# **IRON IN ANCIENT COPPER**

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#### **INTRODUCTION**

Ancient bronze is rarely pure, and of all the ancillary metals found therein, iron is one of the most interesting yet sadly one of the most neglected.

This paper deals with two very different aspects of iron in copper. The first concerns the origin and significance of the small traces of iron found in all copper and its alloys, whilst the second part deals with the unusual but extremely interesting instances where considerable quantities of iron were deliberately induced into the copper during the smelting to give alloys which are without parallel in the modern world.

Programmes of analysis of ancient bronze artefacts have been running for half a century now, and in the past have often concentrated on the trace element content of the metal in an endeavour to group the artefacts on the basis of composition, or to provenance the copper. This work was carried out with only the most perfunctory knowledge of the available ore sources and their mineralogy, and the processes of mining, benefication, smelting, fluxing, refining and alloying etc. that lie between ore and artefact. Over the last twenty years there has been a series of surveys and excavations of early mining and smelting sites (Craddock 1980) coupled with the detailed scientific examination of the smelting debris (Craddock and Hughes 1985). These studies together with a series of carefully controlled and recorded copper smelting experiments (Merkel 1985) have greatly enhanced our knowledge of ancient metallurgy.

This, and the greatly increased analytical data base, has led to a better understanding of the origin and significance of the residual trace elements. With this knowledge it is possible to use the trace element data more intelligently for provenancing problems and to reconstruct the ancient processes by which the artefacts were made.

One of the benefits of running large scale, wider ranging analytical projects generating hundreds or even thousands of analyses from a variety of diverse cultures around the world are the intercomparisons that become possible. Analyses of early copper-base alloys (where the iron content has been determined) show that the copper almost invariably contains measurable iron. When large numbers of analyses from different cultures are considered together, some interesting trends appear (table 1). The iron content tends to rise quite substantially in the copper alloys of any region when the local cultures attain a certain level of technical civilisation, or encounter other more advanced groups.

It has long been understood that iron enters the copper during smelting (Cooke and Aschenbrenner 1975, Tylecote and Boydell 1978), and the explanation for the rise in iron content noted above almost certainly lies in changes in smelting practice, in particular, the introduction of deliberate slag formation within the furnace. Recognition that the low iron content regularly found in metalwork of the European Bronze Age implies a simple

	Sample size	Average % Fe content	% of artefacts below 0.05% Fe
(a) Predynastic-1st dynasty Egypt 2nd Dynasty-New Kingdom Egypt (Cowell 1986)	14 250	0.03 0.33	82 6
(b) Cycladic EB II (principally the Kythnos Hoard BM Reg. 1969, 12-31, 1-10)	16	0.04	55
Minoan, Greek, Etruscan and Roman	3062	0.23	26
(c) Bronze Age Britain	773	0.05	79
Iron Age Britain	56	0.18	29
Ro mano-British	129	0.27	4
<ul> <li>(d) Phoenician Iberian from SE Spain</li> <li>(Morro de Mezquitilla, Giumlia 1985; Tejada, Craddock 1981)</li> </ul>	104	0.27	14
Chalcolithic-Middle Bronze Age SE Spain (Hook <i>et al.</i> 1986)	195	0.05	73
La e Bronze Spain	49	0.04	95

 Table 1 Comparative iron contents of bronzes from various cultures

(a) Iron content of Egyptian bronzes (Cowell 1986) comparing Predynastic and First Dynasty with subsequent dynasties.

(b) Iron content of Cycladic bronzes (Craddock 1976) compared with Later Minoan and classical bronzes.

(c) Iron content of bronze from Britain comparing Bronze Age, Iron Age and Roman (Craddock 1986a).

(d) Iron content of bronze from Spain comparing Phoenician and Iberian culture of south east Spain with the chalcolithic and Middle Bronze culture which had previously occupied the region and the contemporary Late Bronze Age culture from central and north vest Spain.

Source, Craddock and Meeks unless otherwise stated.

non-slagging process and explains why so few remains of smelting, as compared with mining, have been identified in Europe. The evidence is not lost, it probably never existed.

The interpretation given here of the analytical data relies very heavily on the experimental smelting experiments of many others, but especially on the pioneer work of Tylecote and his co-workers (Tylecote *et al.* 1977, Tylecote and Boydell 1978). Langley and Reynolds based at the Iron Age Farm experiment at Butser, Hampshire in England have done important work, as yet unpublished, on primitive smelting successfully producing copper from very high grade ore in the simplest of furnaces.

