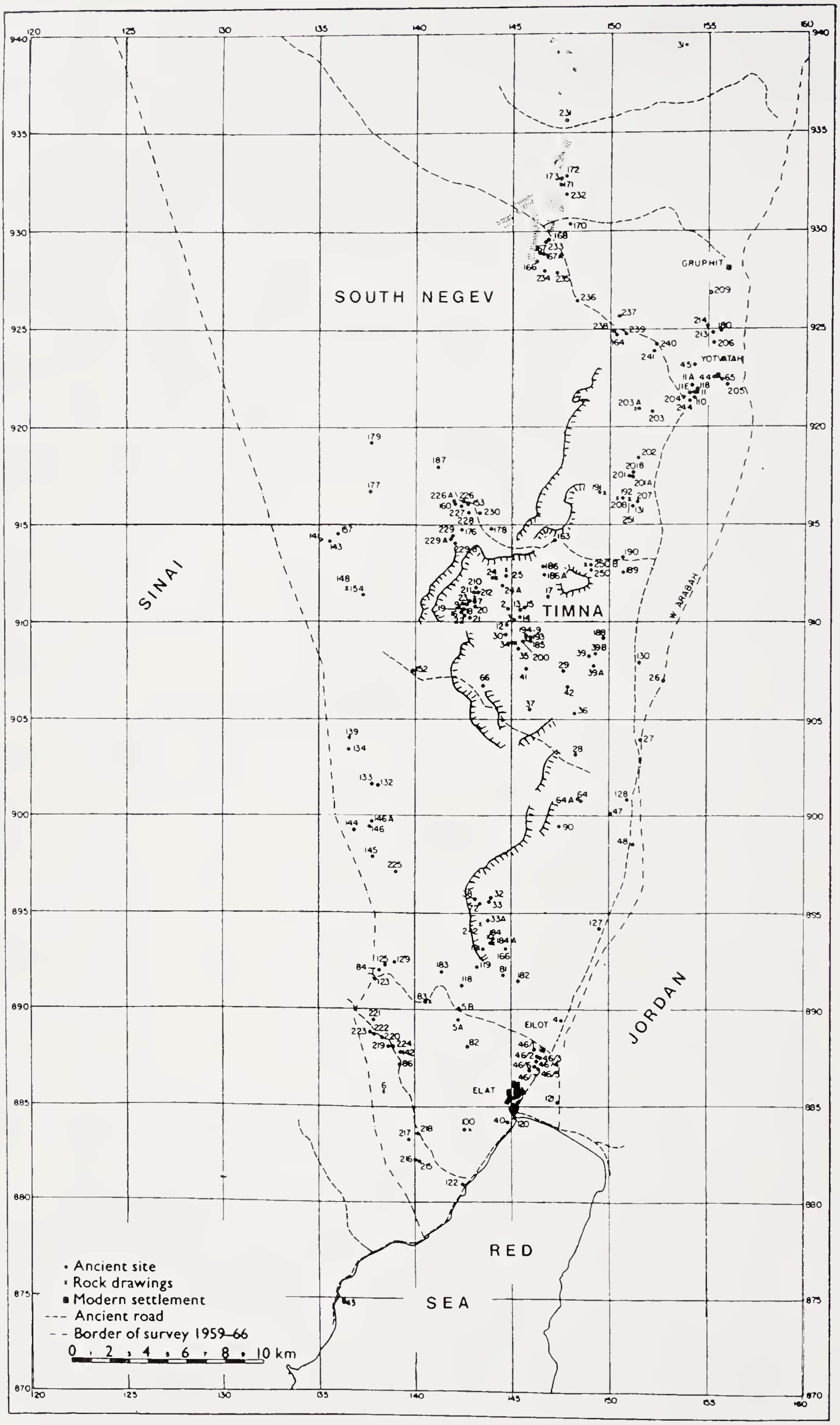

Figure 1. Survey map of the Arabah Expedition's Archaeological Survey of the Southern Arabah and the southernmost Negev.

Excavations at Timna Site 39 a Chalcolithic Copper Smelting Site and Furnace and its Metallurgy

by
Beno Rothenberg

To the memory of Ephrat Yeivin

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I. Introduction

The Arabah Expedition, directed by the author, began its archaeological explorations of the Western Arabah[1] in 1959[2] (Figure 1). This survey and subsequent annual excavations in the Timna Valley since 1964, revealed the existence of large-scale copper mining and smelting operations of many periods. Starting in the Chalcolithic Period, the 4th millennium BC, and reaching its peak in the Late Bronze Age–Early Iron Age I (13th–12th cent. BC), the ancient exploitation of the ore deposits ended with a short-lived Roman enterprise, in the 2nd cent. AD, at Beer Ora.[3]

Whilst until 1970 the main efforts of the Arabah Expedition were concentrated on the smelting camps of the Timna Valley, aiming to reconstruct the ancient processes and to investigate their scientific and chronological aspects, the New Timna Project, which was begun in 1974, has directed much of its attention to the investigation of the ancient mines of Timna.[4] We also began excavations at Site 30,[5] a large walled, Late Bronze Age–Early Iron Age I smelting camp. Work also began at Site F2[6] in Timna and Site 201, in the Arabah[7], north of Timna, as part of a new excavation programme, with the emphasis on early prehistoric metallurgy.

The new picture, which is beginning to emerge from our renewed excavations, reveals a much wider spread of activities than previously assumed. It has now become quite certain that copper mining and smelting began in the Chalcolithic Period (4th mill. BC) and that it was also carried on in the early parts (I and II) of the Early Bronze Age (4-3 mill. BC). Although no metallurgical evidence has yet been found in the Arabah in a Middle Bronze Age I (EB–MB) context, the recent discovery of MBI remains in the Southern Arabah may indicate metal production also during this period.[8]

There is no evidence so far of Chalcolithic shaft-and-gallery copper mining at Timna, though as-yet unexcavated gallery entrances (Site 42) with flint tools and a rilled mining pick (Figure 2), seem to indicate underground workings already being carried out at this period[9]. The earliest mining activities at Timna, tentatively dated to the Chalcolithic Period on the basis of the discovery of flint implements, stone tools and some pottery, were of the nature of rough pit mining, i.e. copper ore nodules, deposited in a thick layer of surface conglomerate, were extracted by irregular trenching and pitting. Chalcolithic Site 39 (see below) and several other sites in the Arabah, not yet excavated, are copper smelting camps, belonging to this earliest phase of metallurgy in the Arabah.

The very beginning of the Early Bronze Age (EB I) is so far represented in Timna by the earliest

Notes and references on pages 14-15

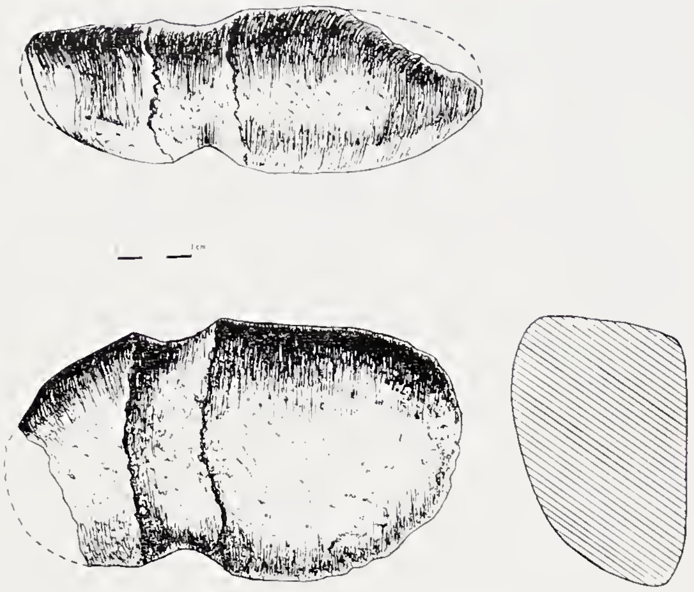

Figure 2. Rilled mining pick from Chalcolithic mining Site 42.

underground mining system, Area T, found to date. It is a real shaft-and-gallery system, hammered out with stone tools—square and round mining hammers, with a biconical shafthole in the centre (Figure 3); it has been dated by pottery found in the underground workings together with numerous typical mining tools, including a typical Early Bronze Age I lamp.

Several primitive smelting sites, of probably EB I date, located in the Arabah near the well-watered oasis of Yotvatah (formerly Ain Ghadian), but not yet excavated, could well be part of an EB I settlement wave, connected with copper production. Many more sites of this period, some also with metallurgical remains (f.i. Site 688[10]), were discovered by our expedition also in Southern Sinai.[11]

No copper mine of Early Bronze Age II has yet been identified in Timna, but this period is represented by several sites in the Southern Arabah, as f.i. Sites 168, 144, 167, 231 and 201, slightly north of Timna. Here, small but fairly widespread slag concentrations and slagged furnace remains, found near habitation and burial remains, together with pottery and flint implements, are evidence of EB II smelting activities.

The EB II smelting sites, like f.i. Site 201A, at present under investigation,[12] show a still rather primitive smelting technique. Their small, stone-built bowl furnaces,[13] standing either right outside the houses or on the slopes of nearby hillocks, produced rather heterogeneous slag, but the flow structure of some of this slag indicated a kind of primitive tapping. At Site 201A a small slag runner and fragments of plate slag, about 1.5–2 cm thick, are certain evidence for such tapping procedure. This is the earliest evidence for tapping found to date, as none of the Chalcolithic slag in Timna could have been tapped.

The Early Bronze Age II sites in the Arabah are of particular interest. During this period, contemporary with early Dynastic Egypt, numerous fortified towns sprang up in the Levant and with such urbanisation the use and need for copper assumed new dimensions. There must have been an enormous increase in population during this period as there is also evidence of many small rural sites, spreading all over the fertile lands, with numerous EB II sites spilling over even into arid areas—and producing metal. Besides EB II sites in the Arabah, our expedition found groups of EB II, as well as Chalcolithic and EB I sites as far south as close to the southern tip of the Sinai peninsula, clustered around or related to local ore deposits.

Many such EB II sites have by now been recorded in the Central Negev mountains, in North, Centre and South Sinai, and also in Syria and Jordan's desert fringes. The location of many of these settlements could only be understood if considered as part of a widespread EB II copper industry[14] with a food-producing hinterland.

It soon became evident that much of the EB II

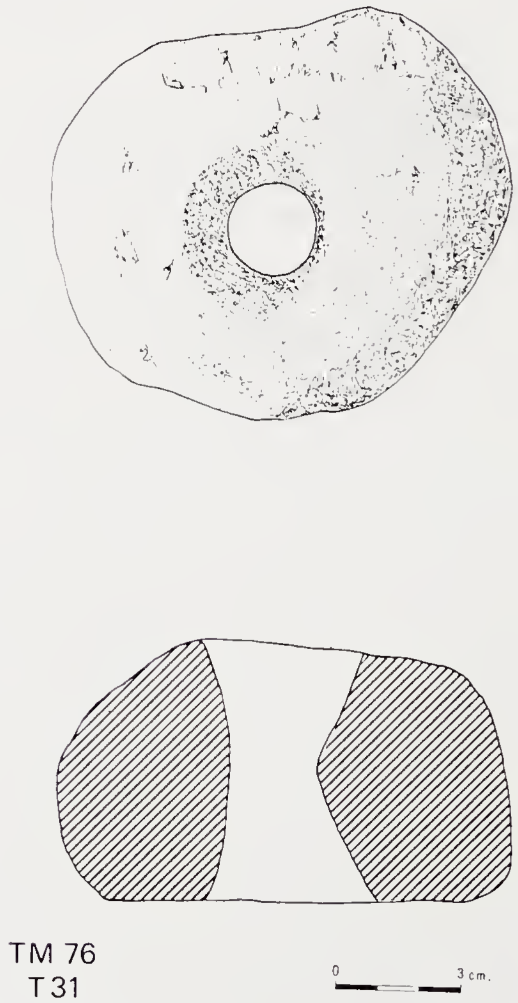

Figure 3. Early Bronze Age I mining hammers, found inside underground workings.

Figure 4. Map of the Timna Valley.

pottery found at sites in South Sinai, was in fact imported from an area of quite different geological setting. Petrographic examination^{15} of EB II sherds from Southern Sinai and the Southern Arabah (including the large EB II site 380, located near the Sheikh Nabi Salah tomb, in Wadi-e-Sheikh, discovered by the author in 1967^{16}) established a clear connection between Early Canaanite Arad, as well as other urban sites in Southern Israel, and Canaanite (EB II) sites in Southern Sinai and the South-Western Arabah.

Comparing the relatively small number of inhabitants of Canaanite Arad (estimated by Mrs. Amiran^{17} to have been about 3 000) with the large number of EB II rural sites, spread all over the enormous area from the borders of Egypt to Israel, Jordan, Syria and Northern Arabia, including thick clusters of settlements around the mining centres of these areas, it does not make much sense to see in South Sinai's EB II sites evidence for mining expeditions sent from Arad to South Sinai, as suggested by R. Amiran and I. Beit-

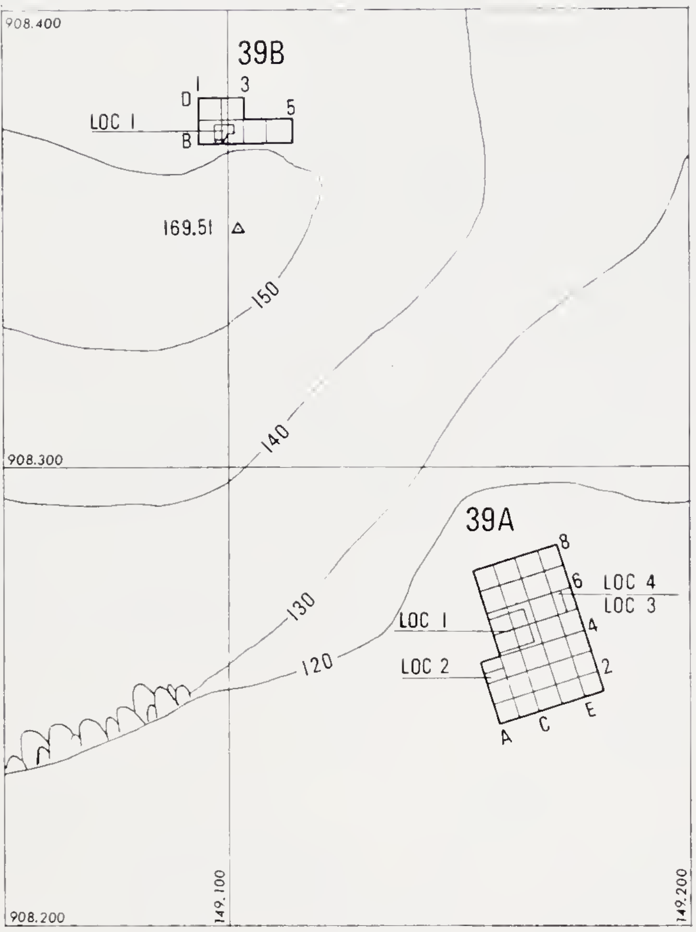

Figure 5. Site 39: Location map of areas excavated.

Arieh[18] and J. D. Muhly (see note 30).

It seems that numerous Canaanite urban and rural sites existed side by side all over the Near East, and extensive trading was carried on apparently over large distances, between the urban centres of obvious technological as well as economic predominance, and the wide network of small, rural settlements. It is obvious that metal, which may have been one of the major factors of urbanization, and was generally produced in arid areas, would need an urban market but, in return, would also require an urban centre of supplies to keep the miner's settlements in the desert supplied with locally-unobtainable necessities of life. Pottery, being the durable, though breakable packing material of such supplies, would therefore travel over long distances and this would, of course, explain the presence of imported Arad-type, Caananite pottery in Southern Sinai.

The prehistoric copper mining and smelting remains of Timna—Site 42 (a Chalcolithic mine), Site 29 (the ore dressing station belonging to Site 42) and Site 39 (the smelting site[19])—represent the earliest metal production complex found to date in the Near East.[20]

The following report on our excavations at Site 39 is, in fact, an introduction to the experimental research report by R. F. Tylecote and P. J. Boydell[21] and provides the archaeological and chronological background to the Chalcolithic Timna smelting furnace, simulated in these experiments. The excavations of Site 39 are here fully published for the first time.[22]

II. Site 39

The Timna Valley (formerly Wadi Mene'iyeh), located alongside the Arabah, some 20–30 km north of the Gulf of Elat-Aqabah, on the Red Sea, is a large erosional cirque, of some 70 sq. km (Figure 4).

Site 39 (Grid Ref. 1493 9085, Israel grid; Figure 5) is located at the foot (39A) and on top (39B) of a solitary hill, standing at the edge of the Arabah, just north of Nahal (Wadi) Nehushtan, and east of the modern Timna Mines. It was discovered by the author in 1960 and excavated in 1965.

Before excavation the remains at 39A (Figures 6, 7) appeared to be an oval-shaped enclosure, 29×23 m, with a wall of about 1.5 m width, and three attached tumuli of 5–8 m diameter, which we assumed to be remains of houses. At the time a number of small mortars of red sandstone, numerous granite pestles and hammers, flint implements and fragments of pottery were collected on the surface. Some copper ore nodules (cf. below, Table 1) and small pieces of slag, also found on the surface, indicated metallurgical activities.

Site 39B (Figure 8) is located on top of the hill right above 39A. There were no structural remains visible at the site, but a concentration of small fragments of very viscous, porous and greenish slag, some slagged stones, flint implements and grinding tools, was evidence of primitive copper smelting activities. The slag was found behind a huge rock-outcrop, shielded from the prevailing, strong north wind of the Arabah.

The flint tools and fragments of pottery found at 39B were the same as the finds at 39A, both groups of finds indicated a Chalcolithic, 4th mill. BC date.[23]

III. Excavations

Site 39 was excavated in March/April 1965, under the direction of the author.[24] The excavations had a dual purpose: 1) To find a copper smelting furnace, an objective of considerable interest and urgency, as no early copper smelting furnace had ever been found anywhere;[25] 2) to secure stratified archaeological evidence for the early date of Site 39 and, thereby, also for the contemporary mines and smelters in the Arabah.

The excavation of 39A presented a unique problem as sulphuric acids, from the nearby modern copper plant, had for many years flowed across the southern half of the structural remains and formed an almost solid, red-brown, acid-smelling mass. We therefore concentrated mainly on the northern half of the 'enclosure'. We excavated the largest (4.5×5.5 m) tumulus, Locus 1,

Figure 6. Area 39A.

and dug several trial trenches across the 'enclosure wall', Loci 2 and 3, and a small structure, Locus 4, to the north of it.

Locus 1 (Figures 9 and 10) was first cleared of a thin layer of wind-borne sand, and a considerable quantity of stone debris which had fallen from the hill above and had accumulated on top of what appeared to be a carefully-laid cover of medium sized field stones. At first, the appearance of this 'stone cover' created the impression of a burial

Figure 7. Site 39A, with Wadi Arabah in background.

tumulus of a type well-known in the area, consisting of a burial cist in the centre of a circular enclosure of rough field stones, often covered by smaller, medium sized stones. However, clearing the debris from the top, it became obvious that the 'stone cover' did not in fact extend right across the whole of the tumulus, but left a roughly circular area, uncovered in the centre.

Removing the 'stone cover', we found a thick layer of fine sterile sand, obviously wind-borne fill, and at a depth of some 40 cm we reached a hard surface. After excavating most of the tumulus, we found a roughly circular wall of undressed stones, with an entrance at its west side. Outside, next to the entrance, we uncovered a small, circular stone-built fireplace, still filled with ashes.

In the centre of Locus 1, a small 'pavement' of small flat stones was found in a shallow depression. The 'pavement', about 80 cm across, was covered by a thin layer of very fine, greenish sand, which also extended over much of the area surrounding it. This stone arrangement resembled a pebble and flat stone setting, found by J. Perrot at Chalcolithic Tell Abu Matar,[26] though many of the pebbles of Abu Matar bore painted marks, not found on our stone setting. Like at Abu Matar, a pit was found next to the 'pavement', about 25 cm deep, full of dark charcoal ash. There was also a small quantity of animal bones.

There were no other structures or installations within the wall of Locus 1, but on its floor—a hard surface found inside as well as outside the wall—were flint implements and flakes, some pottery, and several simple, round hammerstones.

Trying to reconstruct the original structure, it became apparent, that its wall must have been about 1–1.5 m high, and could not have carried any roofing, i.e. it was an enclosure, perhaps around a hut-like structure of wood, skins or cloth. Locus 1 seems to have served as habitation as no sign of any other use were found.

Locus 2 may have been a round dwelling structure, similar to Locus 1, but because of the acidic incrustation, it could not be properly excavated.

Loci 3 and 4 were but small fireplaces, built of small field stones.

The trial trenches at Loci 2–4 (Figure 6) showed that the large, oval 'enclosure' of 39A was, in fact, not a continuous wall, but a circular line-up of small working installations and fireplaces, functionally arranged in the convenient shape of a large 'courtyard'. Hammerstones and mortars, as well as a quantity of copper ore nodules, found at the site before and during the excavation, indicated

Figure 8. Site 39B from north-west. The man stands near the furnace site.

that 39A was a dwelling and working camp, connected with copper smelting. It could well have beeen the place of preparation of the smelting charge for the furnaces, 39B, located on top of the hill, right above 39A.

The actual smelting site—39B (Figures 12-16)—was indicated by a fairly large quantity of small, rough slag fragments, dispersed on the surface over a relatively large area (Figures 8, 13). A solitary large stone, laying amongst the slag attracted our attention (Figure 14). It was a sandstone, not native to this hill and appeared still to be *in situ*; obviously it must have been brought intentionally to this spot for some specific purpose. It was for this reason, and because of the concentration of slag, that this area was excavated.

About 10 cm below the present surface layer of yellowish wind-borne sand, there appeared a layer of greyish, charred sand, mixed with tiny slag fragments and many small, scorched red sandstone pieces. Right in front of the large stone, a pit-shaped hole was uncovered, filled with grey-red sand, bits of slag and charred, small stones. At a depth of about 30 cm, a hard, siliceous grey bottom appeared. The heat discolourisation on the sides of the pit, was sufficient evidence for it having been the actual smelting hearth. In fact, only the lower part of the smelting furnace was found *in situ*, its upper part, probably demolished at the end of the last smelting operation to extract metal and slag, was found scattered around in bits (Figure 10).

The smelting furnace was of a bowl type, 45 cm in diameter, dug into the hard, red sand layer. In 1965 we stopped our excavation of the smelting bowl as soon as we reached a hard, siliceous grey bottom, but subsequent work on the furnace[27] showed, that the smelting pit penetrated, in fact, through the grey sand layer into the rock underneath and was 45–50 cm deep (from present surface, see profile, (Figure 12). A low superstructure of compact sandstone, part of it still found *in situ* (Figure 12, section A-A′), was built over the pit. The furnace had no mortar lining, but 'imported' standstone—not the 'local' granite—was used as refractory material. Many charred and slagged sandstone pieces were found at 39B.

Signs of intense heat were evident at the furnace itself (Figure 15) and at least 50 cm around it. No tuyeres or bellows fragments were found, though bellows of some kind must have been used as the location of the furnace would not allow the use of the prevailing north wind.[28] Perhaps the large stone behind the furnace (Figures 15, 16) served as a base for the operator of bellows or blow pipes.

An area of 4×3 m around the furnace was excavated down to a hard surface, which must have been the working floor, connected with the smelting operations. Charcoal, slag fragments, flint tools and some pottery were found on this floor, right up to the kerb of the furnace.

