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The Occurrence of Metallic Iron in Ancient Copper

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Of the many thousands of chemical or spectrochemical analyses of ancient copper, principally from central and northern Europe, and available in the literature, only a few report iron in excess of 1% and, in general, of these the iron occurs in Iron Age metal. On the other hand, some recent articles report much higher iron, these data being supplemented by our own investigations. These high-iron coppers are from Sardinia, Greece, Israel, Egypt, and India, and range in date from the Chalcolithic and Early Bronze Age through the Iron Age.

Of 61 copper specimens found at Nichoria, a recently excavated site in the SW *Peloponnese, 11 were found to be ferromagnetic, and ranged in age from Early Bronze Age to Byzantine. In a number of specimens, which have been examined spectrochemically and metallographically, the magnetic response is closely proportional to the total iron in the sample.*

Although Iron Age copper that contains appreciable iron can be explained by accidental addition of the impurity, no such explanation is applicable to the much earlier high-iron copper. It is therefore proposed that the iron was introduced as a result of simultaneous reduction of iron oxides in the furnace burden to solid metallic iron during the copper smelting operation. This phenomenon may have been more widespread than is realized.

It is pointed out that in the smelting of low-sulfur copper ores, the iron content of copper prills in an unweathered slag can be used to determine the minimum temperature reached in such an operation and, under favorable conditions, perhaps the maximum temperature reached, thus furnishing a clue to the currently moot question of the temperature attained in an ancient charcoal-fueled smelting furnace.

Introduction

During the Copper and Bronze Ages metallic iron played a rather inconsequential role. However, iron is routinely included among the elements analyzed in early cupreous alloys and is usually listed in analytical tables. Beyond this, it is largely ignored and its presence is usually explained as resulting from iron-bearing slag inclusions or the presence of iron oxides or matte. When studies of early copper metallurgy pay attention to iron, it is exclusively in respect to the handling and removal of this element during the smelting of sulfide ores. Until recently this lack of concern with iron appeared justified. However, in the past few months a surprising series of discoveries has led us to revise our judgement and understanding of iron other than as a normal fluxing constituent in copper smelting.

Our purpose here is to report our findings and to comment on their interpretation and significance. We hope that this account introduces archaeologists to the interesting and important results of metallurgical and metallographic analyses, and that they will seek to have their copper finds analyzed by interactively involving metallurgists. Furthermore, the pre-Iron Age archaeologist should be aware that metallic iron can be present in copper and bronze finds, that it apparently has no serious disadvantages when present in moderate quantities (except perhaps increasing the tendency to corrosion), and that under favorable circumstances it probably can be used to indicate temperatures achieved by the ancients in their smelting furnaces. The metallurgist has long known that iron as oxide was a deliberate addition to the furnace charge as a fluxing agent in the pyrometallurgical extraction of copper, tin, and lead from their ores. Under appropriate cir-

SIMPLIFIED GLOSSARY

α-iron and γ-iron: different crystallographic forms of the metal. Pure α-iron is stable from below ambient temperatures up to 910°C, above which it transforms to γ-iron, stable up to 1401°C. Substances soluble in iron can have a marked effect in changing these temperatures.

Bear or salamander: a mass of unfused material which forms in the hearth of a smelting furnace, usually consisting of a mixture of metallic iron and partially reduced ore.

Blowhole: a cavity or bubble formed in metal or slag by release of gas during cooling.

Centipoise: a unit used in measuring viscosity, that property of a fluid which resists internal flow.

Copper ores: oxidized copper ores, containing cuprite, malachite, azurite and tenorite, are converted to metal by a relatively simple smelting precedure. Sulfide copper ores are mineralogically more complex, contain substantial quantities of sulfur, and require a more complex pyrometallurgical treatment for the same results.

Eutectic: in the simplest binary metallic system, an alloy of fixed composition which freezes at a constant temperature below the freezing points of the constituent metals. Eutectics have characteristic structures (the "eutectic structure"), and more than one eutectic is possible in a binary system.

Eutectoid: physically similar to an eutectic in appearance, but formed by a reaction in the solid state, in the absence of liquid metal.

Flux: see *Slag.*

Gangue: see *Slag.*

Magnetic Transformation; the Curie point: all substances can be classified as being either diamagnetic (in a non-uniform magnetic field they move from a region of high flux intensity to one of lower intensity), or paramagnetic (which exhibit the reverse phenomenon), exemplified by metallic copper and tin. In either case the normal response is relatively weak. A subclass of paramagnetic substances is designated as being ferromagnetic, since their response to even a weak magnetic field is strong. Examples are α-iron, nickel, cobalt, and the non-metallic substance magnetite (Fe_3O_4) which occurs as a natural mineral and as a constituent of many metallurgical slags. When pure α-iron, ferromagnetic at room temperature, is heated to 760°C, it rapidly commences to lose its ferromagnetic properties, and at 770°C has completely transformed to paramagnetic α-iron. The process is reversible, irrespective of the number of heating and cooling cycles, so that is regains its ferromagnetism when cooled to 760°C, which is called the Curie point after its discoverer. The Curie points for pure nickel and cobalt are respectively 358° and 1120°C. On the other hand, γ-iron is paramagnetic at all temperatures at which it is a stable phase.

Metallographic Section: a piece of metal or slag which has been sectioned, ground to a flat surface by abrasive, and smoothly polished to permit the identification of contained constituents through a metallurgical microscope.

Peritectic: an alloy produced by reaction between a solid metal phase and a still liquid portion of the melt.

Phase: a homogeneous, physically distinct portion of an alloy, or a group of substances which are in equilibrium with each other.

Prill or Pellet: a small piece of metal, usually enclosed in a slag.

Slag: the initially liquid product of a reaction, at elevated temperature, between undesirable constituents (gangue) of an ore and reactants (fluxes) specifically added to effect removal of such constituents. In a few ores (self-fluxing ores) the gangue constituents are in the correct proportions to give a fluid slag without the addition of fluxes. A smelting slag is formed in the production of metal from an ore, and its weight is usually considerably in excess of the weight of metal produced. A melting slag is much less in relative quantity, and is added to cover the metal and prevent loss by oxidation.

cumstances some iron may be reduced to metallic form and appear in the smelted copper. Hence an equally important aim is to draw the attention of metallurgical analysts to these phenomena in the hope that yet more data may be gathered for a better understanding of certain aspects of ancient metallurgy.

The Probability of the Formation of Metallic Iron in Base Metal Smelting

It should be noted that even the primitive ancient furnaces used in copper, tin, and lead extraction would be capable of producing metallic iron. In an atmosphere of pure hydrogen, hematite (Fe_2O_3) is reduced to solid iron, at an appreciable rate, at 400°C. Pure carbon monoxide will reduce hematite similarly, but at a somewhat higher temperature. Limonite (impure goethite, $HFeO_2$) is converted to the chemical equivalent of hematite at corresponding temperatures. Of course neither pure hydrogen nor carbon monoxide was used, but the mixture of carbon monoxide and carbon dioxide produced in the combustion of charcoal is an effective reductant for all the metals mentioned. With a large proportion of charcoal in the "burden" or charge to the furnace and an ample supply of air, together with a charge containing more hematite than that necessary to be reduced to ferrous oxide (which reacts with the siliceous gangue to give the fayalite slags so typical of ancient and modern copper smelting) there is no reason to believe that at least some metallic iron should not be produced. Evidence of this has been found in ancient metallurgical operations. Wertime[1] refers to the production of iron "bears" in the traditional Iranian lead-smelting operations, as a result of overdriving (excess charcoal and a high volume air blast). The iron, being infusible at the prevailing temperature, collects as a mass in the furnace and presents an embarrassing problem in removal before ordinary operations may be resumed. Milton[2] refers to iron "bears" having recently been discovered in the early copper smelting operations near Timna, Israel.

In view of the foregoing it is rather surprising that high iron contents of ancient coppers have so infrequently been reported since, as will be shown later, solid metallic iron is readily soluble in molten copper. Although there is no simple relationship between the temperature of the copper and the amount of iron that is dissolved, the generalization may be made that the higher the temperature the more solid iron passes into solution.

Tylecote, indeed, comments on the appearance of iron in Early Iron Age (British) bronze artifacts. "Substantial quantities of iron are now appearing. This may be the result of using chalcopyrite ores, or it may have arisen from the accumulation of iron due to remelting many times and using iron stirring rods or by the accidental incorporation of pieces of scrap iron."[3] Tylecote, Lupu, and Rothenberg make the statement that "Some of the iron would be reduced in the upper levels of the furnace and enter the (copper) metal. But as this metal descended into more highly oxidizing regions, the iron would be oxidized and go into the slag."[4] However, as far as the first quotation given above is concerned, it is obviously impossible to explain the occurrence of metallic iron in some of our early Greek samples, which antedate the use of iron tools.