For the more advanced processes of the Middle East Bronze Age where slagging was regularly employed the work of Merkel (1982, 1983, 1985) is of great importance. The many experiments and detailed measurements of all parameters within his furnace have proved of great value to the authors, as was the opportunity to work with him on some of the smelts, and to be able to examine and compare sections of the metal produced by him under controlled conditions with those from metal produced in antiquity.

The copper produced by the more advanced smelting process regularly contained several per cent of iron and this rendered the primary smelted copper unworkable, thus necessitating a refining process to lower the iron content to acceptable proportions as found in the surviving metalwork but, in certain rare instances, the iron content was actively encouraged



Figure 1 Histogram of iron content of copper and bronze metal from the Late Bronze Age smelting camps at Timna; southern Israel (source, Craddock 1980).

and even boosted to produce copper with between 10% and 40% of iron. Although uncommon, the occurrence of this strange metal is widespread with examples known from China, India, Etruria and even from Britain. The one factor they have in common is their use as some form of currency.

### IRON IN COPPER: AS AN INDICATOR OF SMELTING PROCESS

Some large analytical projects undertaken by the British Museum Research Laboratory have included material from ancient Egypt (Cowell 1986), Sinai (Craddock 1980a), the Bronze Age of Greece (Craddock 1976), Spain (Craddock 1981) and Britain (Craddock 1980b), and the Classical Greek (Craddock 1977), Etruscan (Craddock 1986a) and Roman civilisations (Craddock 1985a). Of all the minor and trace elements regularly found in early copper, iron is the most dependent on the smelting process (Cooke and Aschenbrenner 1975, Tylecote and Boydell 1978). Thus the iron content of the thousands of bronzes covered by these projects were studied for any discernible trends that might be related to the smelting process. The iron contents fell broadly into a single unified pattern, and gratifyingly this was a pattern which agreed with the surviving archaeological field evidence for early smelting. Some of the results are summarised in table 1. It must be emphasised from the outset that there are very considerable variations in the iron content of individual bronzes, and trends only become meaningful when taken in groups of at least ten analyses, and preferably many more. Even so individual high iron contents can distort the average iron content, particularly of the low iron group, and thus the percentage of bronzes with iron contents falling above or below 0.05% have also been included in the figures.

## P. T. Craddock and N. D. Meeks

Basically, copper from very early or relatively primitive societies has much less iron than that from later or more advanced societies (table 1 and figure 1). Thus, for example, copper artefacts from Predynastic and the First Dynasty of Egypt have an average of 0.03% iron, and this rises quite abruptly during the Second Dynasty (around 2900 B.C.) to 0.33% at which level it was to remain with fluctuations at least until the New Kingdom (table 1(a)).

The 16 Cycladic bronzes dating from the early third millennium B.C. analysed as part of the much more extensive Classical bronze programme (Craddock 1976) have an average iron content of 0.04%, compared with the average of 0.23% for the remaining 3045 bronzes dating from the Greek Middle Bronze Age on to the end of the Roman Empire (table 1(b)). In Britain and much of Western Europe the higher iron content did not occur until much later, during the Iron Age, and was probably coincident with the improved smelting technology needed to smelt iron itself (table 1(c)). Sometimes the change-over can be directly associated with the arrival of a more advanced culture. Thus the 49 bronzes from Late Bronze Age Spain have an iron content of over 0.04% whereas the 104 bronzes from the broadly contemporary Phoenician and Iberian settlements of Morro de Mezquitilla (Giumlia 1985) and Tejada (Craddock 1981) in the south-east of Spain have an average iron content of 0.27%. Further, the average iron content of copper from the preceding Millarian and Agaric Bronze Age civilisations, who occupied the same area of Spain and who presumably used the same sources of copper is 0.05% (Hook *et al.* 1986) (table 1(d)).

As a postscript to this section, the frequent occurrence of relatively high contents in Geometric and Archaic Greek bronze tripods should be noted. Craddock (1977) analysed the surviving fragments of a Geometric tripod, now in the Ashmolean Museum, Oxford (cat. 377, Boardman 1961). The handle, statuette and rivet which are bronze, and the bowl and strut which are copper contained between 3.4% and 7.9% iron. Apart from noting that the sheet metal of the bowl with 7.9% iron must have been difficult to work, no further comment was made. Apparently existing in isolation, it was just a curiosity. However, more recently Filippakis *et al.* (1983) have analysed many more tripods from Delphi and Olympia and have found that no fewer than 14 out of 24 tripods in their categories 1–3 contain between 1% and 6% iron. This high iron content is almost certainly the result of using unrefined copper. However, several hundred other Geometric and Archaic Greek bronzes have been analysed (Craddock 1976, 1977) and the extensive use of unrefined copper is completely unparalleled for any other artefact types and is as yet unexplained.