IV. Stratigraphy and dating

A fair number of flint implements and some sherds were collected on the surface of 39A and 39B at the time of the discovery of the site in 1960. These were tentatively dated to the Chalcolithic Period.[29]

The excavations at 39A proved that the structures of Loci 1, 2, 3 and 4 were built on virgin soil We can safely assume that the unexcavated parts of the site represent the same one-phase habitation, without any later, secondary use of its structures.

At 39B, around the smelting furnace, only one working floor was found, close to bedrock, and on this ancient surface, flint implements and sherds were found *in situ*, and dated also to the Chalcolithic Period. The archaeological finds from Site 39 were lately studied in great detail by Avraham Bercovici, of the Institute of Mining and Metal in the Biblical World, Tel Aviv, and this comparative study confirmed the Chalcolithic date proposed by us in 1960.

Site 39 is evidently a Chalcolithic copper smelting site, belonging, probably, to the later part of the 4th mill. BC.[30]

V. On the metallurgy of Site 39[31]

1) Ores[32]: The Chalcolithic smelters used the same ores as the later Bronze Age, Iron Age and Roman copper smelters of the Arabah: occasional thin (1–2 cm) horizontal layers, as well as cupriferous concretional nodules, found in the Upper-Paleo-Mesozoic Nubian sandstone. Although this copper mineralisation consists of (in the thin horizontal layers) malachite, paratacamite, pseudomalachite, brochantite, or (in the nodules) malachite, chrysocolla, dioptase and paratacamite around a core of chalcocite, covellite and (very rare) native copper, the minerals malachite and paratacamite were the major components of extractive significance. A number of ore nodules were collected at 39A and 39B and analysed:

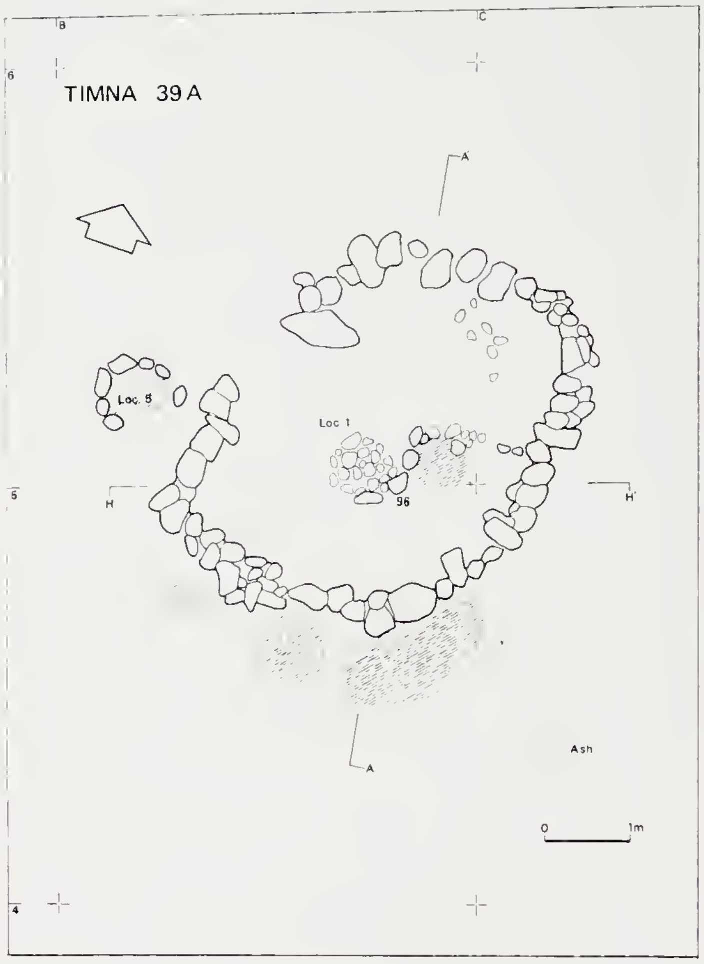

Figure 9. Site 39A: Plan of Locus 1.

TABLE 1

Copper ore nodules from Timna, Site 39 (A. Lupu), (%)

	Cu	SiO_2	Al_2O_3	FeO	MnO	CaO	MgO
1.	41.60	4.92	0.33	0.33	—	1.61	0.12
2.	43.74	10.70	7.84	1.04	—	5.60	1.17
3.	38.20	7.89	4.70	17.72	0.33	—	—

These samples also contained (H. G. Bachmann), in %:
0.1–0.5 Ni, 0.5–1 Zn. No Pb was detected in these samples, but lead is a common admixture in many copper ores from the Timna area.

2) Fluxes: As the copper ores of Timna are siliceous, and as analyses of slag from 39B have shown, iron oxide must have been added intentionally to the smelting charge, to facilitate the separation of the metallic copper from the gangue.[33]

Iron oxide flux was available to the ancient smelters of Timna from the Lower Cretaceous Sandstone layer, overlaying the copper ore bearing Paleo-Mesozoic Sandstone. Here, fossilized plants, often of the shape of large trees, contain up to 85% Fe_2O_3 and only 5–15% SiO_2. Numerous fragments of such fossilized trees were actually found in Timna's ancient smelting camps and must have been brought there intentionally for use as flux.

There is no evidence of the use of manganese flux at Site 39 nor, in fact, at any other Chalcolithic or Early Bronze Age site in the Arabah.[34]

It was previously assumed[35] that limestone, or 'other material rich in lime', was used as flux in addition to FeO. Table 2 shows indeed fairly high (4–23.6%) CaO contents in the slag from 39B. Yet, as no sign of any lime flux was found in the excavation of Site 39, as f.i. in the excavation of the Roman smelting Site 28, at Beer Ora,[36] we propose not to accept this high CaO content as an indication of intentional fluxing with limestone in the Chalcolithic smelting process. The CaO contents could easily have derived from the calcite present in the copper ore, together with the large quantity of CaO contained in the woodash[37] which, of course, goes into the slag.

3) Fuel: Charcoal made of local acacia trees and brushwood, from the nearby swampy area of Yotvatah, was used in the furnaces. A medium-sized acacia tree would produce about 30 kg of charcoal.

4) Slag: Numerous slag samples from 39B were analysed by wet chemistry:

TABLE 2

Composition of copper smelting slag from Site 39 (A. Lupu), %[38].

Sample No.	Cu	SiO_2	Al_2O_3	FeO	MnO	CaO	MgO	S
50a	1.31	30.71	6.83	49.51	2.00	4.06	—	0.22
50b	2.48	39.22	11.11	37.31	0.32	6.39	—	0.32
51	0.024	28.10	21.00	20.99	0.10	23.66	1.77	n.d.
52	5.04	48.42	1.43	22.84	0.27	13.62	2.56	,,
53	5.12	33.21	1.70	41.80	1.40	9.80	0.17	,,
54	2.36	48.25	2.12	35.50	0.20	8.95	0.81	,,
58a	15.12	34.25	—	21.69	—	22.13	1.62	,,
58b	16.60	45.92	17.13	14.20	—	8.80	2.22	,,
59	1.89	21.50	9.06	43.00	1.06	12.04	1.37	,,
60	1.72	30.10	9.00	32.71	0.82	20.13	0.88	,,
64	8.36	16.26	0.37	43.12	0.16	20.80	0.23	,,
69	6.81	40.96	2.96	33.06	—	11.24	1.07	,,
259a	11.10	44.78	3.93	22.38	—	11.42	2.65	,,
259b	4.03	23.21	1.63	33.17	—	19.74	1.48	,,
258a	4.21	28.90	4.77	48.75	0.4	6.32	0.29	,,
258b	2.80	32.75	6.15	43.13	2.23	5.17	1.86	,,

n.d. = not determined.

Most of the samples are from 39B, except sample 64, which is from 39A, and samples 59 and 60 which are surface finds.

All copper slags from Site 39 are of very inhomogeneous composition. This heterogeneity is typical for slags of the Chalcolithic Period, whereever such early slags were found and investigated[39], and due, probably, to lack of metallurgical experience and tradition, makes their characterisation rather difficult. The silica-iron ratio of the slag varied a great deal, but often there is more silica than iron. Most of the slags were very viscous and contained very much entrapped metallic copper (5–15%), i.e. about half the total copper produced remained in the slag.

None of the slag collected showed the flow structure of a tapped slag, but had the appearance of porous, viscous furnace slag, which had to be crushed to small fragments in order to extract the entrapped copper prills and pellets.

5) Metallic copper: Neither copper ingots nor copper implements were found in the excavation of Site 39, but some metallic prills could be extracted from the slag. The metal was found to be impure copper, containing 97.43–98.88% Cu, 0.24–0.30% Fe, some slag inclusions, some Pb and low As.

It is interesting to note the small quantity of iron in the Chalcolithic copper, in contrast to the rather large metallic iron contents in the Late Bronze Age—Early Iron Age I (14th–12th cent. BC) copper smelting slag.[40] There seem to be much less metallic iron impurities in prills from slag produced in a primitive bowl furnace and from a smelting charge with a low FeO to SiO_2 ratio, than in the copper produced in the more sophisticated, well-ventilated Late Bronze Age dome-shaped furnace, as, f.i. at Timna Site 2, and from a smelting charge of a ratio of more than 1 for FeO:SiO_2.[41] With the better reducing conditions in the larger, and hotter furnace, kept hot for many hours to allow the segregation of the copper from the slag, some of the iron flux seems to have been reduced to metallic iron,[42] and some iron was taken up by the metallic copper through its prolonged contact with the slag.

6) The smelting furnace and its operation (Fig. 11): The smelting furnace of 39B was essentially a hole in the ground, with a sandstone superstructure, perhaps narrowing at the top. The original height of the furnace is estimated to have been about 80 cm, with a diameter of 45 cm.

There can be no doubt that a forced draft had to be introduced into the furnace to reach the temperature range of 1180–1350°C, established from the melting range of the slag. This means that bellows must have been used though no direct evidence for such were found at the site. There

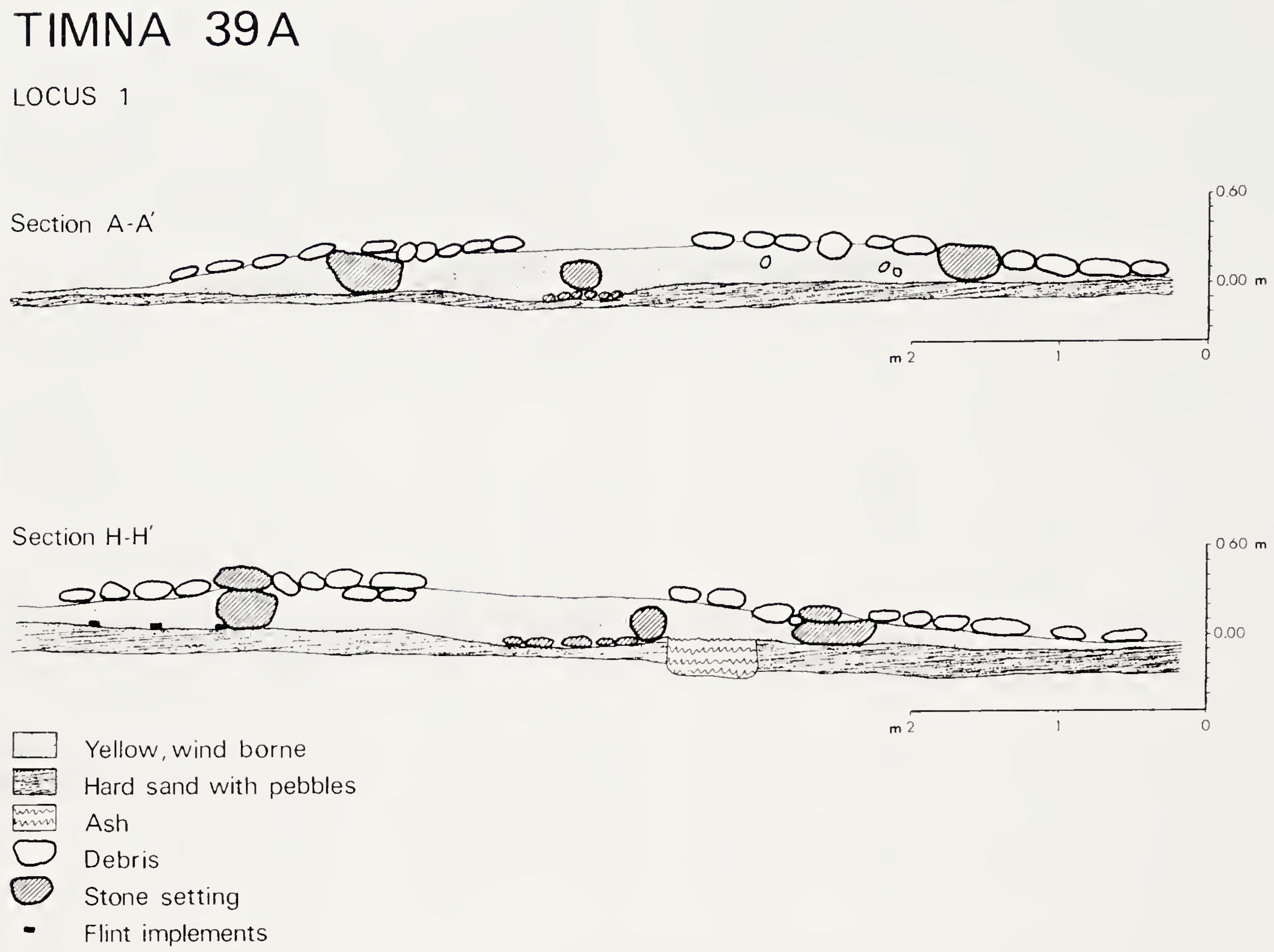

Figure 10. Site 39A: Sections A-A′ and H-H′ of Locus 1.

were no tuyeres, nor any other openings, in the lower two-thirds of the furnace and we assume that several bellows tubes were introduced into the furnace at the height of the present surface, i.e. into its upper third and at an angle of about 20 degrees. The draft would therefore be directed towards the upper half of the furnace and the reducing centre would be slightly above the point of entrance into the furnace of the bellows nozzle.

From the appearance and characteristics of the slag and the furnace remains, we can assume, with a high degree of certainty, that tapping was unknown to the Chalcolithic smelter.[43] At the end of the smelting process, when the furnace was full of slag up to the level of the bellows nozzles, the furnace was left to cool. The slag was then mechanically removed from the furnace and crushed to small fragments. Most of the metallic copper produced in the smelt remained entrapped as small prills and pellets in the slag and had to be extracted with the aid of hammer-stones, some of which were found at the site. It is possible that during the rather lengthy period of cooling, resulting mainly from the well-insulated, dug-in location of the smelting hearth, at least some of the metallic copper settled on the bottom of the furnace and formed a small ingot.

Our reconstruction of the original furnace shape

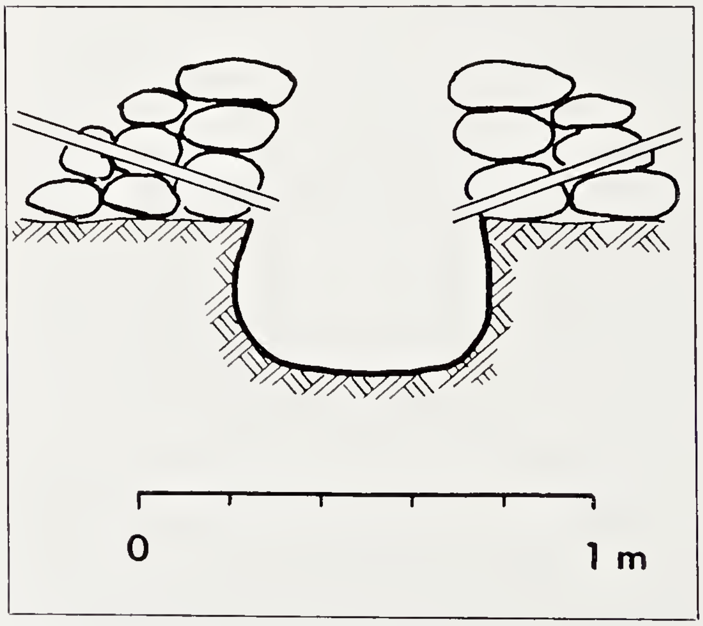

Figure 11. Proposed reconstruction of smelting furnace 39B.

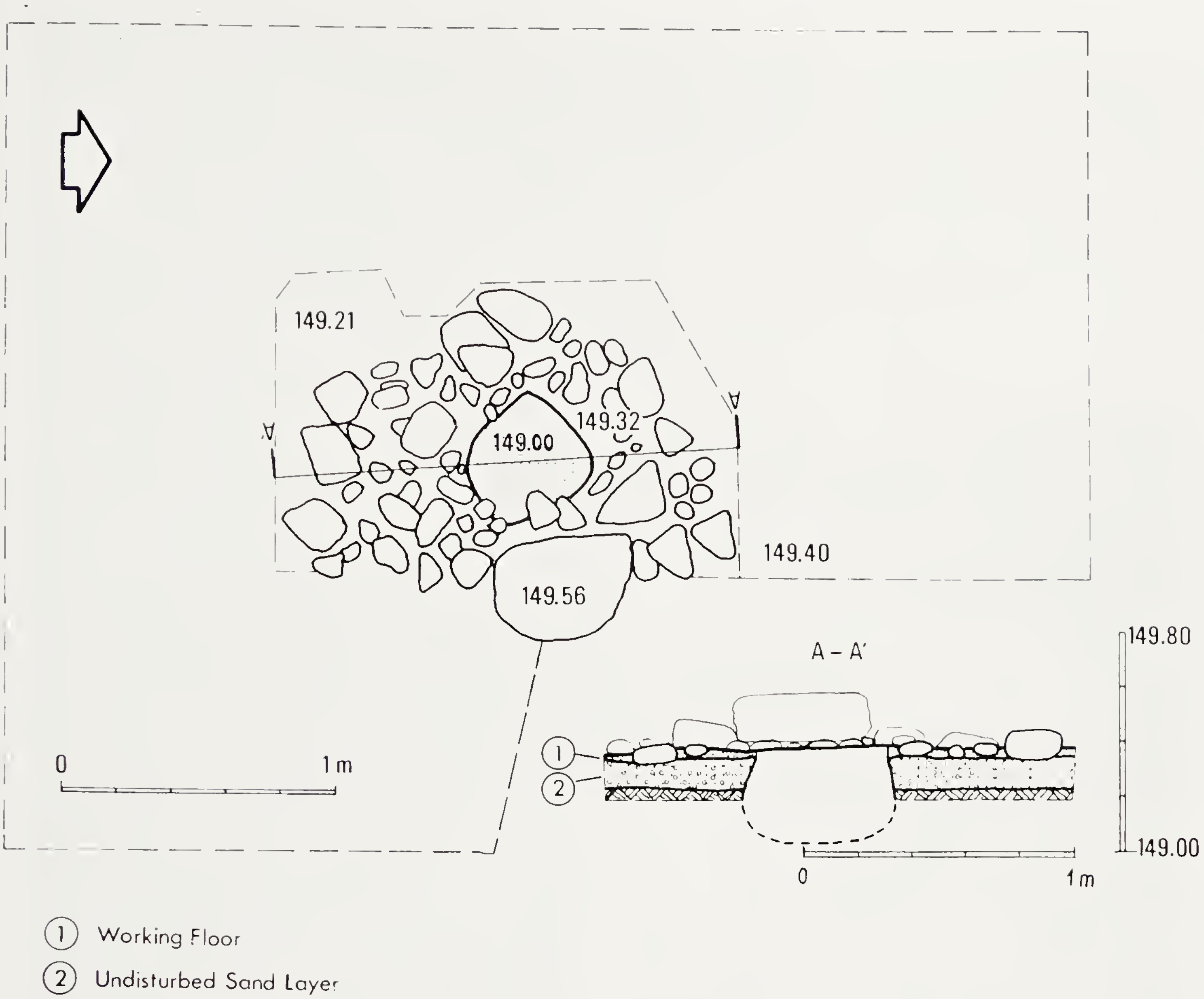

Figure 12. Site 39B: Plan and section of furnace excavation.

and the smelting process is, of course, lacking in detailed furnace characteristics and smelting conditions inside the furnace. These extractive metallurgical details were the subject of the experimental study by R. F. Tylecote and P. J. Boydell, described in Part Two of this publication.

Furnace 39B is the earliest copper smelting installation found up to date. Although it represents a very primitive stage of extractive metallurgy, it is probably not representative of the very beginning of smelting. The operators of the Chalcolithic copper smelters of Timna, though apparently unaware of mortar furnace lining, tuyeres and tapping, were already fully aware of the advantage of the half dug-in, well-insulated smelting hearth, and knew a great deal about fluxing, ore dressing and the preparation of a fairly well-balanced smelting charge. In fact, the Chalcolithic metallurgists of Timna, in constructing their hole-in-the-ground bowl furnace, achieved almost the optimum principle of the dome-shaped smelting furnace in use throughout history, and up to recent times in many parts of the world.[44] The actual extractive principles of copper smelting—though of course not its chemistry—were already well established in Chalcolithic times.

Figure 13. Site 39B at end of excavation. In the background is Wadi Arabah.

Figure 14. Site 39B: Furnace site before excavations.

Figure 15. Site 39B: Smelting furnace as excavated in 1965

Figure 16. Site 39B: Furnace bottom.