Previously Reported Analyses of Iron in Copper and Bronze Finds

With few exceptions the reported iron content of ancient coppers and bronzes is uniformly low, nearly always substantially less than 1%. Among the over 8,000 analyses of European coppers of early age, Junghans, Sangmeister, and Schröder[5] report no more than two or three with somewhat more than 1%. Brown and Blin-Stoyle[6] present 438 analyses of British bronzes of the Middle and Late Bronze Age, and again, with a few exceptions, the amount of iron is in the same range. In 100 analyses of Chinese bronzes[7] the average value for iron is 0.2% and only one has more than 1%. Moorey[8] gives analytical results for 132 prehistoric objects from Western Iran and finds only three with as much as 2.5% Fe.

Despite the strong pattern illustrated by this sampling of the many reports that could be cited, iron values can run much higher. Thus, among Chalcolithic objects from India, Hegde[9] found one with 2.57% and another with 6.48%. From the 12th dynasty (ca. 2000 B.C.) of Egypt, an ingot was found at Bir Nasb, Sinai, with 5.9% iron.[10] Desch also reports, without further comment, a copper object of India (from Odugattar in North Arcot) with 15.75% iron. Again, from the very important metallurgical site of Timna, Israel, four

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[1] T. A. Wertime, "Man's First Encounter with Metallurgy," *Science* 146 (1964) 1257-1267; idem, "A Metallurgical Expedition through the Persian Desert," *Science* 159 (1968) 931.

[2] C. Milton, personal communication, who in return received the information from R. Maddin, University of Pennsylvania.

[3] R. F. Tylecote, *Metallurgy in Archaeology* (London 1962) 51.

[4] R. F. Tylecote, A. Lupu, and B. Rothenberg, "A Study of Early Copper Smelting and Working Sites in Israel," *Journal of the Institute of Metals* 95 (1967) 235-243.

[5] S. Junghans, E. Sangmeister, and M. Schröder, *Kupfer und Bronze in der frühen Metalzeit Europas* (Berlin, 1968).

[6] M. A. Brown and A.E. Blin-Stoyle, "A Sample Analysis of British Middle and Late Bronze Age Material Using Optical Spectrometry," *ProcPS* 25 (1959) 188-208; (=*Analyses in Archaeometry* 2, Supplement, 1959).

[7] R. J. Gettens, *The Freer Chinese Bronzes*, vol. 2 *Technical Studies* (Washington, D.C. 1969).

[8] P. R. S. Moorey, "Prehistoric Copper and Bronze Metallurgy in Western Iran," *Iran* 7 (1969) 131-152.

[9] K. T. M. Hegde, "Metallographic Studies in Chalcolithic Objects," *Baroda (City) Orient Institute Journal* 14 (1964) 84-90.

[10] C. H. Desch, "Report on the Metallurgical Examination of Specimens for the Sumerian Committee of the British Association," *Report of the British Association for the Advancement of Science* (1928) 437-441, and A. Lucas, *Ancient Egyptian Materials and Industries* (London 1948) 3rd ed.

"prills and drops" have been analyzed and contain iron ranging from 5.0 to 9.7%.[11]

Just as there has been only routine attention paid to the iron in ancient coppers, so also there has been no concern with the form or state of the iron, that is, whether it is metallic, an oxide, a matte, or part of entrapped smelting slag. In the case of Hegde, this is somewhat surprising since he made a rather complete metallographic examination of the Indian artifacts. For his specimen No. 5, the iron-rich copper axe from Ahar (Rajasthan), he spectrographically determined its composition (Cu, 90.29%; Fe, 6.48%; Pb, 1.62%; Ni, 0.31%); he found it to be magnetic, and he made transverse and longitudinal metallographic sections; yet he does not identify or comment on the state of the iron, although he remarks that its amount is unusual. Tylecote et al.[12] seem to be the sole exception, for they raise this issue:

> "Microscopical examination showed that it [iron] was not present as metal, and, in view of the low sulphur content cannot be present as matte. There were, however, considerable amounts of oxide phases, including copper oxide, and it would seem that the iron took the form of entrapped fayalite slag or 'FeO'."

We shall return later to this particular case. It suffices to say here that determining the form of iron, especially when its content is more than 2%, can add valuable clues to metallurgical practices.

Additional Examples of Iron in Copper

Our own attention was aroused and focussed on iron-rich coppers by some remarkable coincidences. During initial spectrographic analyses of coppers and bronzes from the Bronze Age site of Nichoria in SW Greece, one fragment (Nichoria 3424) from a level dated to about 1350 B.C. was shown to have > 5% iron. Though this was remarked upon amongst ourselves, nothing more was done for a few months. Then samples from two large Sardinian pieces of metal were spectrographically analyzed and gave an astonishing result of 20% from a 7th-6th century B.C. piece and 2-4% from a 13th century B.C. fragment. The next day's mail added more cases: two Early Bronze Age coppers from the site of Servia in Greek Macedonia had just been analyzed on the new X-ray fluorescence equipment in the British School at Athens and were found to have respectively 8-11% and 10-15% iron.[13]

Table 1. Summary of magnetic tests on various archaeological samples.

Location	Archaeological Date	No. Samples Tested for Magnetism	No. Magnetic Samples
Sardinia	13th and 6th century B.C.	2	2
Olympia (Greece)	9th to 3rd century B.C.	50	2
Nichoria (Greece)	Middle Bronze to Byzantine	61	11
Kea (Greece)	Late Bronze	5	1
Divostin, (Serbia, Yugoslavia)	Neolithic	1	1
Sardis (Turkey)	6th century B.C. to Byzantine	71	9
Sialk (Iran)		1	1
Ali Kosh (Iran)	Mediaeval stray in Neolithic level	1	1

See Table 2 for more data concerning some of these samples.

This prompted us to begin an extensive investigation. It was immediately found that the Nichoria and the two Sardinian specimens were strongly magnetic. Within the day metallographic sections of the Nichoria and the younger Sardinian specimen had been made and were found to contain metallic iron in rather massive quantities. Meanwhile, magnetic tests were commenced on many of the artifact samples available. This brought to light several more magnetic pieces, some of which were taken for metallographic or spectrographic analysis. In all cases this corroborative analysis of magnetic pieces revealed metallic iron and clearly showed that the magnetic properties were not due to magnetite, a common slag constituent. Table 1 summarizes our results of the various analyses and indications of iron. Altogether, 193 coppers were tested of which 27 were found to be ferromagnetic. Five of these were examined metallographically and the iron was found to be primarily in the metallic state. In addition six magnetic pieces were analyzed spectrographically. This suite of samples spans

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[11] Tylecote et al., op.cit. (in note 4).

[12] Ibid.

[13] We gratefully acknowledge the stimulus provided by these two analyses made by Mr. Richard Jones and thank the excavator of the finds, Mrs. Cressida Ridley, for communicating the results to us via Mr. Roger Howell.

Table 2. Composition of iron-rich cupreous archaeological metals.
(Weight percent when numbers are given)

Identification	Sample	Archaeological Date	Cu	Fe*	Ni	Co	Pb	Sn	Ag	As	Au	Mn	Zn	Sb	Bi	Cr
A	Nichoria[14] 3424 (Lump)	LHIIIA: 2 (1350 B.C.)	90+	5+	p.	—	0.91	0.1	—	0.13	n.d.	—	0.05	0.04	n.d.	—
B	Sardinia 75-01-00C (Lump)	7th-6th century B.C.	50-60	20+	1.0	0.1	0.5	0.2	0.005	tr.	n.d.	0.2	n.d.	n.d.	n.d.	n.d.
C	Sardinia 75-80-00D (Lump)	13th century B.C.	85-90	2-4	0.1	0.03	tr.	tr.	0.0005	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	n.d.
D	Olympia 17 (Tripod Foot)	9th-8th century B.C.	90+	+++	—	—	0.4	0.3	.003	—	—	—	n.d.	n.d.	n.d.	—
E	Ali Kosh, Iran	Mediaeval (?)	70-75	6	0.05	0.005	3-4	3.0	0.005	n.d.	n.d.	p.	5-7	tr.	tr.	n.d.

*The iron analyses are not representative due to the segregation reported in this paper.

n.d. (not detected) p. (present) tr. (trace) — (undetermined)

the time period from Neolithic to Byzantine (12th century A.C.) and derives from Sardinia in the west to Iran in the east.

Our findings, namely the frequency of iron-rich coppers and the occurrence of iron in metallic form, are sufficiently surprising in the light of the trend of previous analytical work to warrant some explanation. First of all, it appears that our samples tend to be drawn from a different region than that which generated the bulk of the published analyses noted earlier. The contrast seems to be between Europe on the one hand, and the eastern Mediterranean and the Middle East on the other. Second, and perhaps far more important, iron does not occur evenly distributed throughout copper specimens, but exhibits a marked concentration in certain portions of the specimens. This matter, which is well illustrated by the Nichoria and the younger Sardinian samples, and one from Olympia (TABLE 2, A, B, and D, respectively) will be taken up in detail below. Finally, the failure on the part of previous workers to identify the metallic state of the iron is probably due to the fact that relatively few metallographic studies have been made of ancient coppers. This is, of course, understandable, for metallographic examination is fairly time-consuming. A closely related matter is that tests for magnetism, especially when spectrographic examination has revealed a high-iron content, seem to have been made very rarely. Hegde provides the lone exception.