Other examples could be given but it does seem clear that the enhanced iron content in copper is related to general technical progress either chronologically or culturally in a given area. It is also noticeable that the general level of iron in the early copper or primitive copper (around 0.05%) is much the same everywhere, be it from Egypt or Britain and the same is true of the enhanced levels associated with more advanced copper production where an average level of around 0.3% is fairly typical. This suggests that there is a single explanation for the origin of iron in the copper and for the observed rise in iron content in all the cases observed. The iron entered the copper during smelting and it is now necessary to consider the early smelting processes in more detail.

## Early copper smelting

Knowledge of early copper smelting has been largely derived from the excavation of sites such as Timna in Israel where large heaps of slag and furnace fragments bury the remains of *in situ* furnaces (Rothenberg 1972). However, most of these sites in the Middle East are of the full Bronze Age and few, if any, smelting places have been recognized for the Chalcolithic and Early Bronze Age of the Middle East, or for the whole of the Bronze Age from less advanced areas such as Western Europe. But from both areas come the remains of early mines, and of course copper and bronze artefacts so smelting must have been practised. From the very ephemeral surviving archaeological evidence, or perhaps more correctly its absence, and from some experimental smelting projects, it has been suggested (Rothenberg 1978, 1985, Tylecote 1976) that at the inception of copper smelting the process was very simple indeed.

Copper minerals such as malachite, azurite or cuprite which were easily recognised and occurred in the upper, oxidised zone of the ore bodies would have been carefully sorted (beneficated) by crushing and hand sorting, to pick out the highest possible grade of ore, probably containing 60% or more copper. This ore would have been smelted in a small clay furnace, probably of the size and shape of a small upturned bucket but lacking its bottom. The fuel would have been charcoal with air supplied from bellows. After about an hour of operation sizeable discrete prills of copper, about the size of pigeon eggs or smaller, would have formed in the bottom of the furnace, entrapped in a mass of cinder, ash and possibly some poorly fused slag. The carefully beneficated ore contained only small amounts of iron minerals, and the relatively low temperatures and poor reducing conditions in the furnace would have presented little opportunity for such iron minerals as were present to be reduced to metallic iron and to become incorporated in the copper.

Although this process was very quick it was highly inefficient. Only the highest quality ore could be used and only a small percentage of that was converted to metal in the furnace. By the full Bronze Age of the Mediterranean-Middle East region much more advanced smelting techniques were in use, operating at higher temperatures under more reducing conditions, and with a further, fundamental advance, deliberate slagging. If lower grade ore (of the order of 20-30% copper after benefication (Merkel 1985)) was to be successfully smelted then it was essential to remove the much greater proportion of waste rocky material (gangue) from the furnace or else it would rapidly just choke up. Typically oxide ores are associated with quartz or silica-rich rock, as gangue, and the sulphidic ores with iron minerals. Sometimes the ore contains substantial quantities of each, and where these ores were used in early smelting the iron minerals would have combined with the silica to form a relatively low melting (1200  $^{\circ}$ C) iron silicate slag. By poking a hole in the side of the furnace this could be run off, freeing the furnace of gangue, ready for more ore. The potential of this was realised and where the gangue was silica rich, iron minerals were added (very occasionally manganese) and conversely when the gangue was iron rich, crushed quartz or some other form of silica was added to act as a flux in the deliberate production of a tappable slag. With the ability to clear the furnace of gangue periodically the smelt could be prolonged by the addition of more ore, fuel and flux until a considerable body of copper had built up in the furnace bottom. Scientific studies of furnace fragments from Timna suggest that smelting times of between five and twelve hours were usual (Tite et al. 1982). By prolonging the process for many hours almost all the available copper ore would have been smelted and the copper droplets would have had ample time to drain through the slag to form an ingot of several kg beneath on the furnace bottom. The efficiency of the process is shown by analysis of the slags which typically show copper values of between 0.3% and 1% for slags from the Late Bronze Age onwards, and these figures were not substantially reduced until Post Medieval times. However in the hotter and more reducing



Figure 2 Copper-iron equilibrium diagram (after Daniloff 1948).