NOTES

1. The Arabah, located between the Dead Sea, in the north, and the Red Sea, in the south, is part of the great Syrio-African Rift Valley.
2. B. Rothenberg, Ancient Copper Industries in the Western Arabah, Palest. Explor. Quart., 1962.
3. Cf. first comprehensive, preliminary report on the Timna excavations up to 1970: B. Rothenberg, Timna, London, 1972; with bibliography up to 1970.
4. The New Timna Project, one of IAMS's research projects, is directed by the author, with H. G. Bachmann in charge of analytical research, in collaboration with R. F. Tylecote and P. Wincierz. A. Bercovici is in charge of pottery research. Work is still going on at present, carried out by the Institute of Mining and Metals in the Biblical World, Tel Aviv, under the direction of the author. Field director of the excavations in the Timna mines is Ivan Ordentlich, of the Tel Aviv Institute, with a team from the Deutsches Bergbau Museum Bochum (Director H. G. Conrad) providing specialist technical assistance (during two seasons of work in 1974 and 1976).
5. Excavations of smelting camp Site 30, 1974-76, were directed by the author, with A. Bercovici as assistant director.
6. Paul Craddock, of the British Museum Research Laboratories, supervised this excavation. He is also carrying out a comprehensive analytical investigation of the metal objects found at Timna.
7. Site 201 is a large, widespread habitation site, with intensive copper smelting activities. Excavation of this site started in July 1977, directed by the author, with Ivan Ordentlich as field director.
8. R. Maddin and T. S. Wheeler (Metallurgical Study of Seven Bar Ingots, *Israel Explo. J.*, 1976, *26*, 4, p.170-173) published MBI ingots, which could well originate from a Timna-type copper ore. It is unfortunate that these investigators were unaware of previous metallurgical work done in the Near East, and therefore missed the most significant issues of 'local' archaeological and historical relevance. F.i. the lead content in the ingots, genetically associated with Timna copper ores and/or iron fluxes—and also present in the Timna metallic copper. Unfortunately, Zn was not looked for—another good indicator for the sources of copper in the Near East.
9. B. Rothenberg, *Timna*, 1972, Pl. 2, 3.
10. B. Rothenberg, *Sinai*, *Revue Biblique*, 1975, p.75.
11. B. Rothenberg, Sinai Explorations 1967-72, *Bull. Museum Haaretz*, Tel Aviv, 14, 1972, p. 31-42; idem, Sinai Explorations III, *Bull. Mus. Haaretz*, Tel Aviv, 1972-3, p. 25.
12. See note 7. The New Timna Project plans to excavate a series of sites of prehistoric metallurgy in Timna and the Arabah during 1977-79.
13. The extractive metallurgy of the EB II sites in the Arabah is identical with that of the EB II smelter, excavated by our expedition at Site 590 in Southern Sinai. Cf. H. G. Bachmann, B. Rothenberg, A. Lupu, R. F. Tylecote, *Early Copper Metallurgy in the Sinai Peninsula*, IAMS Monographs, London, to be published in 1978. See also B. Rothenberg, *et al.* Excavations in Sinai, *J. of Field Arch.* (in press); D. Kingery, W. H. Gourdin, Furnace Linings from Rothenberg Site 590 in Wadi Zaghra, *J. Field Arch.* 1976; B. Rothenberg, *Sinai*, *Revue Bibl.*, 1975, p. 73-74.
14. B. Rothenberg, Sinai Explorations 1967-72, *Bull. Mus. Haaretz*, Tel Aviv, 14, 1972; idem, *Timna*, 1972, p. 13-14.
15. Petrographic studies of Sinai pottery and its comparison with sites in Southern Israel (including the important EB II town of Arad), Sinai, Jordan and Saudi Arabia, were carried out in 1971-72 by A. Slatkin. He established that EB II pottery from sites in Southern Israel, including pottery which could have originated in Arad, was found in South Sinai, and that some of the pottery, or some of its raw material, collected in Arad, could well have come from Sinai, thus indicating an exchange of wares and/or raw materials between Canaan and South Sinai. Cf. first report on this study by A. Slatkin, *Hadashot Archaeologioth*, Israel Dept. of Antiq., April 1974, p.24 (Hebrew). These results were later confirmed by J. Glass (cf. R. Amiran, I. Beit-Arieh, J. Glass, *Isr. Explo. J.*, *23*, p. 193-97, published at the end of 1974.
16. B. Rothenberg, An Archaeological Survey of South Sinai, *Palest. Expl. Quart.*, 1970, p. 27.
17. R. Amiran, Lecture on Arad, Museum Haaretz, Tel Aviv, June 1977.
18. R. Amiran *et al. Isr. Explo. J.*, 1973, p. 197. The theory of mining expeditions from Arad to Nebi Salah has been repeatedly propounded by both Mrs. Amiran and I. Beit-Arieh, and maps of the route of the 'mining expeditions' shown, with lines connecting on one end EB II sites in Sinai, and Arad on the other end. Looking at today's distribution map of EB II sites, this theory cannot, of course, be taken seriously.
19. B. Rothenberg, *Timna*, Chap. II.
20. Several more mining and smelting sites of Chalcolithic and Early Bronze I and II date were lately located and excavated by our expedition in 1974-77. See forthcoming report in IAMS Monographs.
21. R. F. Tylecote has been a research associate of the Arabah Expedition since 1966 and dealt mainly with metallurgical aspects of the field work. His experimental work on Chalcolithic copper smelting was carried out as an IAMS research project.
22. Previous preliminary publications: B. Rothenberg, The Chalcolithic Copper Industry at Timna, *Bull. Mus. Haaretz*, Tel Aviv, 8, 1966, p. 86-92; idem, *Timna*, 1972, p. 27-51.
23. Our Chalcolithic dating of the surface finds from Site 39 was confirmed at the time of the survey by (late) Prof. M. Stekelis, by Mrs. Tamar Noy and by (late) Miss Ephrat Yeivin. On the present dating evidence, see A. Bercovici, below.
24. The late Miss Ephrat Yeivin directed the excavations at 39A for several days. Miss Yeivin, due to sudden illness, had to stop her work and the author carried on the excavations at 39A. The author directed the excavations at 38B. Members of the team were: Barbara Hall, Diana Middleton, Colin Emms, Henning Feige, Ronald Simmonds, Haim Albuher, Ephraim Porter and Zvi Ashkenasi (surveyor).
25. Many 'smelting furnaces' of various dates, previously published, could not possibly be installations for copper smelting. They are usually either pottery kilns (f.i. D. Strong, *The Early Etruscians*, 1968, p. 14-15), or melting-casting furnaces (f.i. B. Maisler-Mazar, The Excavations at Tell Qasile, *Isr. Expl. J.*, 1950, p. 74-75), or iron smithies (f.i. Fl. Petrie, Gerar, 1928, p. 14, Pl. 25—this is not even definitely a metallurgical installation). Many archaeologists do not seem to differentiate between smelting and melting and consequently crucibles or tuyeres are almost invariably published as evidence of copper production (cf. B. Rothenberg, Beaker Metallurgy in Spain and Copper Smelting in Crucibles, *Antiquity*, in press).

For Late Bronze Age–Early Iron Age I copper smelting furnaces, cf. B. Rothenberg, *Timna*, 1972; see also R. F. Tylecote, *A History of Metallurgy*, 1976, p. 6-7.

26. J. Perrot, The Excavations at Tell Abu Matar, near Beersheba, *Isr. Expl. J.*, *5*, 1955, p. 167-169, Pl. 21.
27. In 1974, M. Barbetti, Oxford Research Laboratory for Archaeology, took samples for archaeo-magnetic and intensity studies from several of the Timna smelting furnaces. Investigating a section cut out of the bottom of the furnace 39B, at height 149.17 (cf. B. Rothenberg, *Timna*, 1972, p. 50), he found that this material was not consolidated by a thermic

process, i.e. it could not be the bottom of the furnace. A subsequent small excavation, down to 149.00, showed that the hard surface found at the time at height 149.17, and believed to be the furnace bottom, was but sandy fill, consolidated by long exposure and rain, and that the original bottom was about 20 cm deeper and of solid rock.

28. The possible use of prevailing wind for copper smelting operations is still an open question. Although temperatures of more than 1200°C. can be reached in a small furnace with the exclusive use of wind (cf. H. G. Bachmann's experiments at Timna in 1976, to be published in B. Rothenberg ed. *Late Bronze Age–Early Iron Age I (14th–12th cent. BC) Copper Mining and Smelting. Excavations in the Timna Valley, 1974-1976*, (in preparation), it seems doubtful to the present author, that wind was ever used as the only source of draught in a copper smelting furnace. The long time needed for the segregation of the copper from the slag, would require artificial ventilation to keep the furnace hot, and the use of prevailing wind could also infringe the maintenance of the proper reducing atmosphere. However, this problem needs more experimental clarification.

29. Cf. notes 2 and 23.

30. To date we have published several preliminary reports on the Chalcolithic sites of Timna and the Arabah, incl. Site 39. These contained, as dating evidence, drawings of our finds at the sites (B. Rothenberg, *Timna*, 1972, Fig. 10) as well as photographs thereof (Rothenberg, *Pal. Expl. Q.*, 1962, Pl. XV). It is precisely on the strength of these flint implements and the study of the sherds that the sites were dated to the Chalcolithic Period by Prof. M. Stekelis, Mrs. Tamar Noy, Miss E. Yeivin and the author. It is therefore curious to read in J. D. Muhly, *Copper and Tin* (2nd ed. 1976, p. 92-93) that 'it seems doubtful that anything at Timna is really earlier than EB II. This is probably also the date for the slag from Mrashshash (Several 1973)'. I have dealt with the date of the slag from Mrashrassh (the new port site of Elat)—actually a Chalcolithic date was proposed by Mr. Several, on the strength of a misunderstood chemical analysis—in *Isr. Expl. J.*. *25*, 1975, p.39-41, and this slag heap is now actually dated to the Roman period. Mr. Muhly's argument against all but EB II dating of the early Timna smelting sites is without foundation as he has neither seen any of the excavated material nor the sites in the Arabah. Moreover, he appears to have ignored the published dating evidence, which could not possibly be representative of EB II.

This is perhaps the right opportunity to refer to a paper published by another member of Mr. Muhly's 'research group': Th. A. Wertime (*Science*, N.4115, 1973, p. 182), in which he quotes *inter alia* 'B. Rothenberg has shown me a gossan-like formation at Timna in Israel, that was used as flux in ancient smelting and appears as a form of 'petrified' iron, possibly because of its long formation under water'. Mr. Wertime is mistaken. I have never shown him any gossan in Timna: there are no gossan-like formations there.

31. Metallurgical samples from Site 39 were investigated by A. Lupu, P. Fields, R. T. Tylecote and H. G. Bachmann. Most of the analytical work was carried out by wet chemistry, by Mrs. R. Malina, at the laboratories of the Dept. of Mineralogy, Technion–Israel Institute of Technology, Haifa. Cf. A. Lupu, Metallurgical Aspects of Chalcolithic Copper Working at Timna (Israel), *Bull. Hist. Met. Gr.* 1970, 4, p. 21-23; B. Rothenberg, *Timna*, 1972, Chap. IX; R. F. Tylecote, *A History of Metallurgy*, 1976, p. 6–8.

32. Cf. A. Bartura, The Geology and Mineralogy of an Archaeological Sample Area in the Timna Cirque, in B. Rothenberg, ed. *Excavations in the Timna Valley, 1974-76*, IAMS, London (in preparation).

33. It has now been experimentally proved by Tylecote–Boydell (see below) that without the use of iron or manganese as flux, most of the copper would remain finely divided in complex silicate and the extractive efficiency of the smelt would be extremely low.

34. The slag sample N.58c, with a high MnO content (29.33%), published by A. Lupu (*Bull. Hist. Met. Gr.*, *4*, 1970, p. 22, Table II) as coming from Site 39, is in fact a sample from the Roman site N.58 (Ain Zurub) in the Northern Arabah and was mistakenly included in this table. It should therefore be erased from the table published by Lupu.

35. A. Lupu, ibid., p. 25, cf. also my summing up of Lupu's interpretation, in *Timna*, 1972, p. 232.

36. B. Rothenberg, *Timna*, Chap. VII.

37. R. T. Evans–R. F. Tylecote, Some Vitrified Products of non-metallurgical significance, *Bull Hist. Met. Gr.*, *1*, 1967, p. 23, Table II.

38. Cf. note 31. Cf. H. G. Bachmann, below.

39. Cf. f.i. the slags from the Megalithic smelting site at Chinflon, from Masegosa and the Rio Corumbel area in the province of Huelva, Spain; see B. Rothenberg, A. Blanco, J. M. Luzon, *Ancient Mining and Metallurgy in the Province of Huelva, Spain*, IAMS Monographs No. 2 (in preparation).

40. Prills from Early Iron Age I Timna Site 2, contained 3.71–6.37% Fe, much of it metallic iron, and 0.2–1.2% Pb, originating from the ore and perhaps to some extent from the flux as well.

41. Timna Site 2 slag contained 32–41% SiO_2 and 35–53% FeO. Cf. A. Lupu, B. Rothenberg, The Extractive Metallurgy of the Early Iron Age Copper Industry in the Arabah, Israel, *Archaeol. Austriaca*, *47*, 1970, p. 102-3. See also R. F. Tylecote, J. P. Boydell, below, Table II.

42. Most of the iron impurities in smelted copper are removed, intentionally or unintentionally, by the subsequent melting of the copper prior to its casting. Cf. the experiments on iron-copper by Tylecote-Boydell.

On the problem of iron impurities in more recent times, see C. Schnabel–H. Louis, *Handbook of Metallurgy*, *I*, 1905, p.143.

43. The first sure signs of tapping appear at Early Bronze Age II smelting sites (cf. note 13), though it may already have been used, in a primitive way, during EB I.

44. Cf. R. F. Tylecote, *A History of Metallurgy*, 1976.

REFERENCES

Beit-Arieh, I.-Gophna, R.
1976, Early Bronze Age II Sites in Wadi el Qudeirat (Kadesh Barnea), Tel Aviv 3, Tel Aviv.
Ben Tor, A.
1975, Two Burial Caves of the Proto-Urban Period at Azor, Qedem 1, Jerusalem.
De Vaux, R.
1961, Le Fouilles de Tell el Far'ah, Revue Biblique, lxviii.
Dothan, M.
1959, Excavations at Horvat Beter, Atiqot II, Jerusalem.
Koeppel, R.
1940, Teleilāt Ghassūl 4 II, Rome.
Kozloff, B.
1974, A Brief Note on the Lithic Industries of Sinai, Yearb. Museum Haaretz Tel Aviv, 15/16.
Macdonald, E.
1932, Beth Pelet II, Prehistoric Fara, London.
Mallon, A., Koeppel, R., Neuville, R.
1934, Teleilāt Ghassūl I, Rome.
Perrot, J.
1955, Excavations at Tell Abu Matar, Israel Expl.J., 5.
Rothenberg, B.
1972, Timna, London.
Tuffnell, O.
1958, Lachish IV, The Bronze Age, London.
Yeivin, E.
1959, The Flint Implements from Horvat Beter (Beersheba), Atiqot II, Jerusalem.
1976, Note on Flint Implements from 'En Besor, Atiqot XI, Jerusalem.

APPENDIX 1

Flint Implements from Timna Site 39

by Avraham Bercovici

I. Description and comparisons

The flint implements, published here, were found at Site 39, partly in the excavation of areas 39A and 39B and partly on the surface. Since these implements are of uniform character, and the site itself showed one stratum only, it was decided to treat the implements as one group.[1] All the tools on Figures 17–19 are from the excavation, with the exception of Figure 17:7 and Figure 18:3, 6, 7, 8 which are surface finds.

Inventory of flint finds at Site 39

Tool types	Number of specimens found	%
End scrapers	8	14.8
Side scrapers	8	14.8
Fan scrapers	1	1.8
Notches	1	1.8
Burins	5	9.2
Awls	3	5.5
Picks	1	1.8
Adzes	2	3.7
Chisels	1	1.8
Hammering tools	1	1.8
Knives	6	11.1
Retouched pieces	7	12.9
Varia	10	18.5
Total:	54	99.5%
Others		
Flakes	27	
Cores	15	

THE AXES FAMILY:

1. Pick, Fig. 17:1; 18:1

Made on a flake. It has a regular section, which was obtained by steep retouching of the sides. The thick lower part is retouched on the bulbar face. The upper end of the pick has a vertical working edge, produced by dihedral chippings. On both ends of the pick there are hammering marks.

Mallon, A., 1934, Pl. 27: 9, 10
Koeppel, R., 1940, Pl. 99: 2; 113: 1
Yeivin, E., 1959, p. 46; tool No. 302 has a similar description.
De Vaux, R., 1961, Pl. XXXVI: 8 (Chalcolithique Moyen)

2. Adze, Fig. 17:8; 18:2

Made on a flake. Retouched, particularly on the face. The back was finely retouched along the sides. The cutting edge was shaped by two lateral blows.

Koeppel, R., 1940, Pl. 98: 4
De Vaux, R., 1961, Pl. XXXVI: 5
Yeivin, E., 1959, Fig. 2: 6

3. Adze, Fig. 19:8

Made on a core. Broken. Worked on both sides. It has a fine retouch on the left ventral edge and a triangular section.

Macdonald, E., 1932, Pl. XII (Site D^1)

HAMMERSTONE:

1. Fig. 17:6; 18:3

Made on a core, discoidal. Its edge, used for hammering, shows the same marks as the working edges of the pick, Fig. 17:1.

SCRAPERS:

1. Muciform Scraper, Fig. 17:7, 9;18:4, 5

Looks like a bladelet core. The ridges between the primary choppings are emphasized by a secondary retouch of the recesses. Very typical for this industry.

Kozloff, B., 1974, Pl. VI: 7, 8, from the bottom layer of Timna Site 200 (The Timna Sanctuary), cf. also Rothenberg, B., 1973, p. 129, Fig. 42.

2. Thick End and Side Scraper, Fig. 19:7

On a transversal flake; triangular section.

3. Thick, Steep Double-Side Scraper, Fig. 19:9

The trimming is regular and well made. Triangular section. Broken. This steep scraper belongs to the group of scrapers mostly made on rough, primary flakes or halved flint nodules.

Yeivin, E., 1959, p.43, Fig. 1: 16: 'is characteristic of this station and others of the same kind.'
Macdonald, E., 1932, Pl. XV (especially Site E).

4. End Scraper, Fig. 19:6

On transversal flake; striking platform blunted by retouching from both sides.

5. Double Scraper, Fig. 19:5

Made on a thin flake, Bulbar area narrowed by two choppings, one from each side.

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[1] We publish here only a small group of implements found at Site 39 in order to produce evidence for the Chalcolithic date of this site. A detailed description of all flints from Site 39 will be published in a forthcoming report on the Arabah Survey.

Figure 17. Flint implements from Site 39.

6. Elipsoid Tabular Scraper, Fig. 17:3; 19:4

A type belonging to the fan scraper family. On a thin flake (0.6 cm); finely retouched. Striking platform and bulb removed.

Mallon, A., 1934, Pl. 28: 9, 8, 6 (Chalcol.)
Yeivin, E., 1959, Fig. 1: 19 (Chalcol.)
De Vaux, R., 1961, Pl. XXXVII: 20 (Chalcol. moyen)
Ben Tor, A., 1975, Fig. 13: 13, 14 (Proto-Urban)
Yeivin, E., 1976, Fig. 2: 3 (EB.)
Macdonald, O., 1932, Pl. XXIV: 44; XVIII (Site H)
Tuffnell, O., 1958, Pl. 19: 2, 3 (EB.)
Beit-Arieh, I.-Gophna, R., 1976, Fig. 9: 34 (EB. II)

KNIVES:

1. Pointed Knife, Fig. 17:2; 19:1

Blunted along the back. Lower part is narrowed, perhaps in order to fit into a handle.

Koeppel, R., 1940, Pl. 108: 2

2. Knife on transversal flake, Fig. 18:10

Shows signs of use.

3. Knife on thick flake, Fig. 19:3

Cortex along back; fine irregular retouch on the bulbar face.

Koeppel, R., 1940, Pl. 109: 1, 2, 3

4. Knife on rough blade, Fig. 19:2

Cortex along the back; signs of use on the working edge.

BURINS:

1. Burin on denticulated flake, Fig. 17:5; 18:6

Yeivin, E., 1959, Fig. 1: 13, described as an awl, but almost identical.

2. Transversal Burin on truncated notch, Fig. 17:4; 18:8

AWL:

1. Fig. 18:7

Trimmed delicately, a 180° angle at its point.

Koeppel, R., 1940, Pl. 106: 2
Yeivin, E., 1959, Fig. 1: 14
Macdonald, E., 1932, Pl. XVII (Site A); Pl. XXI (Site D); Pl. XXIV: 44 (Site H)

CHISEL:

1. Fig. 18:9

On a small flake. Signs of use on the working edge; triangular section.

II. Discussion

This group of implements, which belongs to the 'Timnian industry',[2] shows a significant technological connection with the industries of the Chalcolithic cultures of Ghassul[3] and Beersheba.[4]

In contrast to the flint industries of Ghassul-Beersheba, the Timnian Industry is almost a pure flake industry. Sickle blades or 'Canaanite' blades[5] are entirely absent, a fact which can be explained by the arid character of the area in which this industry developed and, at Site 39, also by the particular metallurgical function of this site. Another characteristic of this flint industry can be seen in the diminutive size of its implements.

Only a few implements of this group, which appear in the Chalcolithic Period, occur also in the Early Bronze Age industries, as f.i. the elipsoidic fan scraper.[6] This tool is sometimes similar in both periods. However, we are unable to follow, so far, its exact development, because of unsatisfactory descriptions of this tool in the relevant literature and the neglect, in general, of flint studies in Palestinian archaeology over decades.

Other implements, especially the axes family,[7] are almost exclusively of Chalcolithic type, and, therefore, important for the determination of the latest possible date of this group. The occurrence of such axes in the Early Bronze Age is extremely rare, in fact it is not really well documented.

Although we reached the conclusion that our group of flint implements is to be dated to the Chalcolithic Period, datable pottery would be needed to obtain a more precise dating within this period. However, at Site 39 we found only one stratified body sherd of significance and even this sherd was too small to give better chronological evidence than the flints. On the other hand, at Timna Site 200 (the Timna Sanctuary), well below the Egyptian Ramesside structures, a few sherds were found—together with a similar group of Timnian flint implements—including one bowl rim, decorated with thumb indentations.[8] This sherd had its closest parallels in Wadi Ghazzeh, Sites D, O, M, A and H.[9] The occurrence of this rim in all of these sites may indicate its being of a transitional type.[10]

III. Conclusions

The flint implements from Site 39 represent a Chalcolithic culture which existed towards the end of the Chalcolithic Period of Palestine, i.e. during the late 4th mill. BC.

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[2] Cf. Kozloff, B., 1974, p. 47.
[3] Mallon, A., Koeppel, R., Neuville, R., 1934; Koeppel, R., 1940.
[4] Yeivin, E., 1959; Perrot, J., 1959; Dothan, M., 1959.
[5] Cf. Ben Tor, A., 1975, Fig. 13: 11, 12.
[6] Fig. 17: 3; 19: 4.
[7] Fig. 17: 1, 8; 18: 1, 2; 19: 8.
[8] Rothenberg, B., 1972, p. 130, Fig. 42: I.
[9] Macdonald, E., 1932, Pl. XXXII, XXXIII.
[10] The absence of axes at Site H indicates a stage earlier than Site H for our group of implements. Site H seems to be the latest in the sequences of the Wadi Ghazzeh sites. For the dating of Macdonald's sites in Wadi Ghazzeh, cf. also Perrot, J., 1955, p. 178-179.