Metallographic Examination of Some Magnetic Copper Samples

To ascertain the reason for the ferromagnetism of the samples, several were selected for metallurgical examination (see TABLE 2). In addition, some copper-iron alloys and a tin bronze-iron alloy were prepared in the laboratory and will be described later. All of the samples exhibited strong to fairly strong ferromagnetism to the field of a hand-magnet. Spectrographic analyses of the archaeological samples were made from 10 mg. obtained by drilling with a fine drill at randomly selected sites where the metal had been exposed by laboratory removal of the corrosion products.

Sample A

The reported high iron content was tentatively assumed to be due to inclusions of fayalite, magnetite, or

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14. This analysis also appears in Table II of a forthcoming report in *Hesperia*.

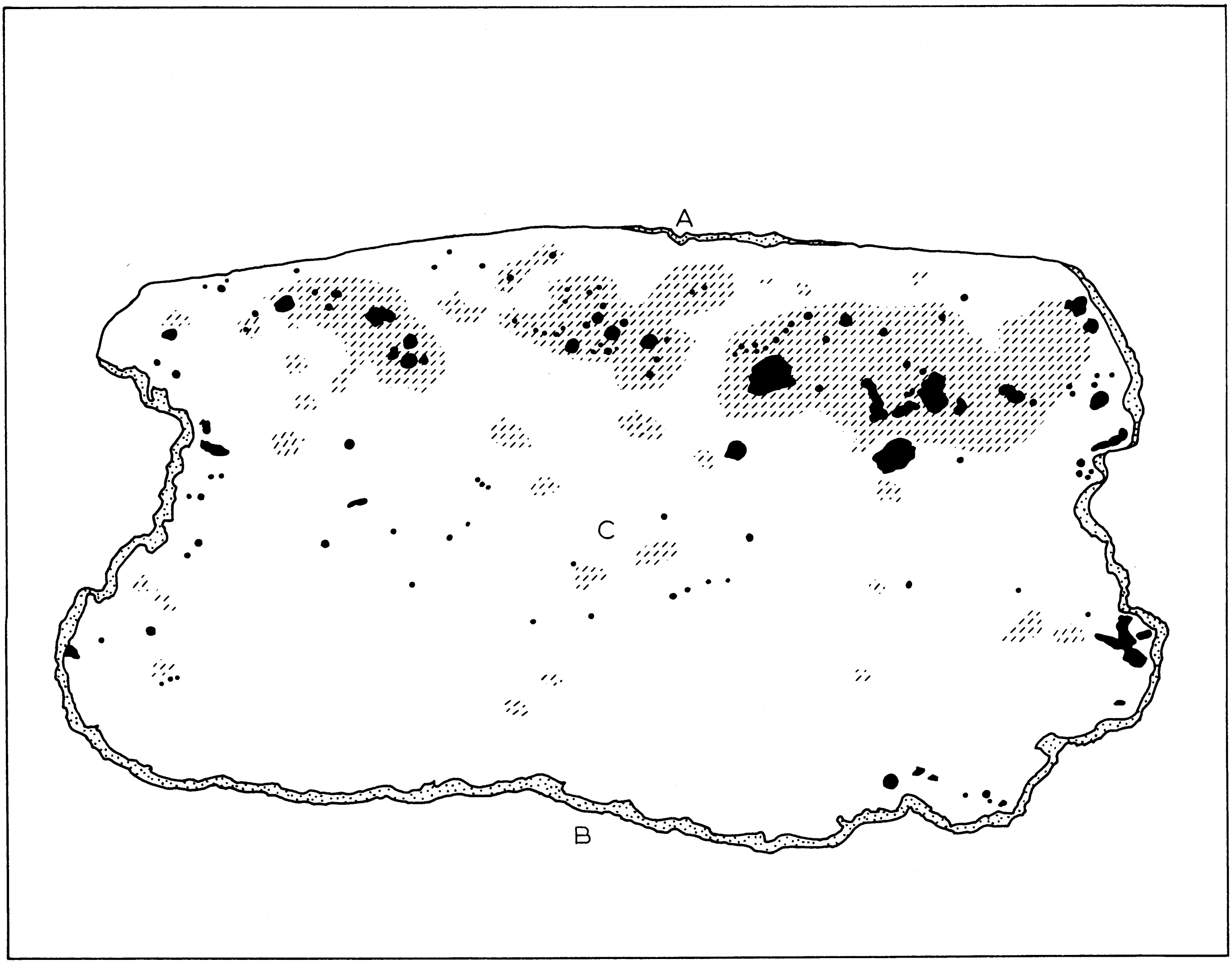

Figure 1. X14. Drawing made from a macrograph of a section of Sample A. Black areas represent blowholes; the lightly stippled areas on the periphery represent the corrosion products, cuprite and malachite. The internal, stippled areas show approximately where nearly complete coalescence of the iron has occurred. In the center, some dendritic iron and a considerable amount of isolated and partly coalesced spheres of iron are fairly common. Only a few isolated spheres of iron occur in the lower part, but very fine iron occurs throughout the copper matrix. The concentration of gas blowholes and the high concentration of iron near the top confirm that this was the upper surface of the specimen as it cooled.

matte unavoidably included in the drilling. As soon as the sample was found to be strongly ferromagnetic it was realized that this could be due only to the presence of metallic iron. The specimen was sectioned and polished for metallographic examination.

Figure 1 is a drawing made from a macrograph of the section. In the following discussion the somewhat convex, lightly corroded edge (A) and the rough and strongly corroded edge (B) will be referred to as the upper edge and the lower edge, respectively. Both edges showed the normal sequence of corrosion products for copper and bronze, i.e., metal-cuprite (Cu_2O)-malachite ($CuCO_3Cu(OH)_2$), but the corrosion is much less on the upper than on the lower edge. A number of blowholes occurred throughout the specimen.

Close to the upper edge, and quite apparent to the unaided eye, were more-or-less continuous bands of a metallic constituent, bluish white in daylight, and contrasting strongly with the red color of the copper matrix.

Under the microscope, besides the cuprite in the corroded areas, chalcocite (Cu_2S) occurs as a minor constituent in the form of spheroidal to irregular blebs which tend to associate with the iron. Only a few slag inclusions occur in the section.

The bands of metal were identified as partially to almost completely coalesced grains of α-iron. Throughout the specimen this constituent occurs in two forms.

(a) As more or less isolated grains, circular to elliptical in cross-section, where not partly coalesced, and ranging in maximum diameter from 20 to 25 microns. These are randomly scattered in small quantity in the proximity of the lower edge, and increase in concentration, accompanied by partial to almost complete coalescence, as the upper edge is approached. A number of coarsely-formed α-iron dendrites occur in the center area of the section.

(b) As very fine particles ranging in size from a maximum of about 1 micron down to a minimum limited by the resolution of the oil-immersion objective (about 0.25 micron). This fine iron occurs uniformly scattered throughout the copper matrix.

Figure 2 was photographed near the center of the section (C in FIG. 1) and shows individual spheroids of iron as well as partly coalesced grains. Visually, fine copper particles occur in the iron, but they are near the limit of resolution. The mottling of the copper matrix is caused by the very fine grains of iron described under (b) above.

In Figure 3, the "upper" edge of the section is on the right. Most of the field is occupied by a mass of partly coalesced α-iron, with some black blowholes and some chalcocite, which also appears black in the sodium D illumination used. Figure 3 was photographed near position A of Figure 1.

Inspection of the whole polished section shows that the average tenor of the iron is about 6%, or reasonably close to the spectrographic analysis. This is due to good luck more than anything else, since a much higher iron content would have been reported if the drill had penetrated from right to left in the section shown in Figure 3. Analyses made by microprobe or X-ray fluorescence of the unsectioned original specimen would have been quite unreliable since none of the iron is exposed at any of the sample surfaces.

A simple experiment was devised to ascertain if the entities in the Nichoria sample could be reproduced. The constituents of a glass with a low softening temperature (Na_2O:CaO:SiO_2 = 32.3/4.2/63.5) were melted together in a dense, prefired fire-clay crucible at 1000°C. The glass formed a deep cup in the bottom of the crucible, in which, after cooling, 1.23 gm. of fine filings prepared from pure iron were placed. Several grams of the same glass flux were firmly tamped around and above the iron. A portion of a copper rod weighing 16.57 gm. was then inserted and more glass flux was tamped around and over the copper. Finally, after plac-

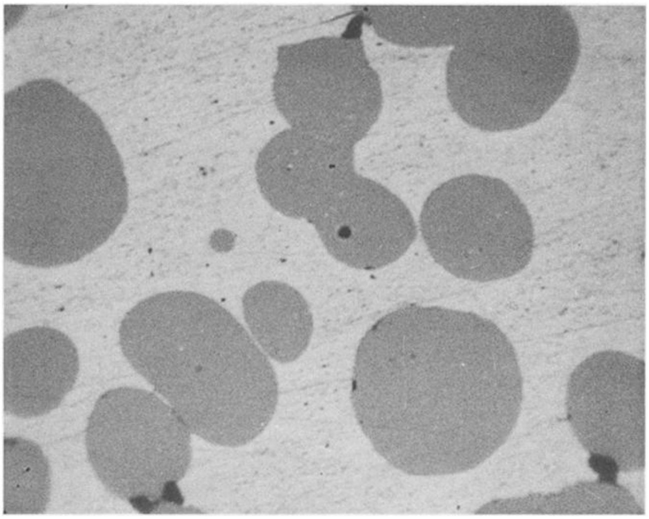

Figure 2. X 2450, oil immersion, Na_D illumination to enhance contrast, Sample A. Dark gray spheroids: α-iron. Light background: copper matrix mottled with iron precipitated from solid solution. Black areas at edges of spheroids: chalcocite, which apparently preferentially "wets" the iron, since this association is common in the specimen. Visually, very fine copper is dispersed in the iron. Just above center a small blowhole (black) occurs in iron. The area shown was photographed near C of Figure 1.