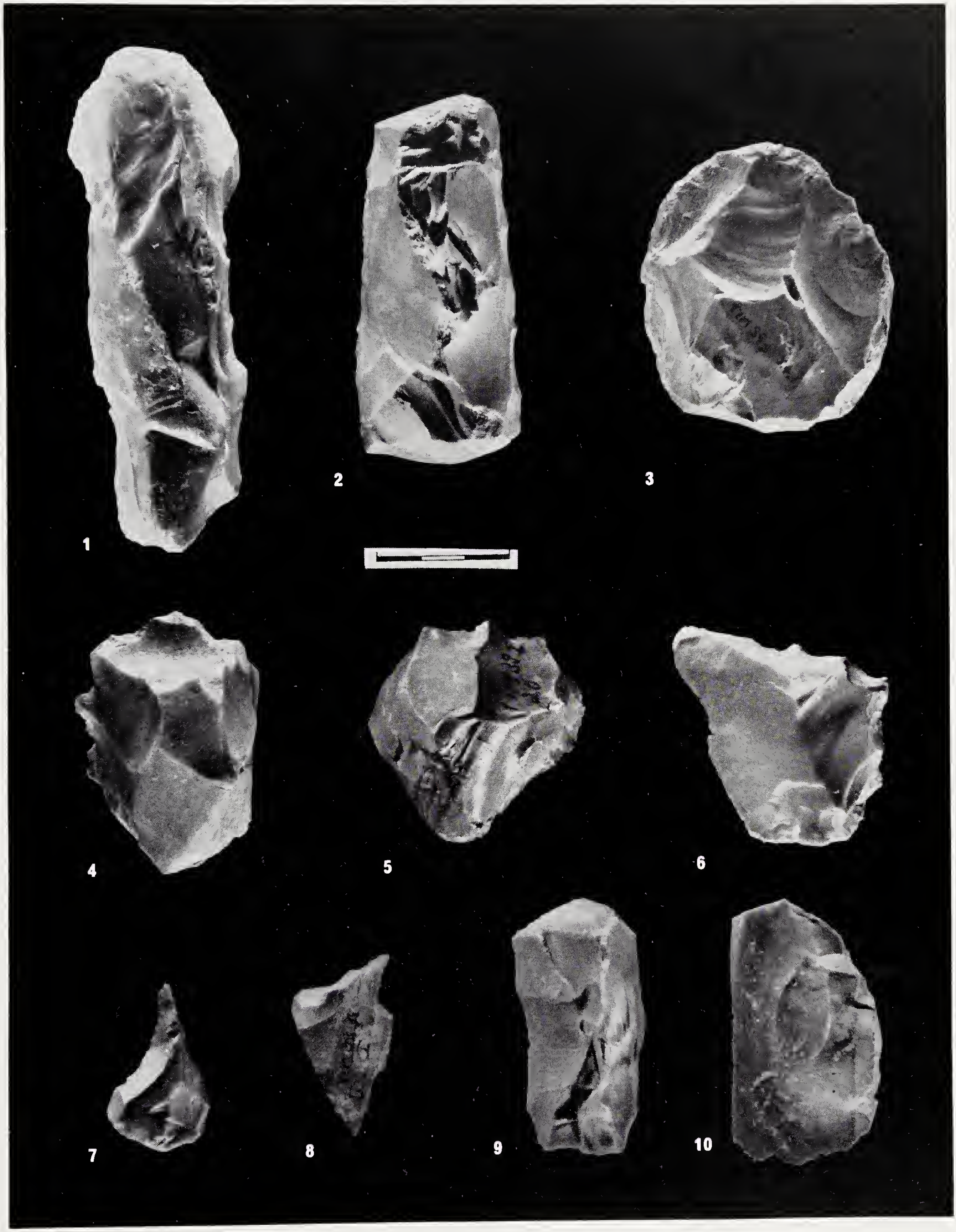

Figure 18. Flint implements from Site 39. Photo: C. Meredith

Figure 19. Flint implements from Site 39. Photo: C. Meredith

APPENDIX 2

The Phase Composition of Slags from Timna Site 39

by Hans-Gert Bachmann

1. Introduction

Copper smelting is a complex pyrometallurgical process, influenced by many parameters. Ancient smelting sites, such as Chalcolithic Timna Site 39, very often reveal the evidence necessary for an understanding of the processes carried out. Apart from excavation results, the discarded waste, i.e. the slags, may yield information on the archaeometallurgy specific for the site under consideration.

The chemical analyses of slags is but one method of characterization. Additional understanding of processes and reactions, that once took place, can be obtained by determination of the phase composition of the slags analyzed. Therefore, a selection of slags from Site 39 were submitted to x-ray diffraction[1] in order to obtain an additional classification criterion.

2. Results and Discussion

The samples investigated are summarized – together with their chemical analyses – in Table 1[2]. The chemical composition[3] exhibit considerable variation in their main components. The SiO_2-range starts at about 20 per cent and exceeds 50 per cent; the same is true of FeO. CaO, taken up by the slags from the gangue, the fluxes, the charcoal ashes and the furnace lining, varies from 4 to 20 per cent. The Al_2O_3-range is less pronounced. The MnO-content is low, excluding the use of manganese oxides as flux, as practised in later times at other smelting sites in the Timna area. Among the major trace elements, zinc and lead are present in all the samples investigated, presumably introduced into the slags from the ores and perhaps to some extent from the fluxes. Other trace elements, like strontium and zircon, are typical of the argillaceous material used as furnace lining. The copper content is low in some specimens and rather high in others. As a whole, the chemical composition range is typical for the type of smelting process outlined by Rothenberg[4]: Charges of sedimentary siliceous copper ores (malachite, paratacamite etc.) plus iron oxide fluxes and charcoal filled into small bowl-shaped furnaces varying from one smelting run to another, gave rise to slags of widely differing compositions. Additional proof of this conclusion is provided by looking at the phase composition i.e. the mineral content, of the slags.

Fayalite, Fe_2SiO_4, the most common and very often the only mineral in early copper smelting slags, is also present in many samples from Timna Site 39, but *always* associated with oxide phases of the spinel type. Spinels are oxides of di- and trivalent metal ions. These compounds may vary in composition and consequently in lattice constants. Among the oxides included in the spinel "family" and present in Site 39 material are: Fe_3O_4, $(Fe,Mn)Fe_2O_4$, $(Fe,Mn)(Fe,Al)_2O_4$ etc. Spinels in slags from Site 39 have already been identified microscopically by Lupu[5]. Another common constituent of the slags from this locality is quartz, SiO_2. The joint occurrence of iron-rich oxides (i.e. spinels) and quartz is an indication of incomplete reactions and unattained equilibria during the smelting process[6]. From chemical analyses one would expect a much higher content of fayalites in the slag, but by phase characterization we are able to distinguish between silicates and oxides. Complete slag identification requires analytical data *plus* phase determination.

All the slags from Site 39 obviously represent a "trial-and-error" approach to copper smelting. The retention times of the smelting charges inside the small furnaces and the temperatures employed were not yet sufficient for the formation of free-flowing slags. These inhomogeneous Chalcolithic

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[1] Guinier technique with Co $K\alpha_1$-radiation.

[2] The numbering of samples published in the tables by Rothenberg (this monograph) and Lupu (Alexandru Lupu: Metallurgical aspects of Chalcolithic copper working at Timna (Israel); Bull. Hist. Metallurgy Group *4* (1970), 21-23) is related as follows:

Rothenberg	Lupu
50a	50
50b	51
59	59
60	60
258a	14x
258b	14b
259a	09

This paper follows the Rothenberg notation. Samples Nos. 217 and 218 (also analysed by Lupu) are as yet unpublished.

[3] Semiquantitative analyses of the minor elements Co, Ni, Zn, Sr, Zr and Pb by x-ray fluorescence; done by the author.

[4] Cf. B. Rothenberg; this monograph.

[5] A. Lupu; loc. cit.

[6] Another oxide phase, present in some of the samples investigated, is delafossite, $CuFeO_2$. It accounts for a change from reducing to partly oxidizing atmosphere during the smelting process. Most of the copper content of the slags is, however, in the form of metallic copper globules. These were isolated from the powdered slag samples prior to phase analysis. Apart from crystalline phases – detectable by x-ray diffraction – most metallurgical slags contain certain amounts of non-crystalline glasses. These glasses are silicates of anorthite-like composition (anorthite $= CaAl_2Si_2O_8$). Most of the CaO content of the samples is probably included in glasses, but part of it can also be taken up by the fayalites.

slags were—on account of their high spinel and quartz contents – highly viscous. They solidified inside the furnaces. They have to be classified as furnace slags, contrary to tapping slags. The high viscosity also prevented a segregation of the copper droplets formed during the reduction process. At the end of each smelting run, the lumps of slag had to be taken out of the hearth and broken up in order to recover the copper prills embedded in the slag matrix. This tedious and rather inefficient procedure stood at the beginning of copper technology. It could only develop into a large-scale production after considerable improvement had been made to the process. At other sites in the Timna region many interesting steps of this gradual development have been preserved.

The Chalcolithic copper technology at Timna Site 39 is typical for an era in which metal tools and weapons were only gradually beginning to replace the use of stones. Slags as the predominant process indicators clearly testify the emerging relation between man and metals.

TABLE 1
Chemical and Phase Composition of Chalcolithic Slags from Timna, Site 39

Sample No.	Composition (Chem. Analysis) Weight Percentages								Minor Elements (Semi-Quantitatively)						Phase Composition
	Cu	SiO_2	Al_2O_3	FeO	MnO	CaO	MgO	S	Co	Ni	Zu	Sr	Zn	Pb	
50a	1,31	30.71	6.83	49.51	2.00	4.06	—	0.22	~0.1	—	~1	~0.1	~0.1	~0.1	FAY, SP, Q + ?
50b	2.48	39.22	11.11	37.31	0.32	6.39	—	0.32	~0.1	—	~0.1	~0.1	—	~0.1	DEL, FAY, Q, SP
59	1.89	21.50	9.09	43.00	1.06	12.04	1.37	N.D.	~0.1	—	>1	~1	~0.1	~1	SP + ?
60	1.72	30.10	9.00	32.71	0.82	20.13	0.88	N.D.	—	—	~0.1	~0.1	~0.1	~0.1	SP + ?
61	Not Analyzed Wet Chemically								—	—	~0.1	~0.1	~0.1	~1	DEL, SP
217	5.89	42.36	N.D.	31.19	N.D.	N.D.	N.D.	N.D.	~0.1	~0.1	~1	~0.1	~0.1	~0.1	Q, SP
218	3.50	51.28	5.31	20.36	N.D.	14.48	N.D.	N.D.	—	—	~0.1	~0.1	~0.1	~0.1	Q, DEL, SP
258a	4.21	28.90	4.77	48.75	0.40	6.32	0.29	N.D.	—	—	~0.1	~0.1	~0.1	~0.1	FAY, SP, Q
258b	2.80	32.75	6.15	43.13	2.23	5.17	1.86	N.D.	—	—	~0.1	~0.1	~0.1	~0.1	DEL, FAY, Q, SP
259a	11.10	44.78	3.93	22.38	—	11.42	2.65	N.D.	~0.1	—	~0.1	~0.1	~0.1	~0.1	FAY, SP + ?

Abbreviations:
N.D. = Not Determined
FAY = FAYALITE, Fe_2SiO_4
SP = SPINELS, Fe_3O_4 etc.
Q = QUARTZ, SiO_2
DEL = DELAFOSSITE, $CuFeO_2$
? = Unknown Phases (Minor Constituents)

Experiments

Acknowledgements

Most of the analytical work in this report was carried out by the laboratories of Borax Consolidated Limited at Chessington. The authors would like to express their kind appreciation for this work, in particular to J. R. Trayler, who has contributed the Appendix detailing the analytical methods used; to R. E. Coulson, C. L. Peers, Dr. R. Thompson (Research Manager) and K. J. Matterson (Manager of Geomet Services).

The full analysis of the slag from B 11 given in Table 7 was kindly undertaken by the British Steel Corporation through Dr. R. V. Riley of the Tubes Division, at Corby, Northants.

Experiments on Copper Smelting Based on Early Furnaces Found at Timna

by

R. F. Tylecote

P. J. Boydell

This work is based mainly upon copper smelting sites found in the Southern Negev by Israeli archaeologists.[1-7] *The sites uncovered have been virtually undisturbed since their use in Chalcolithic, Late Bronze–Early Iron Age and Roman times and reveal simple bowl smelting furnaces as well as developed bowl-shaped furnaces with sophisticated tuyeres and slag tapping facilities resembling closely those used for iron smelting in parts of Europe as late as the medieval period, in both cases producing slags of the fayalite type.*

Two furnaces have been in operation during the course of this work, one large furnace with slag tapping facilities and one smaller bowl furnace without slag tapping facilities, similar to the one found at Site 39, Timna.[2,4,6,7] An attempt has been made to produce plano-convex ingots of copper in both furnaces, using a variety of slagging materials and ores. In the early experiments artificial ores were used, due to the small amount of Timna oxide ore available at the time, to determine the characteristics of the furnaces and to develop the correct techniques.

Metallic copper was produced in both furnaces but, in usable form, only in the small Chalcolithic furnace. Slags of the fayalite type were produced in both furnaces, but tapping of the slag was not achieved.

The metal from the small furnace was remelted in a crucible furnace and refined.

Flow rate, fuel to ore ratio, tuyere size, tuyere number, and bed depth were varied in an attempt to optimize the conditions and temperature, pressure and gas measurements were taken during the smelts.

History of Copper Smelting

It is generally thought the first copper artifacts were made from native, or natural copper – possibly found during the searches for turquoise, obsidian and lapis lazuli during the period 7000-4000 BC and that the first native copper was appreciated as a stone.[8] The native copper probably had a dull green colour and, when scratched, would have given the familiar metallic red copper colour.[9]

The existence of native copper is quite well known, and although it has been suggested that the available quantity of native copper was so small that the metal was not of importance in prehistory, it must be taken into account that copper is the most common native metal, found as prills, nuggets, leaves and veins, and most primary deposits of copper ores produce their share of native copper – often becoming a nuisance in crushing operations. In fact, in 1861 Von Cotta found lumps of native copper weighing up to 15 kg at Recs, not far from Erlan, in the Siebenburgen region of Romania.[10]

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[1] B. Rothenberg, *Palestine Exploration Quart.* 1962, *94*, 5-71.

[2] B. Rothenberg, *Bull. Museum Haartez*, Tel Aviv, 1966, *8*, 86-93.

[3] B. Rothenberg and A. Lupu, *Bull. Museum Haartez*, Tel Aviv, 1967, *9*.

[4] R. F. Tylecote, A. Lupu and B. Rothenberg. *J. Inst. Met.* 1967, *95*, 235-242.

[5] A. Lupu and B. Rothenberg, *Arch. Austriaca*, 1970, *47*, 91-130.

[6] B. Rothenberg, *Timna: Valley of the Biblical Copper Mines*, London, 1972.

[7] A. Lupu, *Bull. Histor. Met. Group*, 1970, *4*(1), 21-23.

[8] C. C. Lamberg-Karlovsky. *Expedition*, 1971, *13* (3-4), 14-21.

[9] J. R. Partington. *Origins and Development of Applied Chemistry*, London, 1935.

[10] B. von Cotta, Die Erzlagerstätten Ungarns und Siebenburgens. *Gangstudien*, Teil IV, Freiberg, 1861, 144, 195.

Figure 1. Chalcolithic furnace from Site 39 at Timna. Scale: tool = 40 cms long.

Copper implements have been found in the New World with annealing twins in them.[11] Well-shaped objects made of native copper, found in the Lake Superior area and dating to between 3000 BC – 1400 AD, have been examined by Schroeder[12] and Winterton.[13] Spearheads of native copper have been examined by Smith,[14] showing work-hardening and hardnesses ranging from 58-108 HV, and the observed structures of annealed material with and without final cold work. Smith concludes that the final shape was obtained by working and annealing, and the finishing touches by cold working.

The annealing temperatures of these objects range up to 800°C, but before melting of the copper was possible a forced draught fire would have had to be set up in order to raise the temperature of the fire above the melting point of copper (1084°C). The temperature of a good wood fire ranges from 600°C-700°C; but with a good strong draught the temperature can reach 800°C and higher.

The next step in the development of copper smelting may have occurred during the firing of pottery. Renfrew[15] mentions that pottery has been found that had been fired at 1050°C in a reducing atmosphere, and here we almost have the conditions for both melting and smelting copper. Mond[16] suggests that firing conditions of 1100°C-1200°C may have been attained in Egypt by arranging the furnace so that the prevailing north wind improved the draught. Speiser[17] gives evidence to show that pottery at Susa and Tape Gawra was fired at temperatures up to 1200°C.

It is almost certain that melting came before smelting and Rothenberg[2] and Renfrew[15] have put forward the idea that the discovery of smelting may have occurred when man noticed that native copper could be melted. Gowland suggested in 1912[18] that copper was first smelted in a camp fire, and this can be confirmed to a certain extent by Rickard[19] who states that a geologist in the Belgian Congo found beads of melted copper on fragments of copper ore that had been reduced in camp fires by the local people. The instability of pottery glazes has been suggested as another route to the smelting of copper. The green glazes used for decorating pottery may have been reduced during the firing process. There is no evidence for this, although Gadd and Thompson found recipes for a green glaze on a clay tablet at Seleucia, dating 1600 BC; both recipes contained substantial amounts of copper.[20] It appears, therefore, that on the whole the discovery of smelting may be regarded as a logical process following on from the melting of native copper.[2]

Furnaces

The first metallurgical furnace must have been worked by either induced or forced draught. The pottery workers in the 4th millennium BC were capable of producing induced draught furnaces giving the temperature needed to melt copper, and if such furnaces were known to the potter, the metallurgist may have adapted them to his requirements. These furnaces could have been used for the *melting* of copper, but as they are pottery furnaces – and the melting area remote from the fuel – the conditions may not have been reducing enough for smelting.

Probably the first forced draught furnace was the simple bowl furnace as found on Site 39 at Timna, this site being of the Chalcolithic period.[2,7] This was a dug out and partly stone-built bowl, blown with one or more tuyeres, but with no facility for tapping slag (Figure 1). The ore was added with the charcoal and after the slag had reached the tuyere level, the furnace was allowed to cool, and the slag and copper removed. The slag was then broken up in order to remove the copper from it. The furnace

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[11] D. T. Easby. *Sci. American.* 1966, *214*, 73-81.

[12] D. L. Schroeder and K. C. Ruhl. *American Antiq.*, 1968, *33*, 162-169.

[13] K. Winterton. Dating of some museum objects by metallurgical means. *Ontario Res. Foundation.*

[14] C. S. Smith. *Acts XI Congres Int. Hist. Sci.* 1965, Warsaw-Krakow, Vol. VI, 237-243.

[15] C. Renfrew. *Proc. Prehist. Soc.* 1969, *35*, 12-47.

[16] R. L. Mond and D. H. Myers. *Cemeteries of Armant*, London, 1937, *1*, 167.

[17] E. A. Speiser. *Ann. Amer. School. Orient. Res.* 1927-8, *9*, 50.

[18] W. Gowland. *J. Inst. Met.* 1912, *7*, 23-49.

[19] T. A. Rickard. *Man and Metals.* New York, 1932, 114.

[20] C. J. Gadd and C. Thompson. *Iraq*, 1936, *3*, 78-96.

at Site 39 had been placed near the top of a hill but this was clearly not for the purpose of using the natural wind for induced draught, as this would not work in the case of such a shallow furnace dug into the ground.

A later step in the evolution of this type of furnace was the development of larger, slag-tapping, furnaces. Excavations on Site 2 at Timna have produced a number of furnaces measuring $\frac{1}{2}$ m×2 m, $\frac{1}{2}$ m deep at one end and rising to ground level at the other (Figure 2). These furnaces were lined with clay which was found to have been slagged during use. Single tuyeres have been found in the back wall of the furnace and none at the sides, but it is possible that more than one tuyere could have been placed in the front wall above the slag tapping point, or in the sides, at a higher level that were not preserved.

The tuyere system was found to be complex, consisting of a 10 cm dia. tube or clay-lined opening in the furnace wall, in which a 3 cm dia. tube was placed – presumably leading to the bellows. The end was sealed with a prepared nozzle of clay (tuyere end) serving as a heat screen to protect the combustible bellows pipe. This has been found to have been well-vitrified with some slag adhesion on it. The tuyere angle was about 40° to the horizontal and was probably directed into the centre of the furnace. At the bottom, a shallow cavity was prepared to receive the molten copper.

Fluxes

The ores used were basically oxides, i.e. oxidized sulphides, and the degree of oxidation could vary considerably. No roasting of the ore was necessary and this is borne out by the fact that no matte and virtually no sulphides were found in the slag. The gangue was highly siliceous and therefore to slag off the silica, haematite, other iron oxides, or manganese oxide had to be added. The slags found have usually been of the fayalite type, $2FeO.SiO_2$, thus having a low melting point (1150-1250°C). These slags contain prills and drops of copper of varying sizes. Analyses of the prills, drops and slags are given in Tables 1 and 2 (from references 4 and 5).

Figure 2. Late Bronze—Early Iron Age furnace from Site 2 at Timna. Scale: each section = 10 cms.

TABLE 1
Composition of Timna (Site 2) Copper Prills and Drops (%)

Specimen No.	Cu	Fe	Pb	S
1	89	9.7	0.8	0.01-0.1
2	92	5.0	0.7	—
3	89	7.2	1.2	—
4	90	9.0	0.2	—

Experimental Procedure

Furnace Construction

Two furnaces were used during the course of this work. The first, furnace A, was based upon the Early Iron Age I Timna Site 2 furnaces, and was constructed from firebrick blocks with a sand seal around the inner circular blocks to eliminate leakage of gas. The internal diameter of the furnace was 32 cm and the height from furnace bottom to top was 76 cm. A single opening in the front of the

TABLE 2
Analysis of Timna (Site 2) Slags (%)

	1	2	3	4	5	6	7
SiO_2	32.7	35.6	29.7	40.2	35.7	32.5	36.1
Al_2O_3	4.8	4.1	9.8	2.2	3.1	2.9	2.3
FeO	14.8	6.5	53.1	43.3	32.9	46.2	40.4
MnO	32.3	40.4	2.5	1.7	2.7	0.4	3.5
CaO	4.1	4.6	4.7	9.3	13.7	2.3	4.5
MgO	2.5	1.5	2.3	0.5	0.3	4.7	3.1
Cu	0.24	0.27	0.27	0.61	2.3	3.8	0.22
S	0.2	0.13	0.20	0.1	0.69	0.14	0.25

furnace was blocked up with bricks and clay-sand; the clay-sand was replaced with refractory concrete in the later smelts (Figure 3).

In the early experiments a single inclined tuyere in the side of the furnace was used, terminating at the furnace edge and not protruding into the furnace, with a diameter of 3 cm at the opening to the furnace. As work progressed, a horizontal tuyere was positioned in the side opposite the inclined tuyere, protruding 2 cm into the furnace. This tuyere consisted of a single aluminous porcelain tube 2 cm in bore diameter.

Four steel probe-tubes of 10 mm diameter were built into the side of the furnace, vertically aligned with the inclined tuyere, for temperature gas and pressure measurements. Two probe tubes were built into the front of the furnace over the front opening.

Temperature measurements were taken using Chromel-Alumel thermocouples sheathed in mild steel tubes 10 mm diameter, which were replaced when necessary. Around and below the tuyere (i.e. probe tubes 1 and 2) the thermocouples were inserted into the furnace for short periods only because of the high temperature, and the thermocouples quickly burnt out if care was not taken. At probe tubes 3 and 4, the thermocouples could be inserted into the charge permanently, although if the thermocouple was inserted far into the furnace the charge tended to "hang-up" and consequently the working of the furnace became erratic.

Furnace B was of smaller size than Furnace A and, like the Chalcolithic furnace (Site 39, Timna), had no slag tapping arrangement. It consisted of fireclay bricks formed into a hearth, 22 cm in diameter and 30 cm deep, and a sand seal was built around the furnace to reduce gas leakage. A single inclined tuyere with a diameter of 3 cm was built into the side of the furnace at an angle of 50° to the horizontal, 16 cm-18 cm above the base of the furnace. Into the front of the furnace three mild steel probe tubes were placed at 9 cm, 20 cm and 28 cm from the furnace bottom. Details of the furnace are shown in Figure 4.

Gas compositions were analyzed with an Orsat apparatus, using a mild steel sampling tube inserted into the furnace through the probe holes. Both the CO and CO_2 percentages could be measured with this apparatus but in several cases only the CO_2 measurement was taken, for control purposes only.

The tuyere design is shown in Figure 5. The tuyere was fabricated from mild steel with a glass eyepiece at one end which could be removed for cleaning. The hot end of the tuyere was of mullite.

Air was supplied from a compressor capable of producing 550 l/min. and the air flow was measured using a 35X Rotameter with a duralumin float. The rotameter was coupled to a mercury manometer in order to correct the flow rate for air pressure to N.T.P. The flow rate was controlled by a gate valve and regulator, and excess moisture was removed from the air by means of a trap.

Ores and Charcoal

Because of the small quantity of Timna ore available, in the majority of experiments a simulated ore was used. Cumberland hematite, silica sand, and manganese ore were used; the analyses are shown in Table 3. The hematite was supplied in pieces ranging from 12 mm-25 mm and the Hotezel

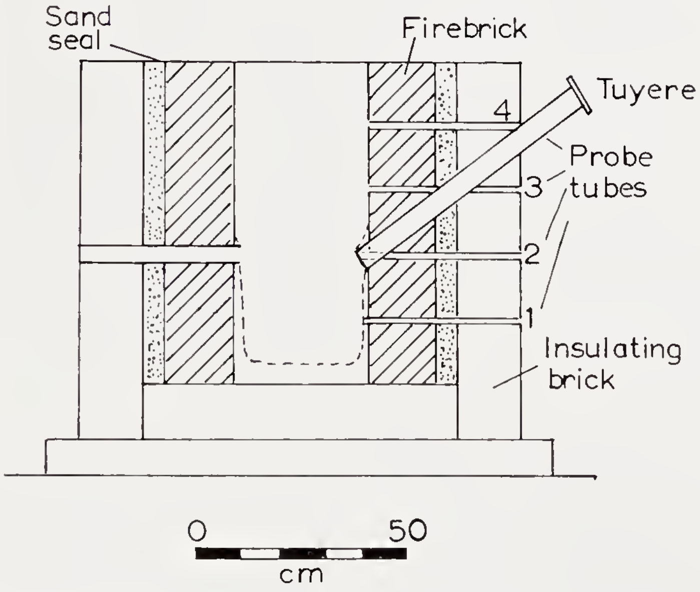


Figure 3. Furnace A, showing probe positions numbered 1 to 4.

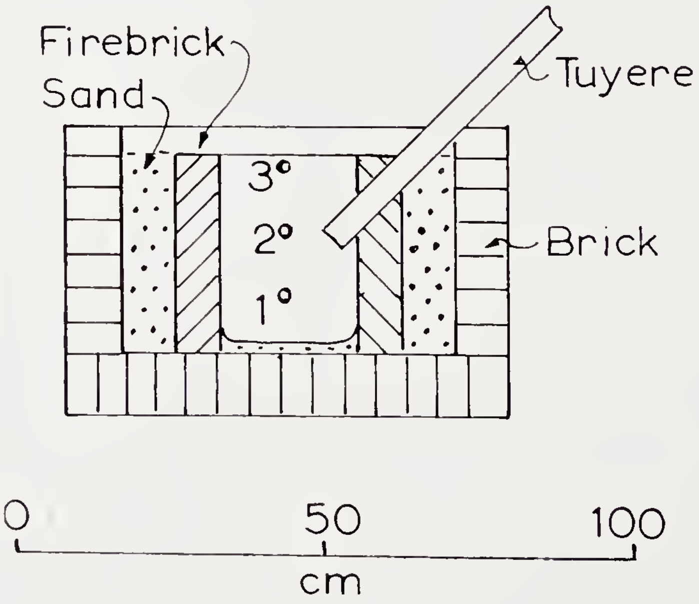


Figure 4. Furnace B.

manganese as massive lumps – although both ores were crushed to sizes not greater than 5 mm before charging to the furnace.

The copper oxide ore was supplied from Timna, and from the analysis it can be seen that it was highly siliceous. To flux the silica it was necessary to add iron oxide in the form of haematite ore, and in one experiment manganese ore was used. The Timna ore was supplied in a size range from fines to approximately 50 mm, but in all experiments the ore was crushed to fines (<4 mm).

The charcoal used was of mixed hardwood and softwood and was assumed to contain 2.5% ash.

Furnace Characteristics: Furnace A

Pressure Losses

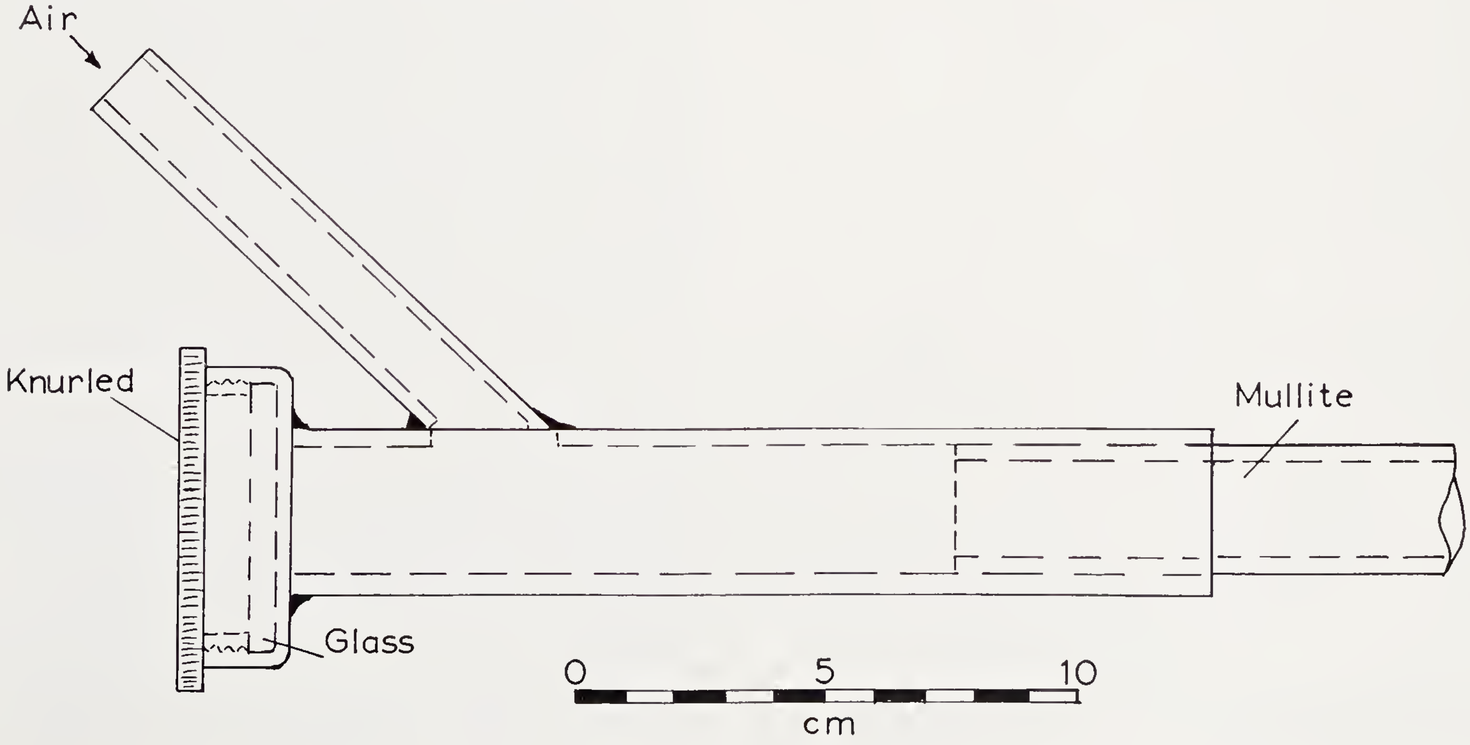
The pressure losses were determined with the furnace filled with unignited charcoal only. A single inclined tuyere with a diameter of 3 cm was used with a bed depth of 73 cm. The pressure on the central axis was measured by means of the probe tubes 1 to 4 using a venturi manometer. The results obtained by varying the air flow rate are given in Figure 6. These results are replotted in Figure 7 to show the change of pressure with position up the bed. It is clear from this figure that there is a more-or-less linear fall-off in pressure up the bed and below the tuyere, as would be expected. In examining Figure 6, it must be remembered that position 2 is immediately in front of the tuyere and a high pressure zone is to be expected in this area. With flow rates exceeding 300 l/min (not shown in the Figures), the pressure was higher than expected at the top of the furnace which suggested a channelling effect at a point 20 cm above the tuyere due to the force of the blast displacing the low density charcoal. However, this effect was not apparent during the normal working of the furnace on a heavier charge of ore and charcoal.

TABLE 3
Analyses of Ores and Fluxes (%)

	Timna Nodular Ore	FLUXES			
		Hematite Typical	Hematite Analysed	Hotezel Mn Ore	Sand
FeO		nil	0.7	—	—
Fe_2O_3		68.6	73.0	15.10	2.43
SiO_2	43.4	17.0	16.6	5.67	90.30
Al_2O_3	3.1	2.0	1.3	—	4.40
MgO	—	0.5	—	—	—
MnO	—	—	—	63.0	—
P	—	0.002	—	—	
S	0.54	0.17	0.17	—	
H_2O	—		—	—	
CO_2	—		—	—	
CaO	0.084	3.0	1.54	—	0.03
Cu	23.70		0.04	1.01	
Fe	7.29		—	—	
Zn	tr				
As	(500)		(100)	(12.5)	tr
Ni	0.013		0.012	—	tr
Ag	tr		—	—	
Pb	0.045		0.005	—	

( ) = ppm

Figure 5. Tuyere design used on both furnaces.



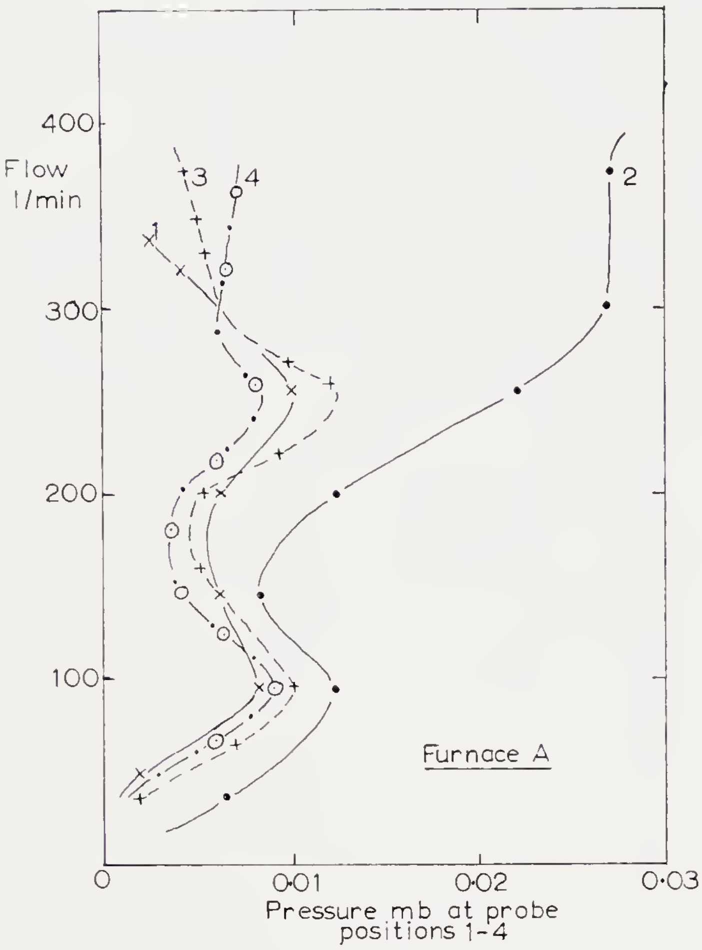


Figure 6. Effect of flow rate on pressure drop in Furnace A.

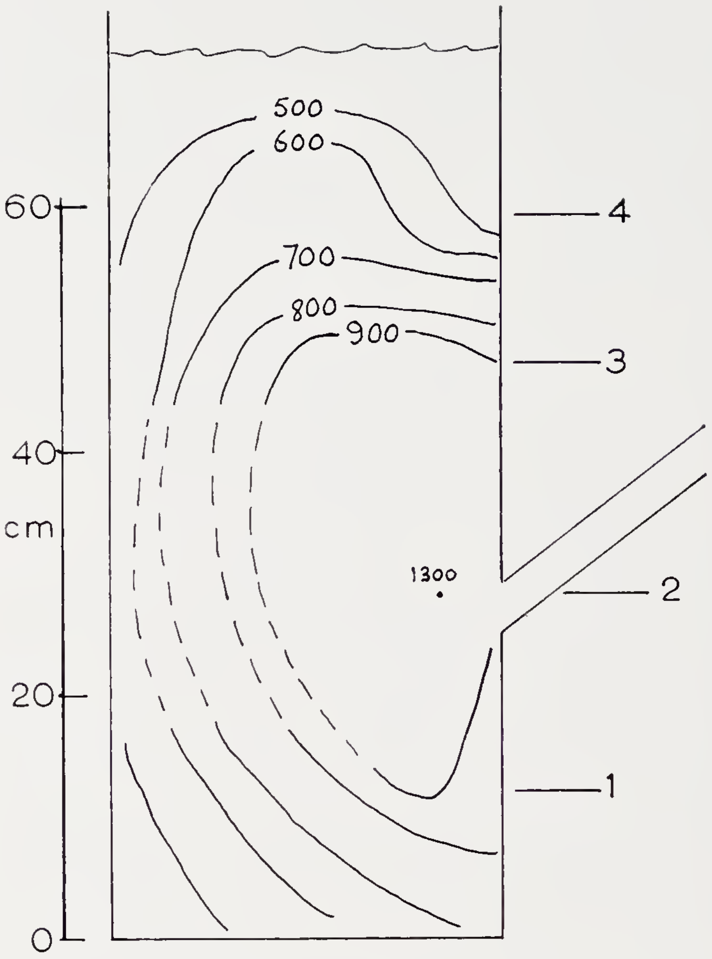


Figure 8. Temperature distribution in Furnace A with 200 l/min of air and one tuyere (°C).

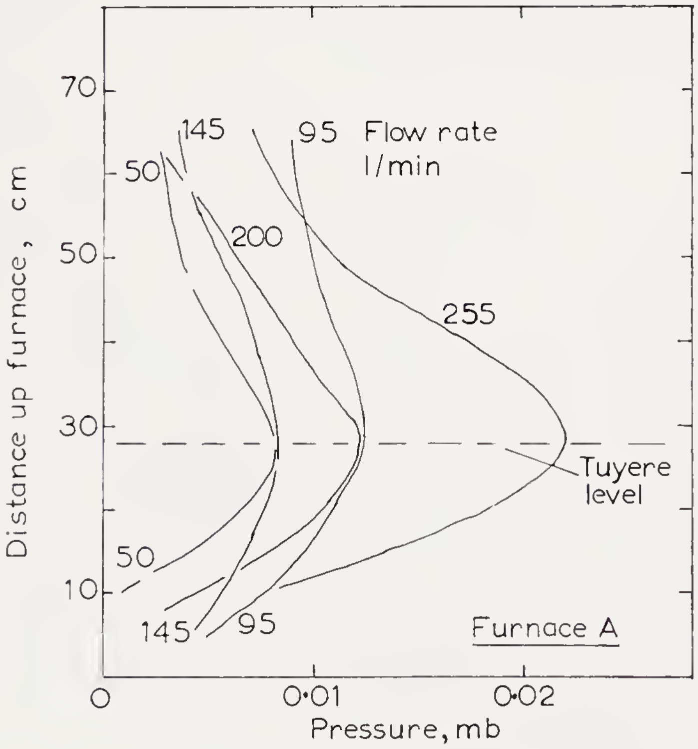


Figure 7. Pressure drop related to bed depth in Furnace A for various flow rates.

Temperature Distribution

Temperature profiles were made for this furnace at flow rates of 160 and 200 l/min (that for 200 l/min is given in Figure 8). The latter was repeated with a hole of 2.5 cm diameter made in the furnace wall opposite the tuyere. With a flow of 200 l/min. air was sucked into the furnace and gave the temperature distribution shown in Figure 9. With a flow rate of 300 l/min. the pressure reversed and gas was blown out. This meant that the air was being diverted across the bottom of the hearth, causing better combustion in this area, and thus resulting in higher temperatures.

Experimental Work on Furnace B

This furnace was intended to be similar in type to that found at Site 39 at Timna. The tuyere was made of mullite with an internal diameter of 1.9 cm and was inserted over the lip of the furnace directed towards the centre of the furnace bottom.

The main plan was to work the furnace on simulated ore charges until success with the Timna ore could be guaranteed. The details of the smelts made with this furnace are given in Table 4.

The example of B1 is typical of the first five runs. The furnace was preheated for $1\frac{1}{4}$ hours and then mixed charcoal was added with a blast of 100 1/min. After filling the furnace, the charcoal was charged in 0.2 kg loads; $2\frac{3}{4}$ hours after the beginning of preheat the first ore was charged and layers of charcoal and ore were charged for a further $1\frac{3}{4}$ hours. (The "ore" consisted of hematite crushed to 4 mm., and copper swarf.) Hematite ore was charged first, and then the copper was added – the object being to see if liquation of the copper would take place. After the last ore addition, the furnace was kept burning on charcoal for a further $1\frac{1}{2}$ hours to allow the ore to reach the base of the furnace.

After cooling, the slag was removed from the furnace and broken up. Small copper globules were found in the upper layers of the slag which had not liquated through to the bottom, suggesting that the furnace was running cold at the bottom.

Metallography of the products showed a fayalite-wüstite slag with Cu and Cu_2O trapped in it; the copper was of high purity with oxide in the grain boundaries.

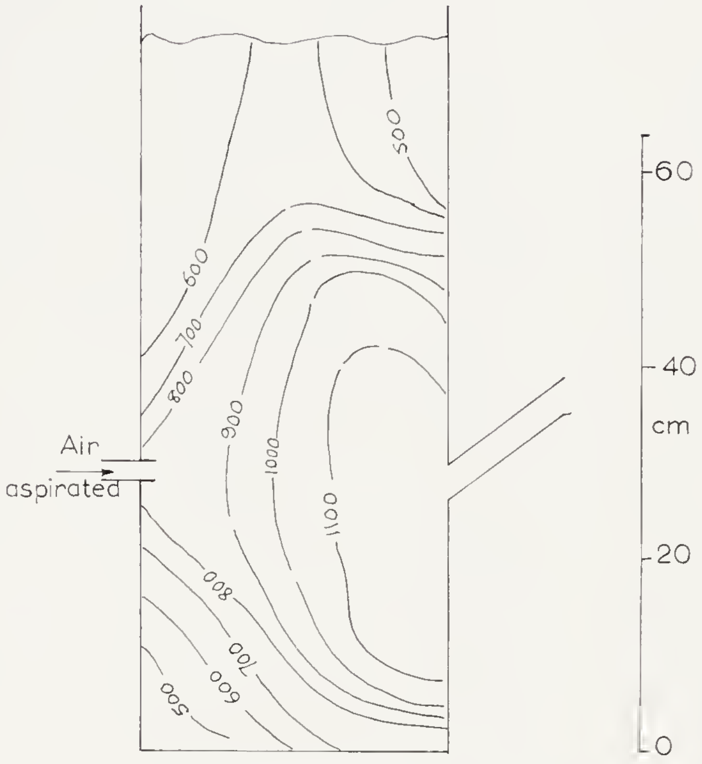
The tuyere was inclined towards the centre of the furnace, thus producing a tendency for the furnace to combust more on one side of the furnace. In B2 the tuyere was directed vertically downwards into the furnace with the tuyere opening 12 cm from the bottom of the furnace; this was intended to distribute the blast evenly across the furnace. There is evidence that the method could have been used in early times because of the 'L'-shaped tuyeres that have been found near some copper working sites.[21] In this case the charge was hematite and reagent grade CuO (18% CuO, 82% hematite ore). The furnace was on blast for $2\frac{1}{2}$ hours after the end of ore charging.

The copper had been caught in the slag and had not liquated through it. If the temperature of the furnace had been higher the slag would have been less viscous and allowed better liquation.

Metallography of the smelt showed a wüstite-glass slag which was magnetic. Most of the copper was present as globules; these contained oxide in the grain boundaries and within the grains.

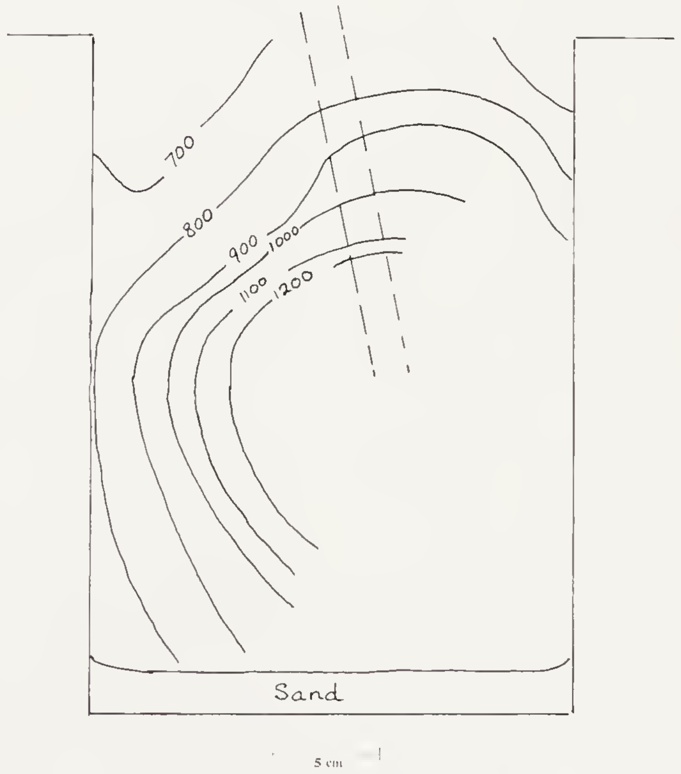
Although this tuyere arrangement worked, the inclined tuyere was more convenient and in B3, and subsequently, the tuyere was positioned as in B1, i.e. at an angle of 50° to the horizontal axis 16-18 cm above the base of the bed. The blast was increased by 20% to 120 1/min and gave the temperature distribution shown in Figure 10.

This smelt was more successful than the previous ones. Copper oxide was charged, and the CuO had been reduced and the copper agglomerated into globules ranging from 0.1 g to 20 g with one globule of 34 g. The copper yield was 94.5% of



A3 Flow 200 1/min
Temperature °C

Figure 9. Temperature distribution with air aspiration through the horizontal tuyere with 200 1/min of air through the inclined tuyere (Smelt A3—°C).



Temperature distribution in Furnace B3
in plane at right angles to tuyere

Flow=120 1/min

Figure 10. Temperature distribution in Furnace B with 120 1/min air (Smelt B3).

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[21] R. F. Tylecote. Observations on Cypriot copper smelting. *Rep. Dept. of Antiqs. Cyprus, 1971.* 53-58.