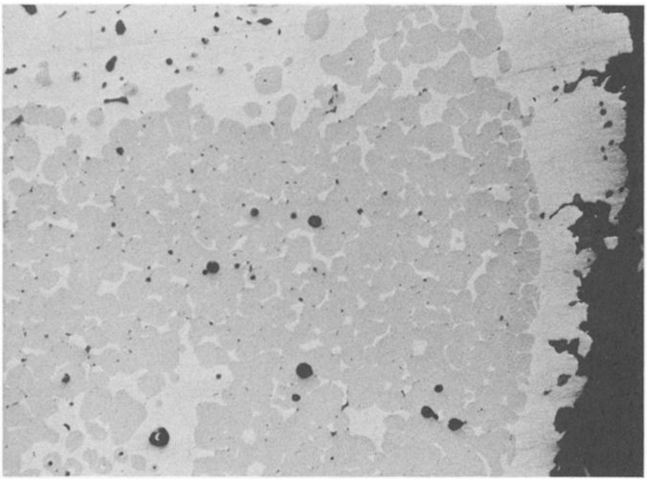

Figure 3. X 95, Na_D illumination, Sample A. Most of the photograph is occupied by α-iron which has largely coalesced. Black areas are principally blowholes, but some of the finer ones are chalcocite. Photographed near A in Figure 1.

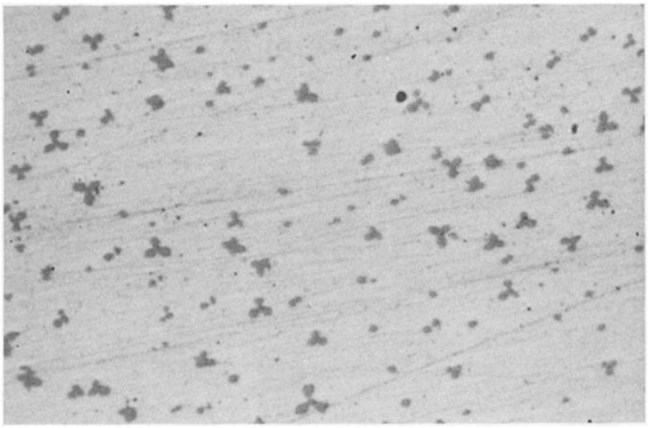

Figure 4. X 830, oil immersion, Na_D illumination. Laboratory prepared alloy. Gray: copper. Dark gray: α-iron precipitated from the copper.

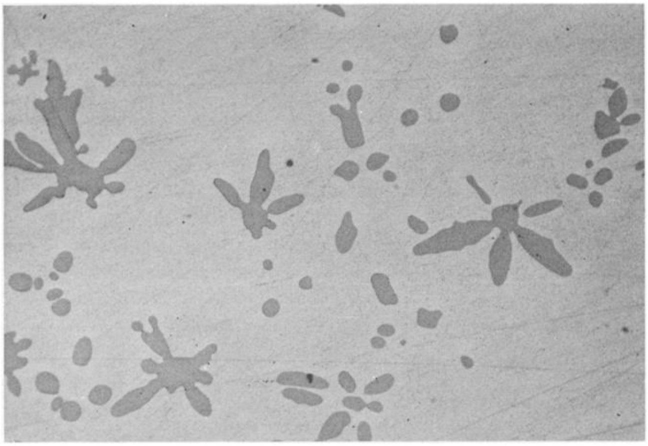

Figure 5. X 120, Na_D illumination. Laboratory prepared alloy. Dendritic iron (dark gray) in copper. The low resolution does not show the iron precipitated from solution, as in Figure 4.

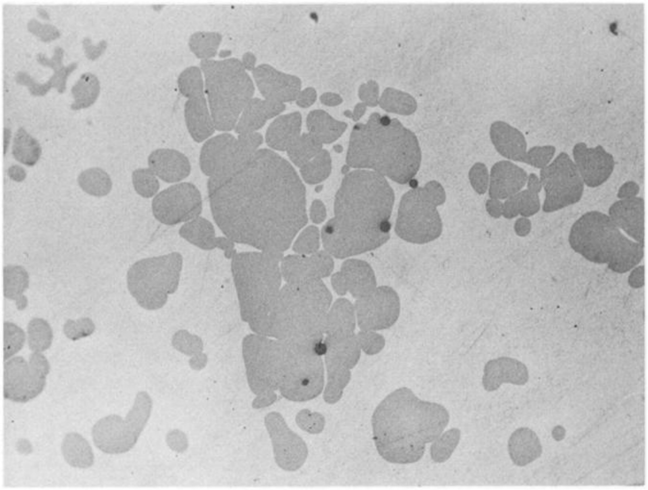

Figure 6. X 120, Na_D illumination. Laboratory prepared alloy. Partly coalesced iron (dark gray) in copper matrix near the top of the melt. Black areas are slag inclusions.

ing a substantial layer of graphite on top of the charge, the crucible was inserted into a muffle furnace at 1300°C. Since the furnace atmosphere could not be controlled, the purpose of the graphite was to maintain a reducing atmosphere in the crucible to prevent oxidation of the iron and copper.

After holding at the stated temperature for 40 minutes the furnace temperature was lowered to 805°C over a period of 2 hours, the crucible was removed, air-cooled to room temperature, and broken open. A button of clean metal, showing no surface oxidation, was removed from a very light-blue and transparent slag. There was no trace of the iron, but the button was strongly ferromagnetic. The complete absence of iron oxide indicated that the atmosphere in the crucible had been sufficiently reducing to prevent loss of metallic iron.

The button was sectioned vertically along a diameter with respect to the position it had assumed in the crucible, and polished for metallographic examination. The copper matrix (FIG. 4) contained hosts of fine iron particles, somewhat coarser than those responsible for the mottling shown in Figure 2. Near the base of the button there were a few small spheroids of α-iron. Near the center the iron occurred as isolated spheroids and as coarsely developed dendrites (FIG. 5). Near the upper surface of the button, marked coalescence of the iron had occurred (FIG. 6). Since no iron had been lost by oxidation, the *average* analysis of the button would be 6.9 % Fe, 93.1% Cu. The copper contained no cuprite. Very finely dispersed copper, small in quantity, occurred in the α-iron. The light blue color of the slag originated from the very minor quantity of cuprite known to be present in the otherwise high-purity copper used to make the alloy.

Reference to the two sections of the copper-iron constitution diagram[15] for, respectively, the high-copper and the high-iron portions shown in Figure 7 provides much of the explanation of the foregoing observations of the Nichoria and the laboratory-produced specimens. For convenience we can assume a molten copper containing 6% iron in solution. As it cools it reaches the liquidus temperature at 1217°C, and solid γ-iron commences to precipitate, containing about 8.3% copper in solid solution. With a slowly dropping temperature (to maintain equilibrium) more iron precipitates, until at 1100°C the precipitating iron contains about 8.5% copper. From the photomicrographs it is a fair inference that the precipitating iron grows on the original nuclei to respectable dimensions, although it is not clear why spheroids should form.

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[15] M. Hansen and K. Anderko, *Constitution of Binary Alloys* (McGraw-Hill, 1958). The data for figure 7 were taken from the publication.

At the copper-rich end of the diagram the composition of the still molten copper alloy follows the liquidus. At 1100°C the copper contains a little over 2.8% iron in solution, and the weight ratio of liquid copper alloy to precipitated γ-iron solid solution is 28.5/1 for the alloy chosen.

At 1094°C a peritectic reaction occurs, which, under equilibrium conditions, means that an isothermal reaction occurs between the liquid and the precipitated iron to give a solid solution of peritectic composition Cu 96.0%, Fe 4%; i.e., the copper takes up iron. Theoretically, for an initial 6% iron-copper melt, a little more than 35% of the *already precipitated* iron reacts with the melt. The product of the reaction forms on the surface of the iron and prevents contact between the two phases, so that the diffusion of the reactants is through the intermediate solid peritectic material, a very slow process. However, given an extremely slow cooling rate, the reaction will be completed. The alloy will now consist of a solid solution of peritectic composition containing the residual γ-iron dispersed throughout its mass. As far as the high-copper end of the diagram is concerned the cooling curve follows line AB, along which γ-iron continues to precipitate. This will be finely dispersed material, since it is precipitated from solid solution.