TABLE 4
Smelts made using the small furnace B

Smelt	1	2	3	4	5	6	7	8	9	10	11	12	13
Charcoal Total kg	5.7	6.5	7.9	8.5	10.3	8.3	8.55	9.05	5.9	8.65	8.85	9.3	11.9
Charcoal rate kg/hr	0.9	1.0	1.2	1.8	1.6	1.5	1.6	1.65	2.0	1.7	1.9	1.8	2.0
Flow 1/min	100	100	120	150	150	150	150	150	150	150	150	150	200
Ore charge kg	1.8H 250 g Cu	1.6H 350 g CuO	1.5H 500 g CuO	2.0H 500 g CuO	1.8H 450g CuO	2.25H 1.25 kg T	1.5T 3.0H	1.3T 2.6H	2.6T	2.3T 4.6H	4.55 slag+Cu (A10)	5.0 T+H+M 0.35+0.58 +0.32	2.0T 4.0H
Tuyere position above bttm cm	18	12	16	16	18	16	18	16	16	16	17	17	16
Fuel/ore ratio	1:1	4:5	1:1	3:5	1:1	1:2	1:3	1:2	1:2	1:2	1:2	1:2	1:2
Temp. °C IC							1080	1130-40		1090	780		700
IIC							1200		1200+	1200	1200		1280
IIIC							1020			1040	1200		820
Cu rec. g	104	137	370	320	290	235			nil	290		135	273
%	42	49	94.5	80	80.5	94				58		45	69
% CO_2												12.7	25.0
Results	Fay.+ FeO	Glass+ FeO	Fay+ FeO	FeO+ glass	FeO+ glass	Fay+ glass	Fay. glass slag+Cu+ Cu_2O.Glbs Fe-free. Filmnts Fe-rich	Fay+ glass Cu as B7	Brittle-porous. Redcd Cu not agglm	Fay+wüst +anorth. Cu_2O in Cu glbs.	Fay+anorth Cu_2O. Cu glbs. and filaments Fe-cntng.	Cu globs +flmnts with iron	Fay+magn.
Remarks							Not well liquated		Unsccsfl due to lack of flux	To much charge 5 kg max.	Failed: tuyere blocked	Good;slag liquation better due Mn ore.	Good liq: top 3 cm of slag Cu free

Key; T=Timna ore H=hematite ore M=manganese ore Temps. C=furnace axis. I, II, III indicate positions up furnace, 7, 18 and 26 cm above the 2 cm thick sand bottom.

TABLE 5
Smelts made using furnace A

Smelt	1	2	3	4	5	6	7	8	9	10	11
Flow: 1/min	200	200	200	300	300	300	370	175+175	140I+210H*	325I+195H*	324I+185H*
No. of Tuyeres	1×25 mm	1×25 mm	1×25 mm	1×25 mm	1×25 mm	1×19 mm	1×19 mm	2	2	2	2
Total Fuel: kg	15	15	18	16.5	20	25	17.5	23.5	26.5	29.1	27.8
Charcoal rate: kg/hr.	1.75	2.0	2.0	3.0	5	3.25	3.0	3.5	4	6.6	6.9
Flux: kg	4	3.5	12.0	8.4	11.5	12.43	8.35**	6.4**	8.0	8.5	10.26
Cu ore: kg	nil	nil	nil	nil	nil	nil	1.15 Cu	1.6 Cu	1.4 Cu	1.7 CuO	1.08CuO
Slag recovered: kg	2.0	2.8	11.0	8.0	10.6	11.5	11.6	7.8	8.7	7.1	—
SiO_2/FeO	44/45	40/60	40/60	35/65	34/66						
Fuel/ore	1:1	1:1.22	1:2.4	1:2.4	1:2	1:2.3	1:4	1:2	1:2.7	1:2	1:1.3
Gas leak	none	none	in	out	out	out	out	nil	nil	nil	nil
REMARKS:	Slag too viscous	Glassy slag+Fe	Fayalite slag+ magnetite	Fayalite slag+ magnetite	Temp. not high enough	Smaller tuyere raised temps. across furnace	Fluid slag some red'd Cu globs. nr. bottom	Satisf. but slag not suff. fluid for liqtn.	Charcoal not burnt at base of furnace	Plano-convex slag bottom. 150 g Cu; rest filament	Slag running through leak in front wall around tuyere

*Horizontal tuyere in front wall **All iron ore; no added silica that expected, i.e. 0.37 kg, of which 36% of the copper had formed globules; the residual copper was in filament (or leaf) form. A size analysis is given in Table 11.

Further successful runs were made under the conditions given in Table 4, so that it was felt that Timna ore could be smelted with a reasonable degree of success. In B6, therefore, the charge was Timna ore fluxed with Cumberland hematite in a ratio of T:H=1:1.8, giving by calculation a slag of 35% SiO_2 and 65% FeO, after anorthite has been allowed for.

The furnace was preheated for 2 hours and then charged with charcoal and worked with a blast of 150 l/min. After 1 hour on charcoal, the Timna ore and hematite, crushed to fines, were charged in 200g loads with 100g charcoal, i.e. a fuel/ore ratio of 1:2. After the final charge, the furnace was run on charcoal for a further 3 hours 20 minutes to allow liquation.

After cooling, the slag was removed from the furnace and broken up. The smelt was very successful, and agglomeration of the copper had taken place although the slag still seemed to have cooled before complete liquation of the copper could take place. There was a 95% yield of copper based on the calculated amount of copper charged, and 84% of the copper produced was in the form of globules.

The slag was fayalite-anorthite with no visible wüstite and negligible metallic copper although oxide particles could be seen. The copper globules contained 15% Cu_2O in the grain boundaries (measured by point count) and the filaments contained iron dendrites and a few iron particles.

Two further runs (B7 and 8) were made with the Timna ore under slightly different conditions. Finally, an attempt was made to see whether the Timna ore was self-fluxing, i.e. whether it would yield copper without the addition of iron ore as a flux.

In B9, the tuyere was positioned as in B6 and B8, with a blast of 150 l/min. and a fuel/ore ratio of 1:2. Half-an-hour after the first charge of Timna ore the tuyere started to block and had to be cleared before further additions of ore could be made.

On cooling, the product was removed from the furnace and found to be a sinter product – i.e. very porous and brittle – and it was quite obvious that the conditions were not right to form a slag from the highly siliceous ore. The copper in the ore had been reduced and could just be seen under the microscope. It was therefore concluded that the Timna ore is non-fluxing.

TABLE 6
Slag Analysis Calculated from charges (%)

Smelt	FeO	SiO_2	Al_2O_3	CaO	FeO/ SiO_2
B1	71.54	20.3	2.4	6.74	3.5
2	70.90	20.4	2.4	6.4	3.5
3	70.00	20.4	2.4	7.1	3.5
4	70.77	20.4	2.4	6.5	3.5
5	69.8	20.4	2.4	7.4	3.5
6	55.8	34.3	4.0	6.6	1.6
7	55.5	34.2	4.0	6.3	1.6
8	55.1	34.3	4.0	6.6	1.6
9	14.53	67.76	7.82	9.9	0.2
10	57.4	33.7	3.9	6.7	1.7
11		See Table 7			
13	55.9	33.8	3.9	6.4	1.7
A1	46.51	48.9	1.47	3.12	0.95
2	59.66	35.47	1.91	2.96	1.7
3	59.78	34.3	1.96	3.96	1.75
4	59.66	34.1	1.97	4.27	1.75
5	62.74	31.2	2.01	4.03	2.0
6	63.53	29.9	2.10	4.51	2.1
7	72.27	20.31	2.39	5.03	3.6
8	71.16	20.36	2.40	6.08	3.5
9	63.53	29.9	2.10	4.51	2.1
10	62.42	30.56	2.10	4.91	2.05
11	62.42	30.56	2.10	4.91	2.05

Assuming 100% yield to slag and:—
Timna ore analysis (%) 9.4 FeO, 43.4 SiO_2, 5.0 CaO, 5.0 Al_2O_3
Charcoal (2.5% Ash) = 25% CaO, 1% Al_2O_3, 8% SiO_2.

The next smelt (B10) was done to determine the maximum ore input to the Chalcolithic furnace, using a hematite flux. The conditions were as in B8, and ore was charged as fines 1 hour 10 minutes after the start of the warm-up on charcoal. After 6 kg of ore and flux had been charged, the charcoal seemed to be burning only on the side of the furnace near to the tuyere. A further 0.9 kg was charged and then the furnace was run on charcoal alone for a further two hours and then allowed to cool.

On breaking up the slag, the copper yield was 58% of the total copper expected, and the solid mass removed from the furnace was 4.4 kg. In the ash at the base of the furnace, particles of unsmelted ore were found; presumably they had moved down the side of the furnace away from the tuyere and escaped reduction. The yield, size of product, and the fact that the furnace ran cold after charging 6 kg, suggest that the maximum working charge for the furnace is approximately 5 kg of Timna ore and hematite flux.

In B11, slag and copper from an unsuccessful smelt in the large furnace was used to see if it was possible to separate the copper and slag by further smelting. The furnace was preheated as before and charcoal was charged 1½ hours before the charging of the slag/copper mix commenced. A flow rate of

150 l/min. was directed through the tuyere as in previous smelts and a fuel/ore ratio of 1:2 was used.

The tuyere became blocked very quickly and after cleaning the tuyere-end by poking, became blocked again, and on cooling of the furnace it was found that separation of slag and copper had not occurred.

Metallographic examination of the copper showed a high iron content in both the globules and filaments; the slag was of the fayalite-anorthite Cu_2O type and was slightly magnetic, thus suggesting a small amount of magnetite.

The experiment failed probably because of the introduction of excess CaO and SiO_2 from the charcoal ash and the resultant depletion of the slag in iron. Subsequent chemical analysis of the slag shows high lime and alkali and low iron content (Table 7). Assuming Morton and Wingrove's assumptions.[22,23] the liquidus of the slag would be 1230°C – according to the FeO-SiO_2 – anorthite diagram – which is considerably higher than the previous slags and accounts for the failure of the slag and copper to separate.

As we see from Table 2, manganese ore was used occasionally. This was successfully tried in B12. (See Table 3 for flux composition). The proportions of the charge were 0.35 kg Timna ore, 0.32 kg Mn ore and 0.58 kg hematite. The progress of the smelt is given in Figure 11. This smelt consumed 9.3 kg charcoal and 5 kg ore and flux, giving an approximate fuel/ore ratio of 1:2. The charcoal rate was 1.8 kg/hr.

The weight of the product removed was 4.0 kg, and from this 135 g of copper were recovered, giving 45% copper recovery. The slag ran well through to the bottom of the furnace and with a 5 kg charge there was no chanelling of the blast up the side. There was, in fact, no noticeable change in furnace conditions due to the use of Mn ore and the viscosity of the slag seemed much the same as before.

The slag was of the fayalite-anorthite type with a third phase present which was probably hercynite, but one piece showed the presence of magnetite. The copper was again present as filaments of copper and iron, and as globules. In the case of the latter, the oxygen content was less than 0.4%.

This run was used to obtain details of the % CO_2 in the furnace. Before charging the ore, the CO_2 level was 3%, but after ore charging had commenced the CO_2 level rose to $>12.5\%$ and dropped back to 3% after charging had stopped (Figure 11).

Most of the smelts on this furnace had been conducted with blasts of 150 l/min or less, and it was thought interesting to increase the flow rate to 200 l/min. to see the effect on the products. In B13, therefore, the furnace was preheated for 1½ hours and the charcoal was then charged for a further hour before the first addition of ore with a fuel/ore ratio of 1:2.

TABLE 7
Analysed composition of slag from smelt B11 being a resmelt of slag and copper from A10

	%
SiO_2	35.6
FeO	22.0
Fe_2O_3	2.4
Fe	8.3
Al_2O_3	3.9
CaO	16.2
MgO	1.29
K_2O	2.04
Na_2O	0.13
BaO	1.26
CuO	3.00
MnO	0.24
P_2O_5	0.53
PbO	0.49
TiO_2	0.30
ZnO	0.30
SO_3	1.29
Total	101.27

N.B. This contains twice the usual amount of fuel ash.

The temperatures at the centre of the furnace were over 1200°C and during the smelt the CO_2 percentage rose from 2.2 to 25.0. After the addition of 4 kg of ore the tuyere became blocked so the furnace was run on charcoal for 50 minutes until the tuyere cleared and was then charged with ore again. During this period the CO_2 dropped from 25 to 2.2 and rose again to 21.2 on the addition of more ore.

On cooling, the solid mass was split open and it was found that the copper had liquated well through the slag; the top 3 cm of slag were free from particles of copper, and large pieces of copper from 39 g to 10 g were found at the base of the slag.

The slag was fayalite – magnetite – anorthite, with a large amount of fine precipitated copper probably due to the formation of magnetite. The copper below was of high purity with 0.4% oxide (i.e. oxide in the grain boundaries). There was only a 69% recovery of copper from this slag which shows that the magnetite impairs the liquation of the copper. This smelt was clearly over-oxidised due to too high a rate of blowing for the fuel/ore ratio used.

Experimental work on the large furnace, A.

This furnace was based upon the remains of the furnaces found on Site 2 at Timna.[3-6] As work progressed it became clear that these remains were not sufficient to produce a workable furnace and that a good deal of important information was lacking.

First Series: Smelts A1 to A7

The first series of tests were worked with a single inclined tuyere (at 37° to the horizontal, diameter 3 cm) and a bed depth of 76 cm. The furnace was preheated with a gas burner for 1½ hours before the first additions of charcoal were made. In smelt A1, charcoal additions in a mixed size range up to 5 cm were started at 11.45 with a blast of 200 1/min, and and at 13.15 the furnace was charged with pieces of hematite not exceeding 0.4 cm, and silica sand (composition given in Table 3) with a fuel/ore ratio of 1/1. This charge gave a high SiO_2 slag, with a calculated composition of 52% SiO_2 and 48% FeO (excluding minor constituents such as CaO and Al_2O_3). This was not liquid at the furnace temperatures, as it melts at approximately 1550°C.

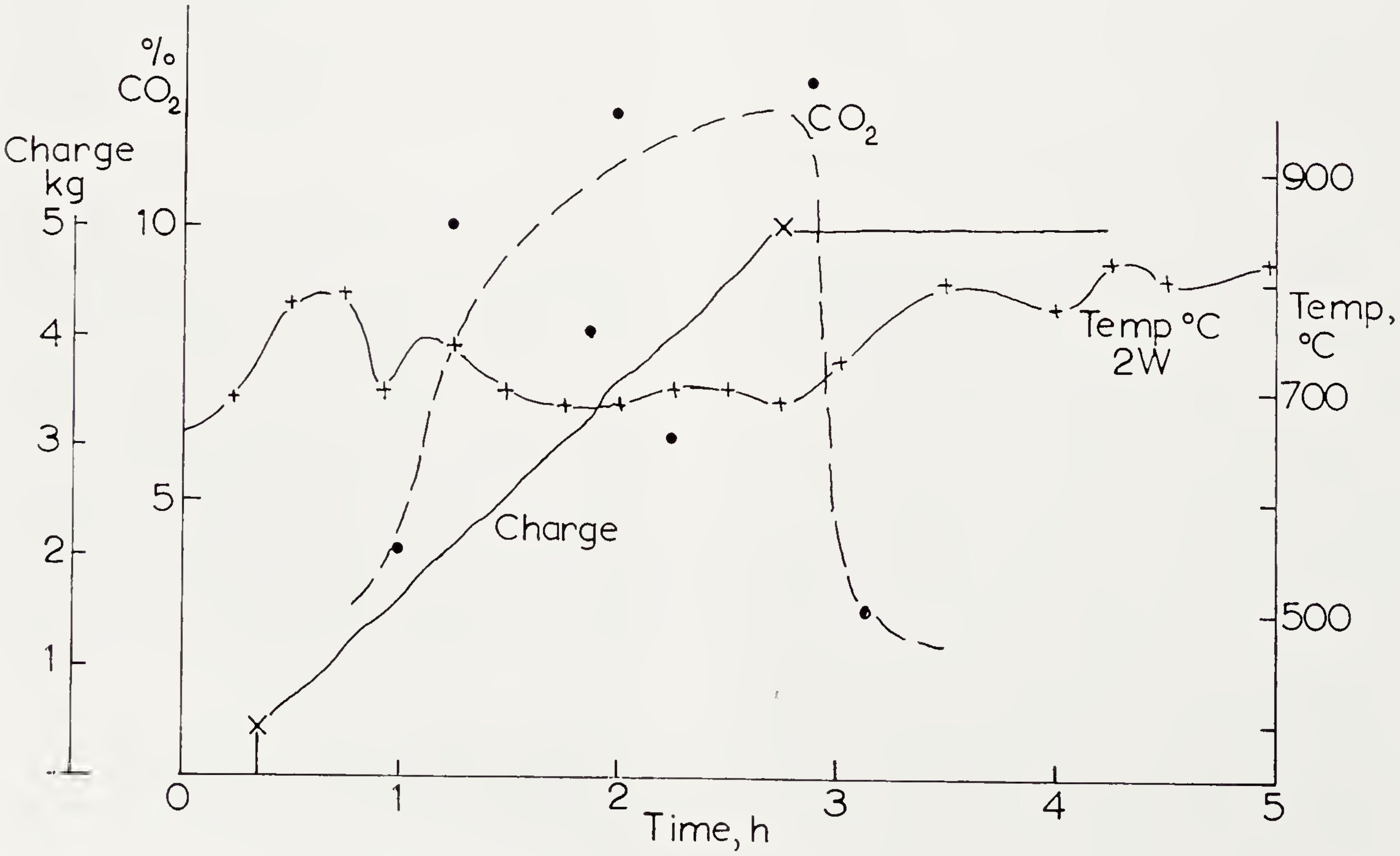
Six more smelts were done with this furnace under slightly different conditions. The results are summarized in Table 5. No copper was charged until Smelt 7, when 1.15 kg of copper turnings were added to the flux charge. As the slag could not be tapped, it had to be removed cold at the end of the smelt with consequent damage to the inner furnace wall. So, a thin, loose, refractory cement lining was freshly inserted for each smelt.

Various tuyere arrangements were tried but it was not possible with a single tuyere to achieve temperatures sufficient to allow metal liquation through the slag, as the slag itself was only molten near the tuyere.

In Smelt 7, the flow rate was increased to 370 1/min through the single inclined tuyere (diameter 1.9 cm); the bed depth was 66 cm, and the charge hematite ore and copper turnings. The hematite was of the right composition to form a slag by itself with a composition which lay close to the fayalite-wüstite eutectic. The furnace was preheated for two hours as before, and charging of the ore started 3½ hours after the beginning of preheat.

The slag appeared to have been fluid at some time during the smelt and had solidified at the base of the furnace near the furnace wall below the tuyere. After removal from the furnace, the solid mass was split in half and, on examination, several small globules of copper were found near the bottom. Copper was also scattered in thin filaments across the section with a layer of copper on the top, thus showing that the attempt to keep the slag fluid throughout the smelt was not successful and the slag was too viscous for complete liquation of the copper.

Figure 11. Progress of Smelt B12. (Temperature measured at position 2W).



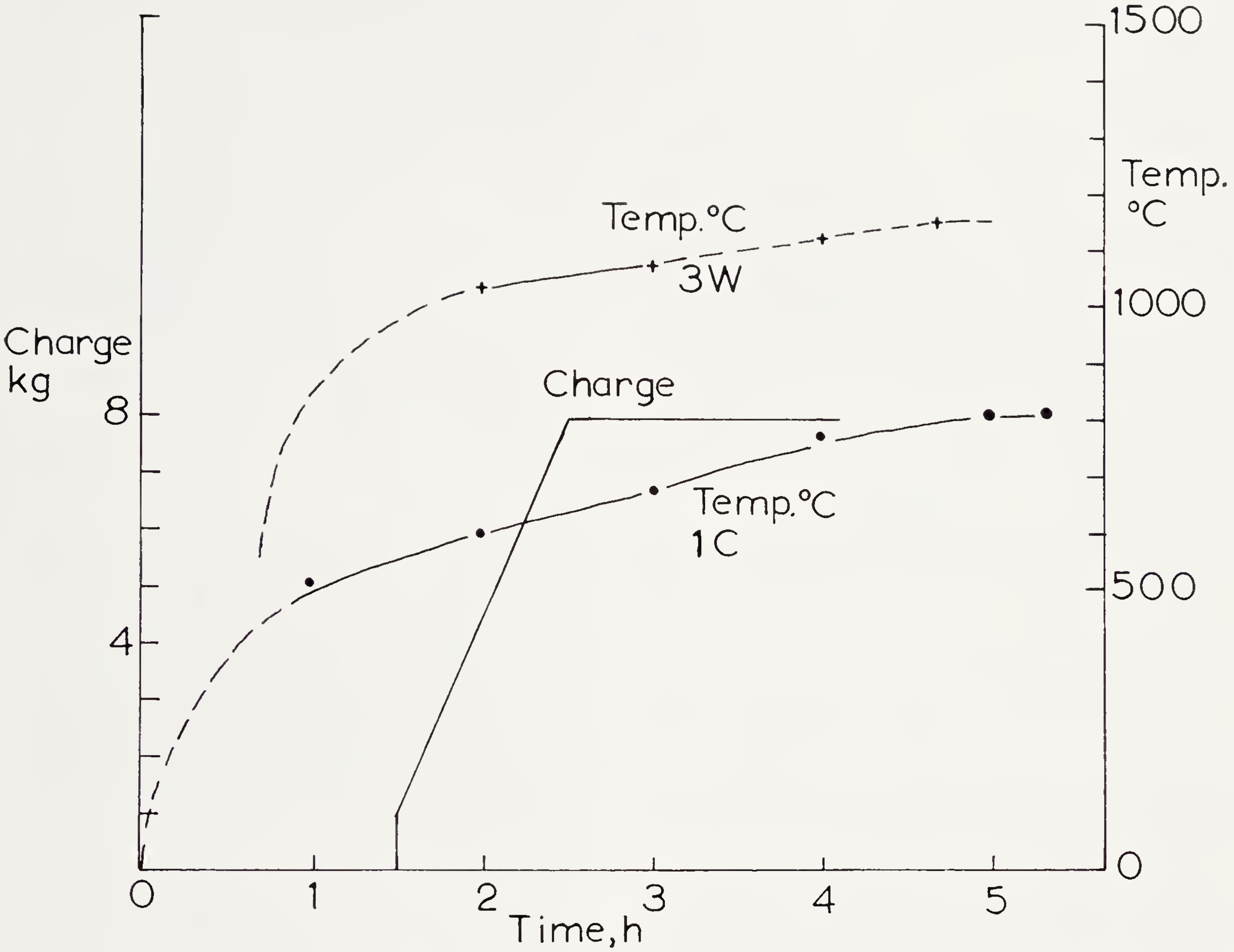


Figure 12. Progress of Smelt A8. (Position 1C is now 1cm inside sand bottom).

Metallographic specimens were taken from four areas of the mass and these revealed:—

- A) A fayalite – wüstite – anorthite slag with no copper present.
- B) Anorthite slag with copper, in conjunction with a fayalite – wüstite slag.
- C) A fayalite – wüstite slag. (A had more wüstite than C.)
- D) Iron with copper in the grain boundaries.

All the slags were magnetic; in the absence of iron this suggests the presence of magnetite with the wüstite.

From the results of the series of experiments A1–A7, it seems that one tuyere was not sufficient to maintain a fluid slag.

Second Campaign on Furnace A

The second campaign on furnace A (A8) was commenced using two tuyeres – the inclined tuyere as used before, and a horizontal tuyere opposite the inclined tuyere.

A blast of 175 l/min was directed along each tuyere and the furnace allowed to heat up, on charcoal only, for 1¼ hours. Temperatures were recorded during this period and are shown in Figure 12. Copper filings and hematite ore were added in 1 kg loads of 200 g copper and 800 g hematite with a fuel/ore ratio of 1:2. After 8 kg of "ore" had been added, the ore addition was discontinued and the furnace was run on charcoal alone for a further 2½ hours before the blast was stopped and the furnace allowed to cool before opening.