A copper containing 4% iron (i.e., initially of peritectic composition) will cool along the liquidus as before, precipitating γ-iron below 1150°C until it reaches 1094°C, when, under equilibrium conditions, it reacts with *all* of the precipitated iron to form the peritectic. The alloy is now completely solid and cooling proceeds along the line AB, with reprecipitation of γ-iron. As it occurs in the solid state the precipitated iron is finely divided, but goes through the transformations to be described later, finally becoming ferromagnetic α-iron. It is this finely divided phase which appears in the copper matrix in Figures 2 and 4.

In the case of a 2% iron-copper alloy, initial freezing commences at about 1090°C, with the ultimate formation of the ϵ-solid solution. With continued cooling nothing further happens until 950°C, when line AB is reached, and γ-iron starts to precipitate, containing about 5.7% copper in solid solution. Subsequently it transforms to α-iron, which ultimately becomes ferromagnetic.

On the high-iron side, Figure 7, the precipitated γ-iron solid solution rejects copper as it cools along DE until at about 835°C it contains 3.5% copper. At this temperature the γ-iron solid solution transforms to α-iron containing about 1.2% copper in solid solution and a eutectoid (a mixture of copper and α-iron) with about 3% Cu. Below this temperature the small amount of copper in solid solution is precipitated from the α-iron. Next, the magnetic transformation from paramagnetic α-iron to ferromagnetic α-iron occurs at 759°C, and it is this change which makes the copper-iron alloys respond to the magnet.

In the foregoing discussion it is assumed that cooling of the metal was so slow that equilibrium conditions were always maintained. This is rarely true, even in modern industrial metallurgy, and in the case of rapidly

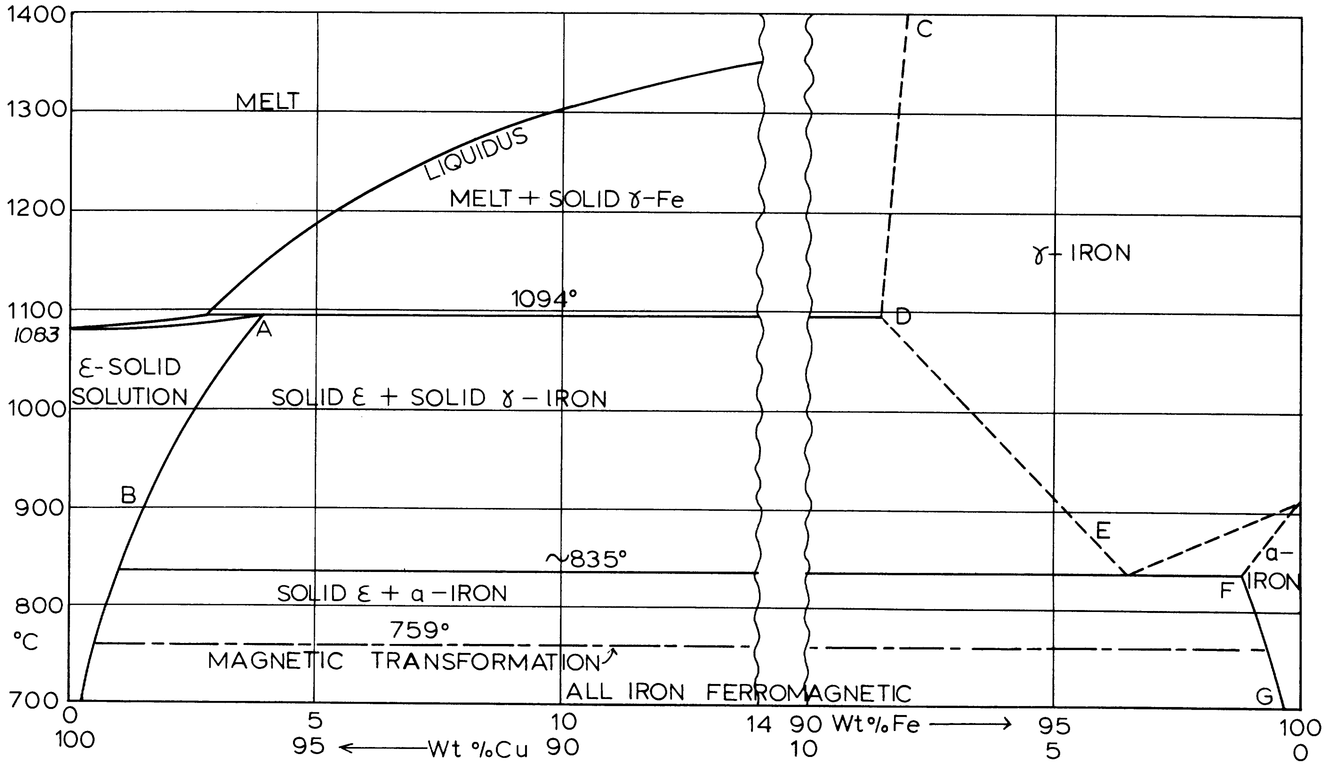

Figure 7. Constitution diagram of the high-copper and the high-iron portions of the Cu-Fe system.

cooled metal, such as in small castings, accidental crucible spills, etc., the constitution diagram can be considered only as a general guide, particularly when part or all of the metal has solidified. For the copper-iron diagram the peritectic reaction may not occur at all, or at best, be incomplete. In the small samples of ancient copper so far examined there is no evidence of a peritectic reaction.

A few experiments were conducted to ascertain if only 2% and 4% iron in copper would make the alloys responsive to the relatively crude hand-magnet test for ferromagnetism. The samples were prepared in identical manner to that of the 6% Fe-Cu alloy previously described, except that an alloying temperature of 1200°C was used. Both specimens weighed about 20 gm. and were furnace-cooled from that temperature to 200°C over a period of 18 hours. Both were ferromagnetic, the 2% Fe alloy being noticeably less so than the 4% Fe alloy. The two specimens were then remelted to 1200°C under reducing conditions, and rapidly quenched in ice water. Their behavior to a hand-magnet was indistinguishable from that of the slowly-cooled alloys and establishes the fact that a copper containing only 2% Fe, and probably less, can be detected with no difficulty by this simple method.

Another experiment was made in which a 10% Sn, 90% Cu bronze was melted with solid iron to give an alloy containing 8% Fe, 9.2% Sn and 82.8% Cu. The alloy, prepared and maintained at 1350°C for 30 minutes, was air cooled in its crucible to room temperature. None of the iron had been oxidized, and the sample was strongly ferromagnetic. In polished section the distribution of the iron was virtually indistinguishable from that of the 6% Fe laboratory-prepared copper, there being, perhaps, a greater tendency to the formation of iron dendrites.

The segregation of the coarse iron in the Nichoria sample is easily explained. In the case of a 10% iron-copper alloy, the density of the melt at the liquidus (1305°C) is about 7.9, and that of the iron commencing to precipitate, about 7.0. The average viscosity of pure molten copper between 1145°C and 1187°C is 3.28 centipoises, and by extrapolation would be about 2.5 centipoises at 1305°C. Since many of the larger grains of iron assume a spheroidal shape, Stokes' law will give the rising velocity. Assuming a diameter of 25 microns, the rising velocity of such an iron sphere in the melt is of the order of 0.012 cm. per second or 0.7 cm. per minute. This, of course, represents a maximum velocity, and would decrease with increasing viscosity as the temperature drops, and with decrease in the particle size of the iron. Because of the increased drag exerted by the many-branched dendrites compared with the spheroids, their rising velocities will be smaller on the same mass basis which probably accounts for their intermediate positions in the Nichoria and the experimental melt.

A comment is required on the apparent color of the iron as seen under the microscope. In tungsten illumination (color temperature 3000°C) the coarse spheroids and the finely divided iron particles appear bluish-white in color. This seems to be largely an effect of contrast with the reddish copper matrix, since upon closing the microscope field iris diaphram to isolate a single large grain, the color approximates that of polished α-iron. As would be expected, illumination filtered to give daylight quality greatly enhances the apparent bluish color as against the matrix.

As noted earlier, Tylecote et al.[16] have reported high iron contents, up to 9.7% Fe, in slags from the Timna area. They unequivocally state that the iron is not present as metal. In a later paper Lupu and Rothenberg[17] report up to 6.37% Fe in copper pellets from Timna, and state: "There are large quantities of copper oxide, some lead, and inclusions of silicates." They include a photomicrograph "showing much oxides," in which the relatively high relief of some of the "oxide" indicates to us that it is actually metallic iron. Milton, Toulmin, Dwornik, and Finkelman, in a paper soon to be published, which Professor Milton has generously permitted us to read, have made an exhaustive mineralogical and compositional study of some slags from Timna. In these they found large pellets of copper containing abundant grains of a substance which was proven by X-ray analysis to be α-iron, and by microprobe to contain 4% copper. A photomicrograph in their paper shows an iron distribution very similar to that in our Figure 3.

Until Milton et al. demonstrated conclusively that α-iron does occur in ancient copper, a conclusion amply reinforced by our own findings, the question once again arises as to why the phenomenon has been overlooked. The test for ferromagnetism is positive, and in the absence of even massive quantities of magnetite, is conclusive. It seems probable that the distinctly bluish color of the iron in contrast with the copper matrix has caused misidentification with cuprite. It is also possible that Hegde[18] was similarly misled.

Sample B

As mentioned previously, two pieces of cast copper

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[16] Tylecote et al., op.cit. (in note 4).

[17] A. Lupu and B. Rothenberg, "The Extractive Metallurgy of the Early Iron Age Copper Industry in the 'Arabah, Israel," *Archaeologia Austriaca* 47 (1970) 91-130.

[18] Hegde, op.cit. (in note 9).

were received from Dr. Miriam Balmuth for examination. Originally intended for neutron activation analysis, the ferromagnetism of the samples called for a closer scrutiny. Both samples contained minor quantities of silicon, magnesium, aluminum, and calcium, undoubtedly from the small amount of included slag. Sample B was strongly ferromagnetic, Sample C weakly so.

Figure 8 is a photomicrograph of an unetched polished section of Sample B. It is unknown if it is a portion of a casting, a spilled piece of metal, or an intentional reject, but it is a highly defective piece of metal found in a "bronze hoard" at Ferraxi, Nioi, Sardinia. (Courtesy of Dr. Feruccio Barreca, Museo Nazionale, Cagliari). The copper phase contains abundant blowholes and some slag inclusions. The iron contains small spheroids of copper, very small blowholes, and consists of two phases, one perceptibly darker than the other. As can be seen, rounded to irregular pieces of iron occur scattered throughout the copper, but most of it occurs as massive metal. Figure 9 was taken, in slightly oblique illumination, of a portion of one of the masses, thereby enhancing the surface relief. Since the sample was polished by conventional methods, and was not etched, it is difficult to escape the conclusion that the massive iron agglomerated completely from spheroids, much as that shown in Figure 3 was in the process of agglomerating before complete freezing of the copper matrix occurred. Variation in polishing hardness across the iron, obvious from Figure 9, is possibly due to the presence of the dark phase shown in Figure 8.

Initially, the dark phase in the iron defied identification, although at high resolution it has all the appearance of an eutectic. A microprobe analysis of the surrounding α-iron and of the eutectic gave the results shown in Table 3.

Table 3. Microprobe analysis of α-iron and the contained eutectic.

	Alpha-iron	Eutectic
Fe	85.4	81.5
Cu	12.3	4.4
S	n.d.	1.0
P	n.d.	12.4
Mn	Tr	Tr
Ti	n.d.	—
Cr	n.d.	—
Ni	n.d.	—
Co	n.d.	—
As	—	n.d.
Sb	—	n.d.
Bi	—	n.d

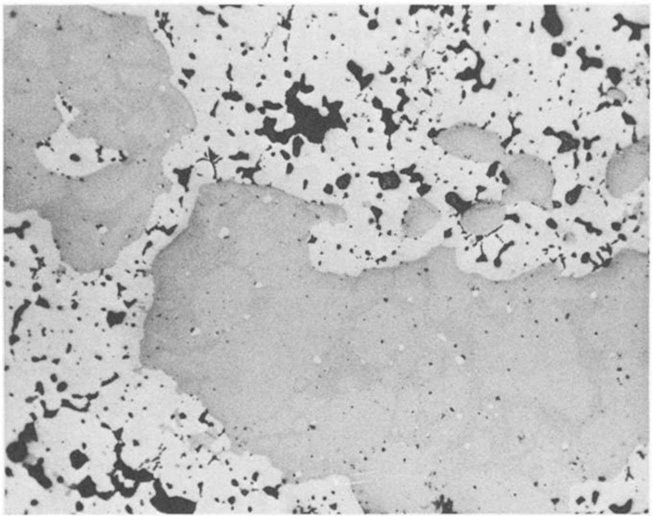

Figure 8. X 120, yellow-green illumination, Sample B. Masses of iron (dark gray) in copper (whitish-gray). Note the large number of cavities in the copper, some of which are slag-filled. The eutectic described in the text appears as darker patches in the α-iron.

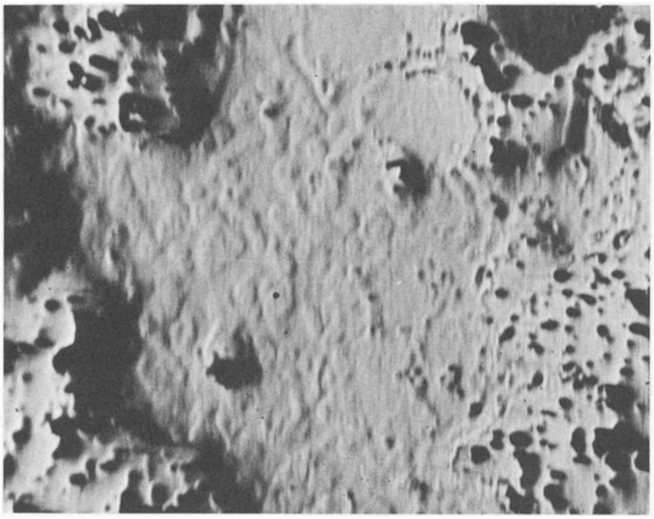

Figure 9. X 120, unfiltered tungsten illumination, slightly oblique. The α-iron occupying most of the center exhibits an uneven surface. Copper is on the right and left hand sides, and contains numerous cavities.

The sulfur distribution in the eutectic ranges from 0.5 to 2.5%. There is a sympathetic variation in the phosphorus content, this element being somewhat higher when sulfur is low, and vice versa. In the binary system Fe-Fe_3P, the eutectic solidifies at 1050°C and contains 10.5% P, but it is a complex system which is reported to be subject to undercooling. The roles played by the copper and sulfur in the eutectic are unknown, but it can be concluded that the dark phase is essentially α-iron and iron phosphide. Using a Rosiwal analysis to

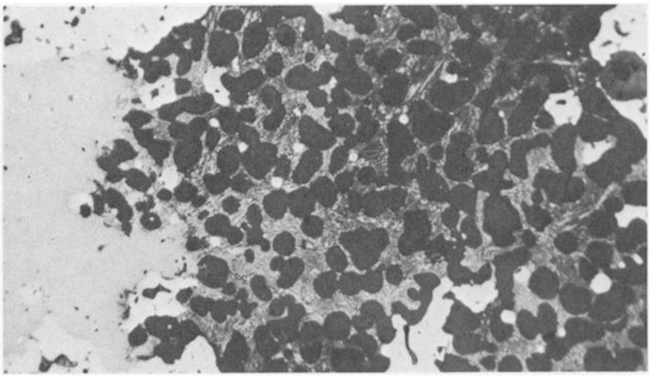

Figure 10. X 120, yellow-green illumination, Sample B. The light-colored phase is copper, the apparently smooth gray phase is α-iron. The inclusion occupying most of the field consists of devitrified slag (dark gray) with black spheroidal to irregular grains of a high-iron, high-phosphorus constituent.

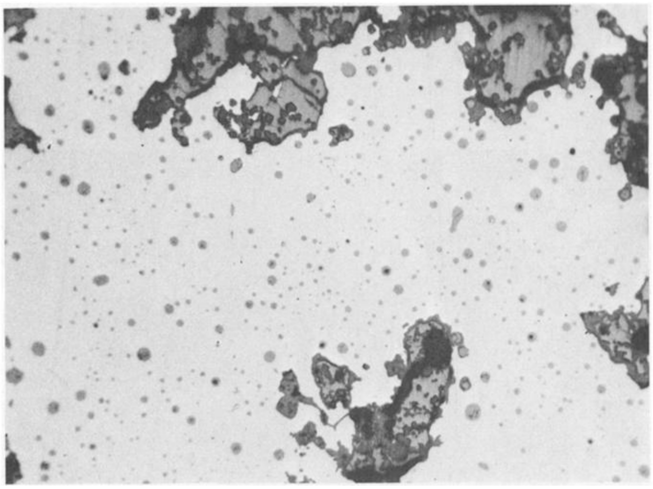

Figure 11. X 120, yellow-green illumination, Sample C. White: copper. Gray spheres: chalcocite containing, in some cases, a dark iron-cobalt alloy. Massive gray areas: chalcocite, rimmed with cuprite, and containing a multitude or iron-cobalt grains.