On opening, the slag and copper (intermixed) had formed as shown in Figure 13. It can be seen that there are two levels to the slag layer, a higher slag level around the horizontal tuyere. Around the furnace there were two distinct areas of slag, one around each tuyere, with the middle of the furnace containing copper intermingled with slag and charcoal, and this suggests that the temperatures at the centre of the furnace could not sustain a molten slag. Furthermore, it was also found by the homogeneity of the slag around the tuyeres that the slag had been fluid in these areas, but the copper

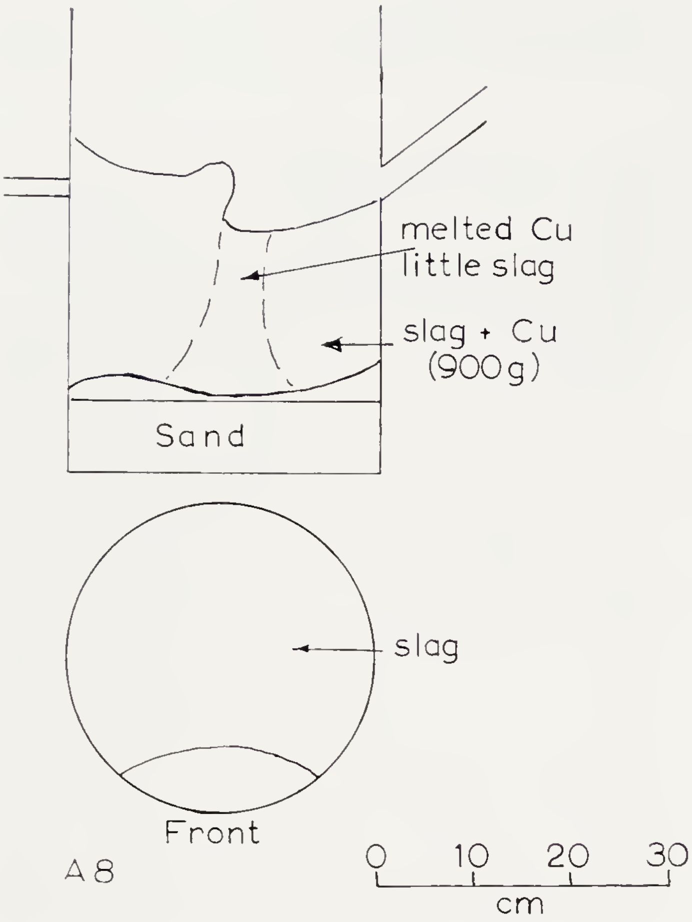


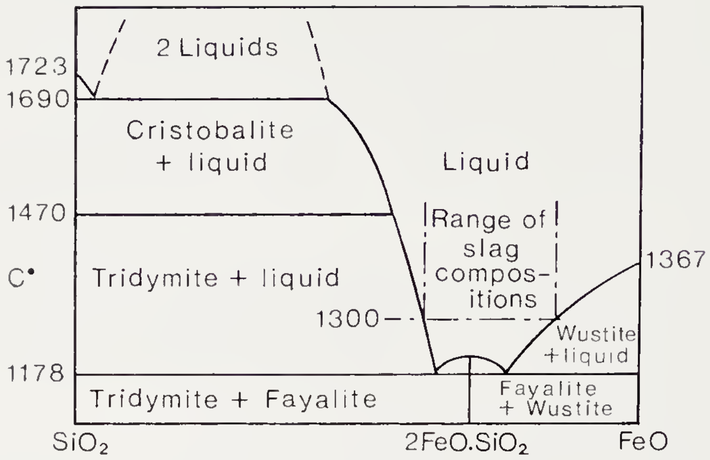
Figure 13. Sketch showing the position of various parts of the product of Smelt A8.

had not separated from the slag as hoped. The slag around the inclined tuyere contained the majority of the copper – a mixture of copper and slag of some 900 g; the total copper around the horizontal tuyere was not ascertained. The top layer (1.5 cm) of the slag appeared free of copper whereas the lower parts of the slag were copper-rich; it was thought that a larger residence time would be needed to produce better separation.

The metallography of the products showed that the copper globules were relatively oxide-free but contained iron dendrites and were highly magnetic. The slag was of the fayalite – anorthite type with a few wüstite dendrites.

Further experiments were made with various tuyere arrangements and slag compositions which are given in Table 5. But it became quite obvious that tapping of slag from the furnace was not possible using a tap-hole remote from the tuyeres, and therefore a horizontal tuyere was placed in the front wall of the furnace aimed at the centre of the furnace; this replaced the horizontal tuyere at the side opposite the inclined tuyere.

During the course of this smelt (A11) the horizontal tuyere became blocked and had to be cleared by 'poking'. This blockage of the horizontal tuyere coincided with the leakage of gas through the front opening of the furnace near the tuyere as the clay sealing the front dried and cracked. (This problem was not encounted during previous smelts and it suggests that the temperatures at the front of the furnace in A11 were higher). Slag began to flow from gaps in the brickwork formed by the distintegration of clay, so the front opening was partially opened and a little slag was tapped. The front opening was then closed and further additions of charcoal were added to allow liquation of the copper through the slag.



The system $FeO-SiO_2$ (Bowen and Schairer: *Amer. J. Sci.*, 1932, 24, 177)

Figure 14. Liquidus temperatures of the $FeO\text{-}SiO_2$ system.

On cooling it was expected to find good liquation because of the fluidity of the slag, but unfortunately this was not so. The slag had formed clear of copper for 2 cm at the base of the furnace but above this level the copper found was predominantly filamentary, although one piece of copper of 100 g was removed from the base of the furnace.

Analysis of the Results of the Smelting Runs

Slags

The Timna ore used during the experiment was highly siliceous (see analysis in Table 3) and therefore to remove this silica the ore was fluxed with hematite ore. A ratio found acceptable was Timna: hematite, 1:2. Workable low melting slags have to have a composition in the region of the compound fayalite, $2FeO.SiO_2$, and the fayalite phase diagram (Figure 14) shows the range of slag compositions which are liquid below 1300°C. Outside this range the liquidus temperature rises rapidly, and for a small composition change there is a large rise or fall in liquidus temperature.

Morton and Wingrove[23] suggest that the lime, alumina, and silica form anorthite, and that for overall consideration of fayalite slags the ternary phase diagram FeO,SiO_2 and anorthite may be considered (Figure 15).

The formula for anorthite ($CaO.Al_2O_3.2SiO_2$) shows that the oxides required for its formation are

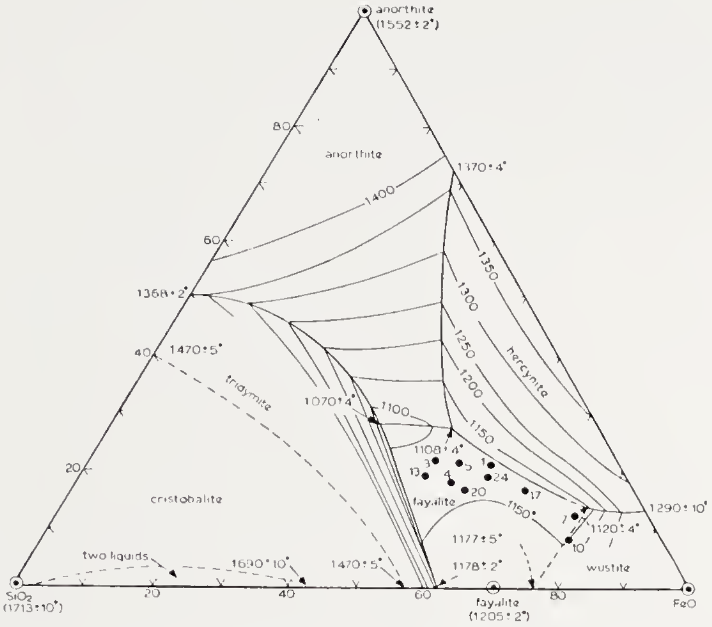


Figure 15. Ternary phase diagram of the FeO-SiO_2-anorthite system. (After Morton and Wingrove).

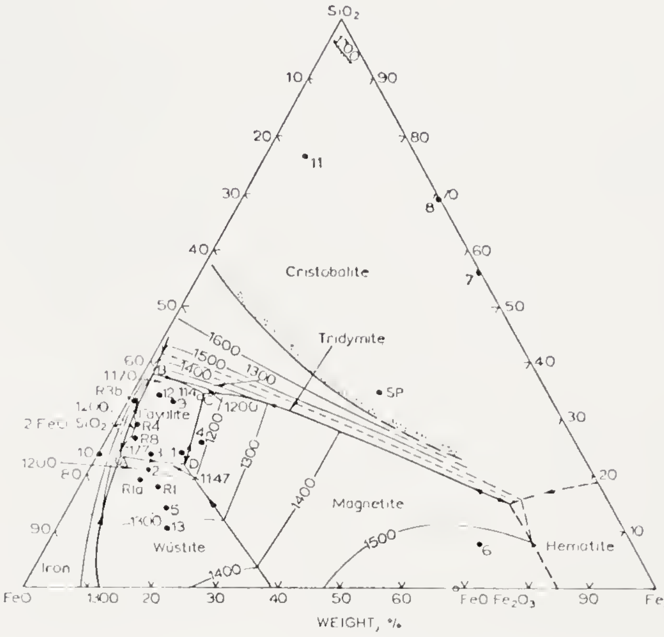


Figure 16. Ternary phase diagram of the system FeO-Fe_2O_3-SiO_2. (After Morton and Wingrove, Constitution of Roman bloomery slags.

CaO Al_2O_3 and SiO_2. Since there is always an excess of SiO_2 in the slag over that required to form anorthite, the amount of anorthite which can be formed will be governed by the available CaO and Al_2O_3. It was considered that the anorthite would probably dissolve MgO and excess CaO or Al_2O_3.

For consideration of the analytical results of the slag, the following assumptions are usually made:

a) Moisture and loss on ignition must not be considered in the calculation, as they would have developed since the slag cooled.
b) The amount of Fe_2O_3 in the tap-slag is insignificant and any Fe_2O_3 in the slag is derived from oxidation after tapping.
c) The maximum possible amount of anorthite is formed from the CaO and Al_2O_3.
d) The FeO, SiO_2 and anorthite contents are assumed to equal 100%.

Slag analysis was carried out on the majority of B furnace slags, and these compare favourably with the calculated analysis (cf. Tables 6 and 8). Examination of the results may be carried out in terms of—

1) FeO–SiO_2
2) FeO–Fe_2O_3–SiO_2
3) FeO–SiO_2–anorthite (Al_2O_3CaO.2SiO_2).

FeO–SiO_2

Examination of the binary system FeO–SiO_2 (Figure 14) shows two eutectics at 1178°, at 62.5% and 77.5% FeO respectively – i.e. at a FeO/SiO_2 ratio of 1.66 and 3.45. The range of slag compositions liquid below 1300°C extends from 60% FeO to 85% FeO, i.e. with FeO/SiO_2 ratios of 1.5 and 5.65 respectively.

The slags were analysed for:—

1) total iron, Fe^{2+}, Fe^{3+}
2) copper
3) manganese.

The residue would be mostly alkali and silica. For examination of the slag on the basis of the FeO–SiO_2 system, the analysed slag was assumed to contain negligible alkalis, but the calculated slag analysis took into effect CaO and Al_2O_3 from both the ores and the charcoal (Table 6).

The analysed slags (Table 9) show that according to this system (including MnO as FeO) only three slags (B3, 5 and 12) have an (MnO+FeO)/SiO_2 ratio which allows them to be liquid below 1300°. As all of the slags in the B furnace were observed to be liquid it must be assumed that the alkali present is having a significant effect on the melting point.

As the chemical analysis of the calculated and "as analysed" FeO in the slags are mostly so near (cf Tables 6 and 9), it is reasonable to take the calculated analysis for the consideration of the results (Table 6).

All of the slags except A1 and B9 have FeO/SiO_2 ratios within the range 1.5–5.65 and should therefore be liquid below 1300°C. The slags from the B furnace all lie within the range 1.66–3.45, i.e. have an FeO/SiO_2 ratio which places their analysis between the two eutectics. The maximum liquidus temperature between the two eutectics is that of fayalite at 1205°±2°C, so the maximum liquidus temperature of any slag from the B furnace, save B9, was 1205°C. As the temperature near the base of the B furnace was greater than 1200°C, all slags should have been liquid and this was the case.

Furnace A slags are slightly different. All slags except A1, A7, and A8, lay between the eutectics, but A7 and A8 lay slightly to the FeO side of the FeO/SiO$_2$=3.45 eutectic, therefore one may conclude that all of the slags in the A furnace were liquid, and from the slag appearance this was thought to be the case at the time. Only slag A11 was tapped from the furnace, this was probably due to the tuyere positioning, but the analysis of the slag differs from the calculated analysis due to liquation or absorbtion of lining.

FeO–Fe$_2$O$_3$–SiO$_2$

The analysed slags (Table 8) were considered on the basis of their Fe$_2$O$_3$ contents using the phase diagram shown in Figure 16. The position of the slags near the cristobalite region suggests that they should not have been liquid. As this was not the case, it is clear that the Fe$_2$O$_3$ was formed during cooling of the slag after smelting had been completed, as has been suggested by Morton and Wingrove.[22,23]

FeO–SiO$_2$–Anorthite

As can be seen from the summaries of the smelts (Tables 4 and 5), most of the slags had a fayalite-wüstite or a fayalite – wüstite – anorthite (glass) structure. Some had a little magnetite also. These phase compositions can be reconciled with the analyses given in Table 9 and, with the exception of the copper content, are very similar to iron slags shown by Morton and Wingrove.[22,23] On the whole, the phase composition fits the FeO-SiO$_2$-anorthite diagram[24] shown in Figure 15.

Except for A1 and B9, the slags concentrate around the low temperature area in the fayalite region. Slags made with Timna ore and flux fall into the same region as slags made from rich iron ores (see Morton and Wingrove[22]), and the slags made with hematite alone fall in the same region as Roman iron slags.

Therefore, from the phase diagram, it can be seen that all the slags used in the experiments should have been liquid and of similar analysis to those recovered from the excavations (Table 2). All the slags in this range of compositions should produce a fayalite – wüstite – anorthite structure.

TABLE 8

Estimation of iron oxides from analysed iron (%)

	Analysed			Calculated	
Smelt	Total Fe	Fe^{2+}	Fe^{3+}	FeO (combined)	Fe$_3$O$_4$
B2	44.6	31.9	12.7	32.6	26.3
3	45.8	42.3	3.5	51.8	7.2
5	54.1	47.6	6.5	56.8	13.4
6	28.7	24.1	4.6	27.9	9.5
6B	40.9	38.4	2.5	46.7	5.2
7	43.1	37.6	5.5	42.9	11.4
9	20.6	6.4	14.2	nil	29.3
10	41.4	38.4	3.0	47.1	6.2
12	28.0	24.2	3.8	28.6	7.8
13	41.5	36.2	5.3	41.4	11.0
A11	35.5	33.5	2.0	41.0	4.0

Assume Fe$_3$O$_4$ contains all Fe$_2$O$_3$ and some FeO (=1.45 × Fe$_2$O$_3$). $Fe^{2+} \times 1.28 =$ Total FeO
Combined FeO = Total FeO – (0.45 Fe$_2$O$_3$)

Effect of Increase in Blast Volume

At low air flow rates of 100 l/min on the smaller furnace, the furnace temperatures appeared to be on the low side, and the copper recovery was low (around 40%). As the flow rate increased, the copper recovery increased accordingly and the slag appeared to contain less copper (as shown in Table 9). A satisfactory copper recovery was reached with an air flow rate of 150 l/min., i.e., a copper loss to the slag of 1.1–2.5%, with the exception of B7 which was smelted using a fuel: ore ratio of 1:3 which lowered the temperatures in the furnace. On increasing the flow rate to 200 l/min., the temperature in the furnace rose, but the conditions were more oxidising than before because the fuel:ore ratio was unaltered. Although the higher temperature should have produced a less viscous slag, and thus allowed better settling of the copper, the magnetite (Fe$_3$O$_4$) in the slag increased.

Magnetite in slag increases copper losses to the slag by:—

i) promoting the formation of copper ferrites (e.g. CuO.FeO)
ii) increasing the viscosity of the slag.
iii) hindering separation of slag and metal.

Ruddle[25] has found a strong correlation between the oxygen pressure and the copper oxide content of slag – i.e. a copper loss to the slag at high oxygen pressures corresponds to the separation of magnetite.

Therefore the optimum blowing rate for the small furnace is 150 l/min.

On the larger furnace the blowing rate was increased from 200 l/min to a final flow rate of 420

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[22] G. R. Morton and J. Wingrove. Constitution of Bloomery Slags: Part I, Roman. *J.I.S.I.* 1969, *207*, 1557-1564.

[23] G. R. Morton and J. Wingrove. Constitution of Bloomery Slags: Part II, Medieval. *J.I.S.I.* 1972, *210*, 478-488.

[24] E. M. Levin, C. R. Robbins and H. F. McMurdie. Phase Diagrams for Ceramists. 1964, *Columbus*, Amer.-Ceram. Soc.

[25] R. W. Ruddle and A. P. Bates. *Trans. Inst. Mining and Met.* 1966, *75*, C1-C12.

TABLE 9
Probable analyses of slag as tapped (%)

Smelt	FeO	MnO	SiO_2	Cu	$\frac{MnO+FeO}{SiO_2}$
B2	57.0	—	39.65	3.35	1.43
3	58.5	—	38.74	2.76	1.51
5	69.5	—	28.06	2.44	2.47
6	52.2	0.17	46.48	1.16	1.12
7	55.5	0.09	41.5	3.20	1.33
9	26.4	0.07	52.04	21.50	0.51
10	53.0	0.15	45.19	1.69	1.17
12	35.6	21.0	(23.00)*	1.87	2.02
13	53.0	0.22	44.07	2.76	1.2
A11	46.4	0.26	52.89	0.51	0.8

* Estimated

l/min with only a little success. Even at the high flow rates the slag could not be kept liquid across the base of the furnace. The experiments were, however, showing signs of improvement as the experimental period came to an end. A movement of the tuyeres to a position over the tap-hole would be considered advantageous and would almost certainly allow most of the slag to be tapped from the furnace. This was shown in A11 where a tuyere was positioned at the front of the furnace and slag was tapped.

The blowing rates for the copper furnaces, as compared to the iron smelting furnaces, show that more air is required for copper smelting per unit cross section of furnace than for iron.[26] (Table 10). This is largely because iron smelting is a step-by-step accretion process where the iron is built up into a bloom and the slag runs away. This does not require so much heat at the bottom of the furnace since the accreted iron can cool down as soon as it is formed. In copper smelting, the metal has to liquate through the molten slag which has to be kept at a high temperature (over 1200°C) throughout the process. This requires considerable heat which is provided by the consumption of additional air and charcoal.

Effect of Fuel: Ore Ratio

It can be said that the small furnace B ran well on a fuel:ore ratio of 1:2, although a smelt (B7) was tried with a fuel:ore ratio of 1:3. The reduction in fuel caused the tuyere to become blocked during the smelt because of the subsequent drop in temperature, and it also resulted in poor liquation of the copper through the slag.

The use of a fuel:ore ratio of 1:2 on Furnace B suggests that this ratio should prove satisfactory in the larger furnace because the higher stack would allow the material to be held in the stack for a longer period and thus prevent any cold material falling into the tuyere zone. Unfortunately, although temperatures around the bottom seemed sufficient to support a fluid slag, liquation of the copper did not take place. Raising the fuel:ore ratio to 1:1 was considered, but the first experiment on Furnace A had shown that considerable iron was likely to be produced under the more reducing conditions.

Effect of Ore Size

All ore charged to the furnace was fines, i.e. crushed to a maximum size of 4 mm in a jaw crusher. This was mainly to enable a uniform

TABLE 10
Conditions for iron and copper smelting

	Iron smelting. Forced draught shaft furnace	Copper smelting Furnace A	B
Furnace dia. cm.	30.5	30.5	23.0
Furnace cross-sectional area cm^2	735	735	420
Air flow; l/min	300	~ 500	150
$l/min/cm^2$	0.41	0.68	0.36
Charcoal burning rate; kg/h.	3.5	6.7	1.6

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[26] R. F. Tylecote, J. N. Austin and A. E. Wraith. *J. Iron and Steel Inst.* 1971, *209*, 342-363.

sizing of the Timna ore which, being very siliceous, tended to break up very easily. The use of a high fines material in the furnace could have had an effect on furnace performance. On occasions the furnace tended to 'hang' and then 'slip', but this happened only very infrequently. In experiments on iron it was found desirable for the ore to be in a size-range up to 12 mm to obtain a larger residence time.

Charcoal Consumption

From Table 10 it can be seen that the charcoal consumption rate in the large furnace is greater than that in a similar furnace producing iron. This is due to the large slag volume that has to be maintained in the case of copper. No doubt, as practice became more sophisticated, and slag could be tapped at regular intervals from the furnace, the charcoal rate was reduced.

Furnace B showed a smaller charcoal rate than the other furnace, but it is apparent that the charcoal rate is in proportion to the air flow in 1/min.

TABLE 11
Details of Copper Recovered

Smelt No.	Wt of Cu Recovered g.	% Cu Recovered	% Globules in Sample	Mean wt of Globules g.	Standard Deviation
B1	104	42.0			
2	137	49.1			
3	370	94.5	32.8	2.27	5.27
4	320	80.0	15.3	0.96	1.91
5	290	80.5	61.0	2.80	8.73
6	235	85.0	84.4	2.75	9.09
7	—	—	—		
8	—	—	—		
9	none	—	—		
10	290	58.1	75.0	1.35	2.45
11	—	—	—		
12	135	45.0	54.5	0.68	1.13
13	273	69.0	78.0		

Copper

The copper produced during the smelts varied from thin filaments up to some massive pieces of 34 g in weight. The most easily recoverable copper was in the form of spheres. To gain some comparison between several smelts the copper was sorted and sized, and a mean and standard deviation performed on the results. The figures in Table 11 show that the copper from smelts B5, B6, appear to have the largest mean size, and this corresponds to the calculated slag analysis for B5 and B6 showing them to be low melting point slags near the two eutectics according to the FeO–SiO_2 diagram.

It appears therefore that up to 85% of copper smelted can be recovered easily from the slag as globules and can then be subsequently remelted and cast.

Chemical analysis of the copper is shown in Table 12. The main impurity in the globules is iron, and this can be seen easily in dendritic form under the microscope with up to 2.4% iron in B10. The iron content of the filaments is much higher reaching 29% in the case of B13. An examination of the distribution of iron in copper follows later.

The trace elements in the copper are of great interest to an archaeologist. The consistency of the arsenic content of the metal shows that variations in fluxes and slight variations in smelting conditions produce no change in the arsenic content of the metal, and that the arsenic content of the metal reflects the arsenic content of the ore, i.e. $>50\%$ of the arsenic is recoverable in the metal.

The recovery of silver would be 100% and the recovery of nickel nearly that. Manganese is probably picked up from the flux, and the high manganese in the metal of B12 reflects the manganese content of the flux and slag. The manganese content of the metal seems to be related to the manganese in the slag: the higher the slag manganese, the higher the metal manganese.

As the copper filaments produced contained up to 29% solid Fe they would be extremely viscous and this is probably why they did not agglomerate. The Cu-Fe phase diagram (Figure 17) shows that with a temperature in the furnace of 1300°C, the metal should contain solid γ iron (austenite) and liquid copper. As the metal cools, the γ phase will precipitate out of the liquid until the peritectic at 1084°C is reached, where the phase γ iron$+\varepsilon$ copper will form, giving solid ε copper particles in the iron. At lower temperatures, the austentite (γ) will transform to ferrite, and the metal will finish up as ferrite and copper.