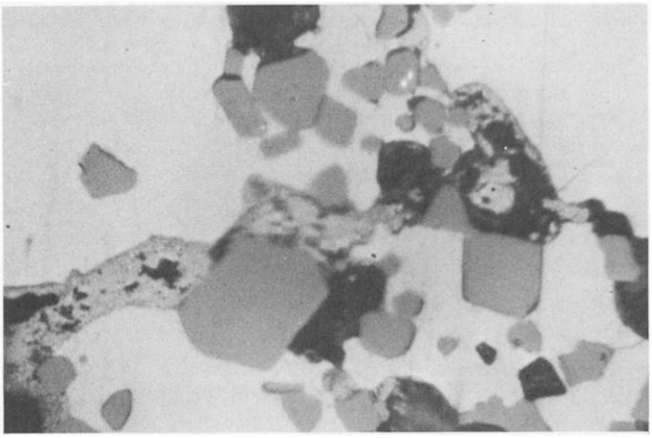

Figure 12. X 1000, yellow-green illumination, Sample C. White: chalcocite. Mottled gray: cuprite. Dark gray: spheroidal to euhedral grains of iron-cobalt alloy. Black: holes.

determine the relative proportions of iron and eutectic, the average phosphorus content of the total iron phase should be about 2%. This would be very high if the phosphorus originated in an oxide or a sulfide copper ore, but it may have originated in a high-phosphorus iron ore used for fluxing.

Figure 10 shows a rather puzzling section of this specimen. On the upper right-hand side, but not shown, the surface of the metal is deeply corroded, the corrosion products being in contact with the area shown, which contains dark spheroids and polyhedra. The matrix is a devitrified slag. In ordinary vertical illumination the dark constituent is gray in color, anisotropic, and under nearly crossed nicols has a deep red internal reflection, similar to that of hematite, (Fe_2O_3) or in some places, to that of goethite ($HFeO_2$). A number of these grains were examined with the microprobe, and gave an iron content ranging from 59 to 67%, and, rather unexpectedly, a phosphorus content of 10.3% which varied by about 1% from grain to grain. Since no other elements were found except traces of Mn and Ti, and since the sum Fe + P amounts to something between 60 and 77%, the deficiency can only be accounted for by invoking oxygen or hydroxyl. If this is correct the original constituent may have been metallic iron plus iron phosphide, which upon oxidation gave rise to substances of unknown constitution, but probably containing hematite and goethite.

Sample C

This sample of metal was said to have been originally associated with slag. Thanks to the excavator at Nuraghe Albucciu in Arzachena (Dr. M. L. Ferranese-Ceruti) and through the courtesy of Dr. Ercole Contu and Dr. Fulvia Lo Schiavo, Museo Nazionale, Sassari, the sample was made available to us by Dr. Miriam Balmuth. It consists of a piece of copper containing an abundance of chalcocite (Cu_2S) as spheroids, and as considerably larger irregular pieces (FIG. 11). The larger pieces are invariably rimmed by cuprite (Cu_2O), but very few of the spheroids are so encapsulated. Within all of the larger irregular pieces of chalcocite are hosts of near-spheroidal to polyhedral grains (FIG. 12), a material having a perceptibly higher polishing hardness than any other entity in the metal. Some of the chalcocite spheroids also contain this material, but rather infrequently (FIG. 13). Since both the microscope and the microprobe showed that there was no iron in the copper matrix, the origin of the ferromagnetism of the sample presented a problem until a microprobe analysis of the hard constituent was made. A number of grains gave the following average results: Fe 73.2%, Co 27.8%.

This material, which to our knowledge has never before been reported in an archaeological context, presents a number of puzzling features. (a) It occurs only in the chalcocite and appears to have little or no contact with the surrounding copper matrix; (b) occasional grains of the iron-cobalt alloy enclose small spheres of metallic copper (FIG. 12); (c) although the spectrographic analysis indicates iron in the range 2 to 4% for the drill sample taken, the same analysis gave only 0.03% Co. If the Fe-Co alloy were uniform in composition, we would expect something like 1% cobalt to report spectrographically. Although we cannot explain this discrepancy, there is no doubt that the alloy is responsible for the ferromagnetism exhibited by the specimen. (d) In many respects the Cu-Co constitution diagram is similar to the Cu-Fe diagram, with unlimited miscibility of the two metals above a liquidus resembling that of the last-mentioned in shape, but located at a lower temperature. However, since chalcocite is so abundant in the specimen, it is conceivable that the metallic alloy was preferentially "wetted" by this substance, thus inhibiting contact between the alloy and the molten copper. In this connection, attention is called to Figure 2, in which chalcocite, althought present in small amounts, seems to segregate at the iron boundary. Chalcocite melts at 1100°C, or only 17° above the melting point of pure copper. A cobalt-iron alloy containing 25% cobalt has a melting point of approximately 1460°C, so that the two metals must have alloyed in the solid state in the furnace.

Sample D

This specimen is a portion of a rather massive casting identified as a tripod foot. Two pourings were made to fill the mold, the first having solidified before the second addition was made. The chilling effect of the mold gave a finer grain size to the initially cast metal, but being poured into an already heated mold, the second part of the casting cooled more slowly, giving a much coarser grain size. Other than this difference, the two pourings seem to have been quite similar in composition, especially with regard to the iron content. An analysis of a sample drilled into part of the second pouring is reported in Table 2. The iron occurs in patterns similar to those of Figures 2 and 3, and also includes dendritic forms. Primary cuprite is scattered throughout. The junctures between the first and second pourings are obvious, since no welding occurred, and considerable corrosion has occurred along the junctures, with the normal formation of secondary cuprite and malachite. Figure 14 shows all the features described above. Figure 15 shows a massive agglomeration of α-iron spheres in the second casting.

Sample E

This specimen was listed as "part of a ring" and was sent to us by Dr. Frank Hole of Rice University for in-

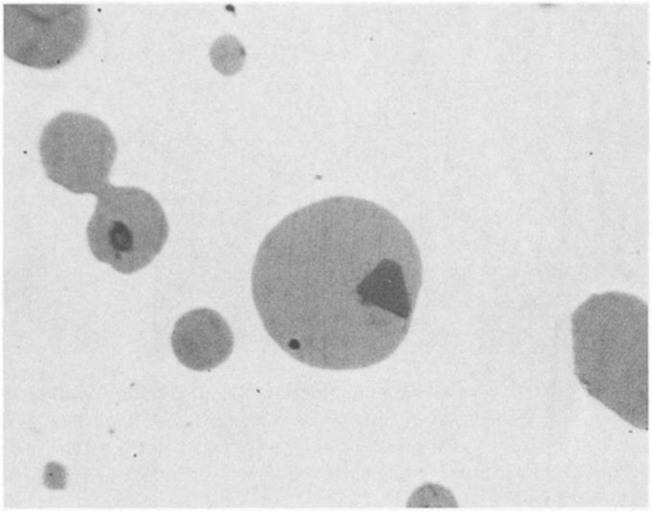

Figure 13. X 1200, yellow-green illumination, Sample C. Spheroidal chalcocite grains in a copper matrix. The central piece of chalcocite contains a small pit and an euhedral grain of iron-cobalt.

Figure 14. X 37, yellow-green illumination, Sample D. Etched with ammonium hydroxide and hydrogen peroxide, to illustrate the grain structure of the first pouring (left), and of the second, more slowly cooled, pouring (right). Corrosion has occurred along both sides of the juncture between the two pourings, with production of cuprite next to the metal, and malachite further out. The black material in the juncture is an infilling of an organic polymer to permit smooth polishing across the juncture. Irregular spheres and dendrites of α-iron (white) occur in both pourings. Some secondary cuprite (dark gray) occurs in both pieces of copper, adjacent to, but not at the juncture.

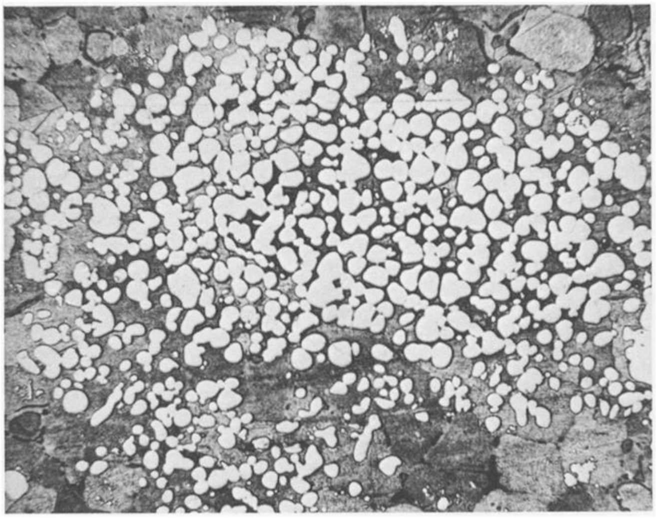

Figure 15. X 50, yellow-green illumination, Sample D. Portion of second pouring, etched as in Figure 14. The copper is of different shades of gray due to varying crystallographic orientations within each grain. The α-iron is white and exhibits its tendency to agglomerate.

vestigation in our continuing program of neutron activation analysis of ancient metals. It was tentatively dated to 6500-7000 B.C., but besides being magnetic, it was brassy yellow in fresh section. A spectrographic analysis showed the presence of substantial amounts of tin, zinc, lead and iron. In polished section the iron was distributed in the same patterns exhibited by Samples A and D, except for being finer in grain size. Etching showed that the sample had been worked into its present shape. Dr. Hole believes that this sample was a mediaeval artifact which had been carried to a lower horizon by burrowing animals or ants. The presence of metallic iron confirms the previously described laboratory experiment with a 10% tin bronze and iron.