The difference in the iron content between the globules and the filaments permits some conclusions regarding the partitioning of the trace elements (Tables 12 and 13). Nickel and zinc are about evenly distributed between the iron and the copper. Cobalt and manganese, as would be expected, are iron-related, while silver is copper-related. Arsenic is also evenly divided.

Metallography of the copper globules shows cuprous oxide and iron dendrites. The oxygen concentration in the metal can be seen from the oxide formation. According to the Cu-Cu_2O phase diagram, the oxide only forms in the grain boundaries when less than 0.4%, but precipitates as a primary phase within the grains when greater than 0.4%.

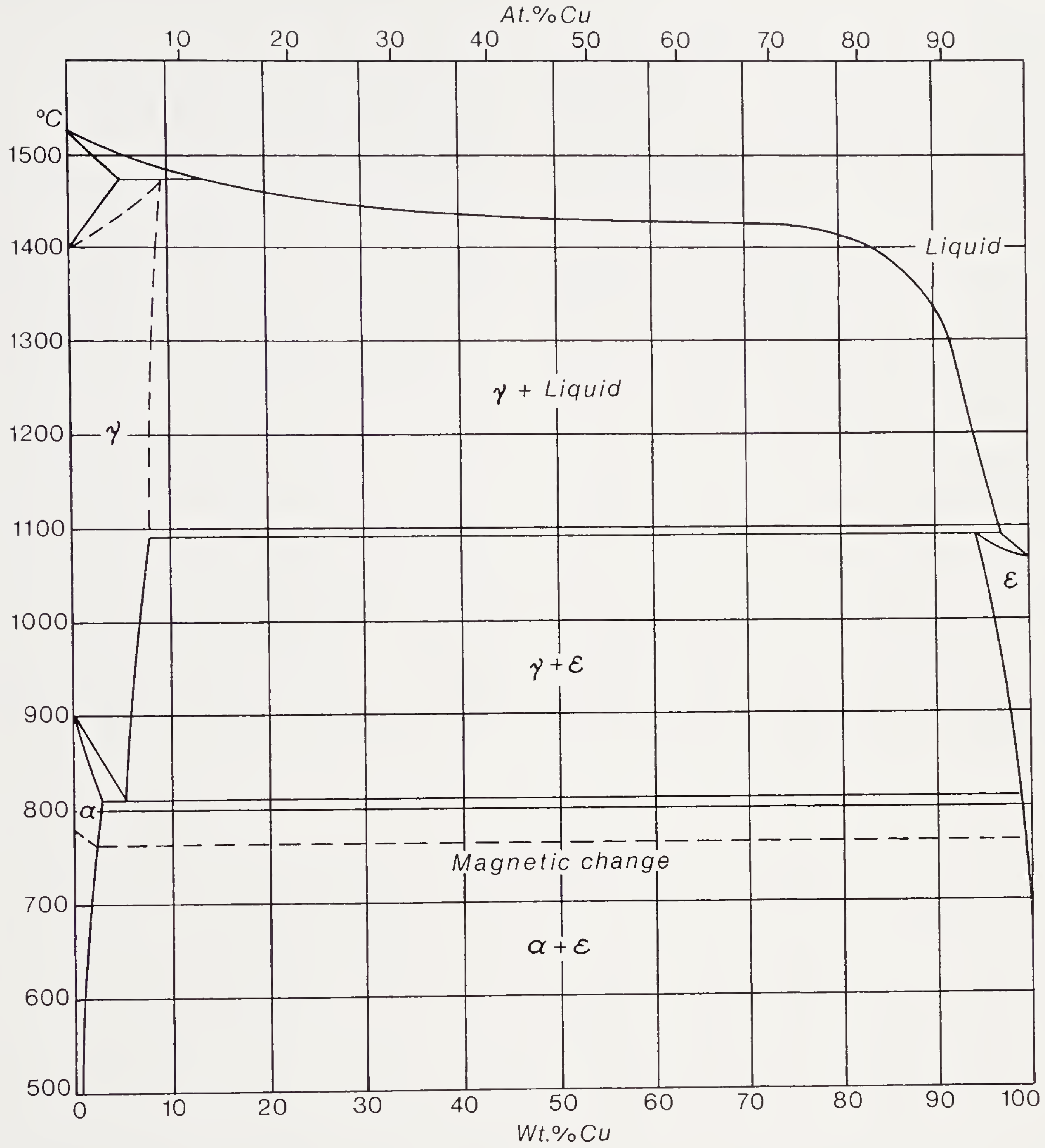

Figure 17. Binary phase diagram of the Cu-Fe system. (After Smithells Metals Reference Book, Vol. 2, Butterworth's, London).

Experiments on the Removal of Iron from Copper by Crucible Remelting

Iron occurs in the smelting of copper either in the slag in the smelting furnace, or as a major impurity in the metal which may be eliminated from the copper by crucible remelting (and recovered as iron). It is possible that some of the earlier iron finds arise from this process.

Iron and copper are on the borders of immiscibility. According to the iron-copper phase diagram (Figure 17), about 3% of iron is soluble at 1100° in liquid copper; about 8% of copper is soluble at 1084°C in solid iron, and the mutual solubility of copper and iron is almost negligible at room temperature. In spite of these restricted solubilities, iron is readily diffusible in liquid copper, as is well-known to foundry technologists who have to protect iron stirring-rods for copper-base alloys by a refractory envelope. Experiments with iron and copper, involving melting copper in a steel tube, show that after slow cooling, dendrites of iron-rich solid solution form in the copper. Table 14 shows the effect of iron on the hardness of copper.

In molten copper, at 1150°C, iron may diffuse from the slag and precipitate out on nuclei within the melt; this precipitate grows dendritically, reducing the concentration of iron in the liquid copper surrounding it. This produces a concentration gradient for further diffusion of iron into the liquid copper. Thus, iron transfer seems virtually unlimited, the iron dendrites growing in the copper until the copper is so saturated with them that copper ceases to be a separate phase and is merely present in dilute solution in the iron. In a quiescent melt the differences in density lead to the iron dendrites floating to the surface and forming a layer, and whether they will remain as solid iron depends on the atmospheric conditions above the melt. If these are reducing the iron will become carburized and revert to the liquid phase (Fe with 4.4% of carbon melts at 1150°C). If oxidizing, the iron will form FeO or higher oxides, and in refractory crucible melting this may form a slag with material from the crucible.

Smelting experiments have shown how easy it is to pick up iron from the fayalite slags. It is clear from analysis that much of the copper produced in the Chalcolithic period was free of iron, so experiments were made to see if the iron could be removed by crucible remelting under various conditions.

Results of Crucible Remelting Experiments

C1: copper from smelt B3, produced from CuO and hematite flux, was melted in a graphite crucible in a high frequency furnace which meant that it was inductively stirred. In spite of this, the iron separated out on the surface as molten cast-iron due to carburization from the crucible. The hardness of the iron was 300 HV. It was a white cast-iron with pearlite and cementite – the latter being in acicular form. The copper still contained some iron in dendritic form and some cuprous oxide; the hardness was 86 HV 5.

C2: this was made with copper from smelt B4 which was made in the same way as B3 (above). It was melted in a fireclay crucible in the same furnace. This melt produced a fayalite-wüstite slag by reaction between the iron and the crucible under oxidizing conditions. Some iron (HV=118-218) and FeO was left in the copper which had a minimum hardness of 48 HV 5 (range 99-48).

C3: metal from smelt B5 (made with CuO and hematite) was melted in a fireclay crucible in a gas-fired furnace to avoid inductive stirring. There were three layers produced in this melt; the top

TABLE 12a

Analysis of Copper globules and filaments from Furnace B

		Fe	Co	Ni	Mn	Ag	Zn	As	S
B1									
2	Globs.			(<50)		(100)		(1500)	
3	Globs.			(<50)		(130)		(<300)	
7	Globs.	2.1	(62)	0.02	(10)	(500)	0.04	0.31	1.65
7	Fils.	23.9	(130)	0.017	(117)	(194)	0.013	0.36	—
10	Globs.	0.4	(17)	0.028	(5)	(245)	0.012	0.29	1.0
10	Fils.	24.0	(171)	0.022	(211)	(13)	0.011	0.21	
12	Globs.	0.3	(12)	0.040	(876)	(278)	0.009	0.40	2.05
12	Fils.	26.6	(248)	0.036	1.52	(179)	0.03	0.23	
13	Globs.	1.2	(33)	0.024	(34)	(237)	0.023	0.29	0.55
13	Fils.	28.9	(213)	0.025	(288)	(109)	0.030		

( ) ppm. Rest %.

was an FeO-rich fayalite slag, the next Fe-Cu alloy (HV 109-197) and the bottom purer Cu with a hardness of 84 HV 5.

C4: as above, but the charge was 150 g copper powder and 30 g of iron powder giving 16.7% Fe. The iron was segregated to the top. Hardness (HV 5) of Fe-containing regions=94, 100, 146, 139; Cu and oxide=69, 86.

C5: as above, but some sand was added to slag the iron. Some iron was removed to the slag, but some was left in the copper. (Fe: HV=229). The hardness of the copper was 84 HV 5.

C6: as above, but intentionally oxidized with an air blast on top. This reduced the iron content in the centre, but the bottom got cold and trapped the iron. The hardness of the copper was 74-88 HV 5.

C7: used metal from smelt B13 (*c*.30% Fe) which was made with Timna ore and hematite. An air blast was applied to the melt in a fireclay crucible in a gas injector furnace. The iron segregated to the top and there was a hole down the centre due to the force of the air blast. The hardness of the copper was 81-87, and that of the residual iron near the surfaces of the hole was 152 HV.

C8: 50 g of cathode (lump) copper was melted with 57 g of iron powder in a plumbago (graphitic clay) crucible in a gas-fired injector furnace. The crucible had a lid and the melt was covered with charcoal.

TABLE 12b
Additional elements in copper from Smelts B12 and B13

	ppm. B12	ppm. B13
Uranium	nd	nd
Thorium	nd	nd
Bismuth	2	2
Thallium	nd	nd
Mercury	nd	nd
Gold	nd	nd
Platinium	< 0.3	< 0.3
Iridium	< 0.2	< 0.2
Osmium	< 0.3	< 0.3
Rhenium	< 0.3	< 0.3
Tungsten	< 0.6	< 0.6
Tantalum	< 6	< 6
Hafnium	nd	nd
Barium	1	0.3
Caesium	nd	nd
Iodine	nd	nd
Tellurium	< 5	< 5
Antimony	200	200
Tin	1	1
Indium	< 0.2	< 0.2
Cadmium	< 0.5	< 0.5
Palladium	nd	nd
Rhodium	nd	nd
Ruthenium	nd	0.4
Molybdenum	1	0.4
Niobium	nd	nd
Zirconium	< 0.1	< 0.1
Yttrium	—	—
Strontium	< 0.2	< 0.2
Rubidium	nd	nd
Germanium	15	1
Selenium	30	40
Zinc	50	30
Cobalt	1	1
Chromium	0.3	< 0.1
Vanadium	< 0.1	< 0.1
Titanium	0.2	0.1
Phosphorus	0.2	0.1
Sodium	4	0.6
Fluorine	nd	nd
Boron	0.1	0.1

nd = not detected — = no estimate
< = less than

TABLE 13
Recovery of Arsenic in Copper Globules Based upon 500 ppm in the ore.

Smelt	Weight g. In charge	Weight g. In copper	% Recovery
B 10	1.77	0.84	48
B 12	0.96	0.54	56
B 13	1.40	0.79	57

TABLE 14
Effect of Iron on Hardness of Copper after slow cooling in Air

% Fe	Hardness HV
0	45
1.12	60
3.20	76
4.17	80
4.46	79

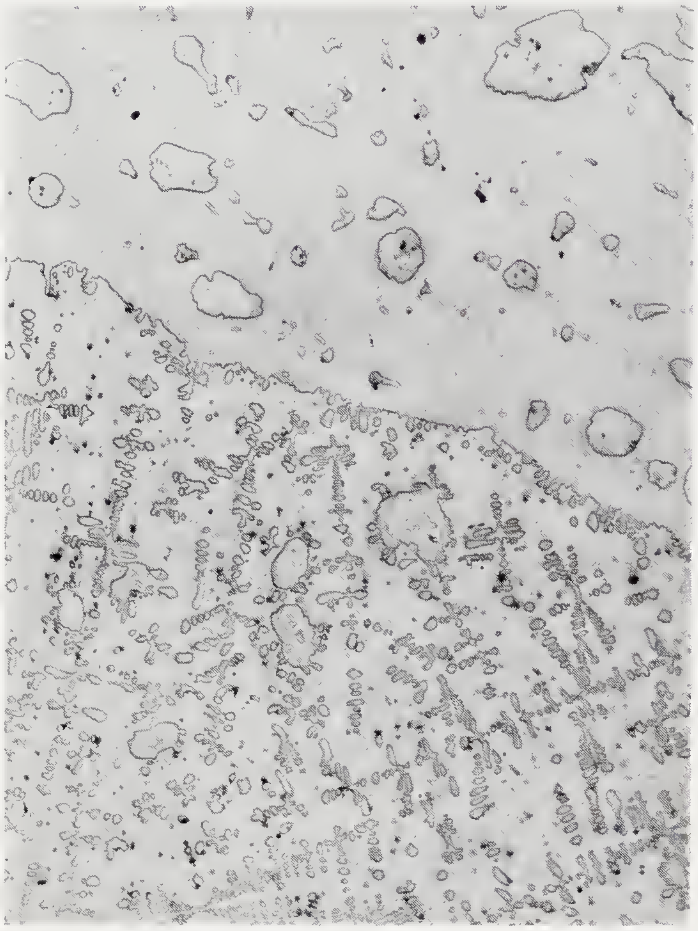

Figure 18. Photo-micrograph of copper-iron interface of the result of C8. (Iron with some copper, top; copper with iron dendrites, bottom). Scale: ×50.

During the 2 hours melting period, the melt separated into two layers; the upper was of steel which, when quenched, was found to have a hardness of 362-396 HV (single phase – possibly bainite); the lower was of copper containing iron dendrites and had a hardness of 100-105 HV 5. Figure 18 shows the area of the interface. On top is the steel with some more or less circular copper inclusions in it. Below is the copper with dendrites of iron, but also some masses of iron floating upwards. Some of the dendrites probably formed during solidification when the solubility of iron decreases from 8 to less than 1%.

The iron was separated and annealed to give a hardness of 252 HV 5 and seemed to be 100% pearlite (0.8% C). This steel, with its copper inclusions, was forged at 900°C to a thin disc weighing 43 g. The structure after forging is shown in Figure 19. The hardness at this stage was 206 HV 5. It is clear that iron or steel can be recovered from copper in a malleable state.

These experiments have not resulted in very pure copper since the average minimum hardness of the copper was about 80 HV, and the hardness of high purity, as-cast, copper is nearer 40 HV. To some extent this is due to the oxygen content which could, of course, be removed by poling, but some at least is due to residual iron which could certainly be removed by longer treatment.

The cast iron from the first experiment (C1) could be easily removed by cutting it off and this possibility could be the explanation of the find of white cast iron at Geoy Tepe.[27] It would be of little use to early man as it would not be forgeable.

But we can also separate the less carburized and more ductile iron produced in other experiments. Experiment C8 shows that it is possible to obtain an iron product which can be forged. This has to be done below the melting point of copper (1084°C) to make sure that any residual copper films do not cause fragmentation of the iron. The residual copper might explain some of the early occurrences of iron-copper alloys, the existence of which has been explained by assuming composite artifacts.

Figure 19. Iron with some copper recovered from the top of C8. This iron contains some copper and carbon. Scale: ×50.

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[27] T. B. Brown. *Man*, 1950, *50*, (4), 7-9.

Conclusions

1) Ores crushed to fines (<4 mm) produced satisfactory results on both furnaces, and were heavy enough to resist the up-draught in the furnace. The fines seemed to have little, if any, effect on the permeability of the bed and were more easily reduced than the larger sizes of ore.

2) Cumbrian hematite was satisfactorily used as a flux with the Timna ore and gave a good fayalite slag. Manganese ore was as good, but more work on this flux is necessary for any conclusions to be reached. The use of Mn ore increased the Mn concentration in the copper (from 10 to 867 ppm) and therefore metal smelted with manganese fluxes should be readily identifiable.

3) Charcoal of an 'as received' size range was used during the smelts and screening of the charcoal (for <6 mm) was undertaken only when a high fines content was noticed in the charcoal. Previous work[28] has shown that the size of the charcoal charged to the furnace has little effect on these small furnaces provided the maximum is less than 50 mm.

4) Copper requires more air/unit furnace cross section than iron. The smaller furnace, B, provided most of the results.

5) The copper produced contained iron as the main impurity. This iron can be reduced by proper furnace control, i.e. by short time in contact with slag, or it can be removed from the copper by subsequent remelting and refining.

6) Plano-convex ingots have not been produced at all during the work, the products of the furnace being in globular form. This leads to the question of whether the plano-convex ingot can be formed within the smaller smelting furnace. This aspect may be connected with the furnace temperature gradient and further work will be done on this aspect.

7) The arsenic content of the copper reflects the arsenic content of the ore and may not be due to arsenical additions to the molten copper.

8) In the smaller furnace, 0.3 kg of copper may be recovered in two hours, i.e. $\frac{1}{2}$ hour smelting time and $1\frac{1}{2}$ hours settling time, with a maximum working charge to the furnace of 5 kg of ore and fluxes.

Work on the larger furnace failed to produce satisfactory working conditions.

9) More work is needed before the large furnace can produce satisfactory results. The positions of the tuyeres should be moved to the front of the furnace over the furnace opening and a suitable tap-hole constructed.

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[28] E. J. Wynne and R. F. Tylecote. *J.I.S.I.* 1958, *190*, 339-348.

APPENDIX 3

Estimation of Total and Ferrous Iron in Smelting Slags

by J. R. Trayler

1. **Application**

This method has been applied to copper smelting slags. Where metallics occur in the slag a preliminary separation can be carried out. (See Note 2)

2. **Principle**

The sample is dissolved in an acid mixture containing sodium fluoride, in a vessel from which the atmosphere is excluded by a bunsen valve. Ferrous iron is estimated by direct titration with potassium dichromate, and total iron after reduction with stannous chloride.

3. **Reagents**

3.1 Barium diphenylamine sulphonate indicator 0.3 per cent.

3.2 Hydrochloric acid Sp. gr. 1.16-1.18.

3.3 Hydrochloric acid, 1 + 1.

3.4 Mercuric chloride solution, saturated.

3.5 Orthophosphoric acid Sp. gr. 1.75.

3.6 Stannous chloride solution, 10 per cent. Dissolve 10 g of stannous chloride dihydrate in 50 ml of hydrochloric acid, by warming. Dilute to 100 ml with water.

3.7 Sodium carbonate (anhydrous).

3.8 Sodium flouride.

Standard Solution

3.9 Potassium dichromate 1 ml = 0.005000 g Fe (0.08953N). Grind about 6 g of potassium dichromate and dry in an oven at 140°C for one hour. Cool in a desiccator. Weigh out 4.3898 g. dissolve in water. Make up to 1 litre in a volumetric flask and mix well.

3.10 Potassium dichromate 1 ml = 0.001000 g Fe. Pipette 100 ml of potassium dichromate solution 3.9 into a 500 ml volumetric flask and make up to the mark, mix well.

Note 1: All reagents must be of recognised analytical quality. De-ionised water must be used throughout.

4. **Procedure**

4.1 Weigh accurately by difference about 0.5 g of sample into a 500 ml wide mouth conical flask.

4.2 Disperse the sample with a small amount of water.

4.3 Add about 0.15 g of anhydrous sodium carbonate (to expel air when acid is added to the sample).

4.4 Add about 1.5 g of sodium fluoride (heaped spoon spatula).

4.5 Add, by measuring cylinder, 50 ml of 1 + 1 hydrochloric acid.

4.6 Close the flask with a rubber bung fitted with a bunsen valve.

4.7 Heat for 30 minutes on a hot plate. The solution should boil gently.

4.8 Cool the solution quickly in a water bath.

4.9 Transfer to a 250 ml volumetric flask, make up to the mark and mix well.

4.10 Keep the flask stoppered. Ferrous iron should be estimated immediately.

Ferrous Iron

4.11 Pipette 50 ml of solution into a 250 ml conical beaker.

4.12 Add 5 ml of orthophosphoric acid and 3 drops of indicator solution 3.1.

4.13 Titrate with potassium dichromate (1ml = 0.001000 g Fe) to a purple end point.

$$\% \text{ Ferrous Iron} = \frac{\text{Titre} \times 5 \times 0.001 \times 100}{\text{Sample Weight}}$$

Total Iron

4.14 Pipette 50 ml of solution into a 250 ml conical beaker.

4.15 Add 10 ml of concentrated hydrochloric acid.

4.16 Heat nearly to boiling point.

4.17 Add stannous chloride solution dropwise, with mixing, until the yellow iron colour is destroyed. Add 2 drops excess.

4.18 Cover the beaker and cool immediately in a water bath.

4.19 When cold add 10 ml of saturated mercuric chloride solution. (A silky white precipitate should form). Mix well.

4.20 Allow to stand for 1 minute and add 5 ml of orthophosphoric acid, and 3 drops of indicator solution.

4.21 Titrate to a purple end-point with potassium dichromate solution (1 ml = 0.001000 g Fe).

$$\% \text{ Total Iron} = \frac{\text{Titre} \times 5 \times 0.001 \times 100}{\text{Sample Weight}}$$

Note 2: Some smelting slags contain metallic globules which are difficult to comminute and difficult to dissolve under the solution conditions used in the method. If the metals do dissolve reduction of ferric iron could well occur.

It has been found advisable to grind

copper smelting slag samples in a tema pot for 1 minute and to screen at 60#. The —60# is analysed for total and ferrous iron and the + 60# analysed by atomic absorption for copper and iron.

Estimation of Metallic Iron in Slags

1. **Application**

The method is suitable for many types of ferrous and non-ferrous slags.

2. **Principle**

Metallic iron displaces copper from copper sulphate solution; excess copper is precipitated by aluminium, and ferrous iron in the resulting filtrate is titrated with potassium dichromate.

3. **Reagents**

3.1 Aluminium turnings.
3.2 Barium diphenylamine sulphonate indicator 0.2% w/v.
3.3 Copper sulphate solution 10% w/v.
3.4 Orthophosphoric acid sp. gr. 1.75.
3.5 Sulphuric acid sp. gr. 1.84.

Standard Solution

3.6 Potassium dichromate solution. Dissolve 0.8779 g. of solid, dried for 1 hr. at 120°C, in water and make up to 1 litre. Mix well.
1 ml. = 1 mg. iron.

Note: All reagents should be of analytical quality and de-ionised water used throughout.

4. **Procedure**

4.1 Weigh accurately 1 g. of finely ground slag into 100 ml. tall-form beaker.
4.2 Add 10-20 ml. of 10% copper sulphate solution, heat to boiling and simmer for 1 hr.
4.3 Dilute to 30-40 ml. and filter through a Whatman No: 4 paper washing beaker and paper thoroughly.
4.4 Add 10 ml. of suphuric acid to the filtrate and mix. Add a few aluminium turnings and boil the solution until colourless.
4.5 Cool and filter through a Whatman No: 41 paper washing as before.
4.6 To the filtrate add 5 ml. of orthophosphoric acid and 3-4 drops of barium diphenylamine sulphonate indicator.
4.7 Titrate with potassium dichromate solution to a purple end-point.

$$\%\ \text{metallic iron} = \frac{\text{Titre}}{10^3 \times 1} \times 100$$

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