Summary and Conclusions

1. Metallic iron, sometimes in substantial quantities, occurs more frequently in Iron Age and pre-Iron Age copper than has been formerly recognized. Since the magnetic response of an iron-containing copper is closely proportional to its bulk iron content, and is sensitive down to at least one percent iron, it affords a simple method of detecting this element in a sound piece of ancient copper, although useless with a completely corroded sample. Spectrochemically, some ancient coppers indicate very large amounts of iron, but this is illusory, since in our experience the metal is highly segregated in the copper matrix, and the validity of the analysis depends upon the location of the drill hole from which the analysis sample is taken. Again, there is always the possibility that the specimen is not representative of a finished product, but is instead material that has been discarded during refining or remelting. Of the five samples described in this paper, only the Iron Age tripod foot from Olympia, and the portion of a finger-ring from Ali Kosh are obvious parts of manufactured objects.

2. Iron in Iron Age copper can be attributed to a number of factors, such as the use of iron manipulative tools and stirring rods in remelt operations. However, it is probable that the coating of iron oxide formed on heated iron at the implied temperatures would act as an effective barrier to solution of the underlying metal. It is also possible that copper ores were on occasion smelted in pre-existing iron bloomery furnaces, thus affording an excellent opportunity for remnant iron to be taken up by the copper.

Another possibility is that general improvement in furnace construction and operation that came with increased sophistication in pyrometallurgy led to higher temperatures and increased reducing conditions in copper smelting. Under moderate conditions, excess of ferric oxide used as a flux appears as the common slag constituent, magnetite (Fe_3O_4), or under more drastic conditions, as wüstite (FeO). Increase in the charcoal content of the furnace burden and a high air-blast rate is capable of causing reduction of any of these oxides to metallic iron in the solid state. With simultaneous reduction of the copper minerals to copper, the liquid copper will dissolve the iron on contact. It seems to the authors that the foregoing is a valid explanation for the occurrence of many high-iron coppers from the Bronze Age down through the Iron Age.

3. In sulfide copper ores, iron occurs as iron sulfide (mainly as pyrite), and the copper as its sulfides, chalcocite and covellite. There will also be present iron-copper sulfides such as chalcopyrite and bornite, and usually other sulfosalts. Unless such an ore is thoroughly pre-roasted prior to smelting, there will always be available a certain amount of sulfur. During smelting, there will be a partition of the iron between the siliceous gangue constituents of the ore, yielding slag, and the sulfur, giving iron sulfide. Some copper sulfide will react with the iron sulfide to form matte. However, both iron and copper sulfides may enter the copper. Thus Maddin and Muhly[19] have shown that an ox-hide ingot from the Cape Gelidonya wreck averages 10% iron, some occurring as an iron-copper sulfide, the remainder as poorly slagged hematite included with the copper. They infer from their observations that the ore was smelted at too low a temperature.

On the other hand there is the evidence of metallic

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[19] R. Maddin and J. D. Muhly, "Some Notes on the Copper Trade in the Ancient Mid-East," *Journal of Metals* 26 (1974) 24-30.

iron in the copper prills occurring in the Timna slags.[20] From the mineralogy of the ores used at Timna, it appears that they were either low in sulfur[21] or contained a mixture of copper carbonate and iron sulfide which would make them, in part at least, self-reducing, so that most of the sulfur would pass off as sulfur dioxide in the furnace gases.

In one of our samples (A) chalcocite occurs in relatively small amounts, in close physical association with the metallic iron, but with no evident interaction. In a second sample (C) there is abundant chalcocite encapsulating an alloy of iron and cobalt. It therefore seems that moderate amounts of sulfur do not prevent the formation of metallic iron. In some Mycenaean Cypriote smelting slags there has been found no metallic copper, but there are complex copper-iron sulfides and free iron sulfide. In many Roman Cypriote slags, iron-free copper prills are associated with copper sulfides and complex copper-iron sulfides. These slags are all typical fayalitic copper-smelting slags. Quite evidently there was sufficient sulfur to prevent formation of metallic iron, although frequently both magnetite and wüstite are abundant slag constituents.

The implication of the foregoing discussion seems to be that the high-iron coppers we have examined were produced from essentially low sulfur ores, i.e., oxide and carbonate ores, mixed at most with small quantities of sulfides.

Alternatively, a quite thoroughly pre-roasted sulfide ore could have been employed for smelting, but we are unaware of any existing proof that this procedure was employed in the Early Bronze Age.

4. It should be stated that a long-term investigation of copper-smelting slags currently under way at the University of Minnesota has brought to light no examples of metallic iron in copper prills, nor of metallic iron in the slags themselves. However, slags produced as a result of smelting simple copper oxide ores seem to be rare. These, presumably antedating the use of high sulfur ores in any given locality, are either buried under the later slags, or, as in the case of the "Phoenician" slags of Cyprus, are so thoroughly oxidized that they contain no material identifiable as former metallic iron, even if it has been originally present. On the other hand, if metallic iron were produced as a result of overdriving a copper smelting furnace, it is quite possible that the relatively large amount of copper would have dissolved the iron and removed it from the slag.

5. Although we have, as yet, very restricted data to work from, there appears to be a marked regional difference between the relatively high iron content of the circum-Mediterranean coppers and those from central to northern Europe. If correct, the difference may be explained by either a difference in smelting techniques or by a difference in the available ores. Unfortunately, any such broad generalization suffers from an inadequate number of analyses from the Mediterranean and insufficient metallographic studies from both areas.

6. It should prove extremely interesting to physically separate the necessary number of iron-bearing prills from unoxidized Timna slag to permit exact conventional chemical analysis. Spectrographic analysis and surface physical methods are useless, because of marked segregation of the iron in the copper. Milton[22] refers to such prills about 1 cm. in diameter, or approximately 4 gm. of metal, more than sufficient for analysis of all major elements, and assignment of the elements according to the mineralogical entities identified microscopically. This in turn, through use of the data of Figure 7, should provide an answer to the much-vexed question of the temperature reached in an ancient copper-smelting furnace, certainly a minimum value, and with some luck, a maximum temperature. In this regard, our finding of well-developed euhedral crystals of low-iron, low-manganese spinel, the first mineral to crystallize in some ancient copper-smelting slags which we have examined, is indicative of higher furnace temperatures than have been previously accepted.

7. If it can be shown that an appreciable number of pre-Iron Age artifacts (as contrasted with material which was spilled or deliberately rejected) contain the substantial amounts of metallic iron reported for the few samples discussed in this paper, then there follow some obvious implications regarding the operation of the smelting furnaces. In fact, a number of Late Bronze Age artifacts from Nichoria are ferromagnetic, but have not as yet been examined metallographically. If our conclusion No. 2 is correct, then an artificial air-blast is imperative, necessitating the use of bellows. Archaeologists should pay close attention to the recognition of such objects as tuyeres, tuyere nozzles, possible remnants of bellows (although from the nature of things, with wooden and leather constructure, only the nozzles are likely to be found), to furnace grouting, and to furnace wall thickness, the last two being relevant to conservation of heat energy. The use of a dense hard charcoal would also be beneficial in attaining high temperature.

8. Laboratory experiment shows that a 10% tin bronze readily accepts metallic iron to give an alloy containing 8% iron. The microscopic disposition of the iron is very similar to that in the copper-iron alloys.

9. Since it calls for an extensive separate investiga-

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[20] Ibid.

[21] Tylecote et al., op.cit. (in note 4).

[22] Milton, op.cit. (in note 2).

tion, no determination of the effects of iron on the mechanical properties of copper were made. A few percent of iron would not be expected to have any marked effect upon malleability, work-hardening, etc., nor upon casting properties.

Acknowledgments. We wish to gratefully recognize the help provided by Mr. Bruce Nielson in making the microprobe analyses reported in the paper and by Dr. Paul Weiblen for providing time on the microprobe. Grateful acknowledgment is due to Professor George Rapp, Jr., for his financial assistance through the Science and Archaeology Fund and for his continued interest in this work. Thanks are owed to Miss Jennifer Moody for her careful reproduction of the original line drawings for Figures 1 and 7, and to Miss Sandra Meixner for typing what at times must have been a difficult rough draft. The analyses of the Sardinian samples were made possible by Grant No. 6798 from the Penrose Fund, the American Philosophical Society.

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Stanley Aschenbrenner was born in Spokane, Washington, in 1929. He received a B.A. (Philosophy) in 1951 from Willamette University, Salem, Oregon, and an M.A. and Ph.D. (Anthropology) in 1968 and 1971 from the University of Minnesota. Since 1969 he has been with the Minnesota Messenia Expedition and its excavations. He is a Research Associate in the Science in Archaeology group at the University of Minnesota.