conditions prevailing in these more advanced furnaces some of the iron minerals, now inevitably present either in the ore itself or added as a flux, would be reduced to metallic iron. Iron has considerable solubility in molten copper (about 6% at 1200 °C, see below p. 198 and figure 2) and during the long smelt there would have been ample opportunity for the copper to pick up iron whilst the small droplets drained slowly through the iron-rich slag. The forming ingot in the base of the furnace could contain therefore several per cent of iron and indeed spills and droplets of copper from smelting sites are regularly rich in iron. The tange of iron contents in metalwork found at Timna (mainly artefacts) is shown in figure 1. (Full analyses are given in Leese et al. (1986).) In fact the question should rather be why do most copper alloy artefacts from the Bronze Age on contain so little iron? The answer is that copper with this amount of iron is almost impossible to cast or hammer to shape and the necessary refining techniques are very simple. The raw copper was melted in an open crucible and the iron allowed to oxidise and then form a slag by sprinkling clean sand or crushed quartz on to the surface. The distinctive crucible slag could then be skimmed off the surface and discarded. Tylecote et al. (1978) found it easy to reduce the iron content by this method to about 0.5%, but further reduction was progressively more difficult. Merkel (1982) made copper using a reconstruction of the Timna furnaces (see below for a further description) and was able to reduce the iron content to only 0.014% by subjecting the molten copper in the crucible to an air blast. Analyses of Bronze Age and later metal show that the smiths rarely bothered to carry refining this far, probably because the further increase in purity achieved would have made no perceptible difference to the meta].

The differences in iron content discussed above (table 1) almost certainly arise through differences in the smelting process, those averaging around 0.05% having been made by the short simple process and those averaging around 0.3% having been made by the more sophisticated process involving slagging. Thus the iron content in the surviving datable bronzes does give an indication of the contemporary copper smelting technology in the relevant area.

The recognition that the low iron content in copper indicates a smelting process without slag formation can perhaps explain the apparent absence of smelting sites in much of Western Europe in prehistory. Ancient copper mines are known from all over Europe but few away from the Mediterranean area have yet been found associated with smelting debris dating before the Iron Age (Craddock 1986b). This has proved hard to explain. Most smelting was done in the vicinity of the mines as it was much more economic to transport metal rather than the ore no matter how well beneficated. Also most ore deposits tended to be in mountainous or marginal lands where large tracts of woodland needed for charcoal survived the pressures of agriculture. If smelting had produced slag in the vicinity of the mine it is difficult to understand why it should not survive. It would have been produced in quantity; it is virtually indestructable and is only rarely worth reusing. As the mines tend to be in marginal areas away from agriculture there should be little plough damage. The usual explanation given is that later workings will have totally destroyed the earlier evidence. Later activity can sometimes of course damage or disturb the early workings but rarely obliterates them completely. Furthermore, if this is the explanation, why do the mines themselves survive and mining tools remain on the surface to be picked up to this day, and why does slag and smelting debris survive so prolifically in the Middle East and the Mediterranean areas which should be subject to the same agencies of disturbance and destruction? If the explanation of the lower iron content in most of the copper melted in prehistoric Europe presented here is correct then the absence of slag is also explained. Slag heaps are not found associated with the prehistoric mine workings quite simply because they never existed. The primitive process in use up to the end of the Bronze Age at least in much of Europe, as documented by the surviving metalwork, did not produce tap slags.

Smelting experiments carried out by Langley and Reynolds at the Butser Iron Age Farm project in Hampshire, England using a high grade malachite ore in a very primitive furnace such as is envisaged here proved very illuminating. Copper metal was produced satisfactorily but within a fortnight of the experiment there was no recognisable trace of the smelt. The furnace walls had completely disintegrated and no tap slag had been produced. The ash, cinder and non-vitreous slag which had formed in small quantities had been broken up to extract the small prills of copper and then further crushed and scattered underfoot. Only if the furnace fragments and other refractories had become incorporated in a growing slag heap immediately after the end of the smelt could recognisable fragments survive for weeks, let alone millennia. (Addendum: a sample of copper from ore of the Butser smelting experiments contained 0.08% iron.)

### IRON AS A MAJOR METAL IN COPPER

In the previous sections it has been shown that several per cent of iron can routinely enter copper during the smelting. The percentages in figure 1 from the copper smelting site of Timna, or in the Geometric Greek tripods with up to 10% iron, mentioned above, are quite

			T.	ible 2 C	ompositio	10 (%) u	copper-h	ase metal	with high	iron cont	ent*					
Description		() u	Εċ	Sn	Чd	ΑŖ	Sh	N	Чи	C.	4. A	<i>P.</i> 3	Bi	7.n	Мn	S
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Ingot from Anhui. Rth 3rd century B.4 (Zhang Jingguo et a A base Dobunic silv coins, from Bredon England, dating to Ist century B.C. A (Sutherland 1955)	China C. A. 1985) A. 1985) Arrier Hrithe D.	62.88 73 83 55 55	34.35 <i>Fe</i> 19 29 29	<ul> <li>relative to</li> <li>(21)</li> <li>(8)</li> <li>(15)</li> <li>(35)</li> </ul>	0.06 Cia	8 10 12 10 8	0.233									2.08
<ul> <li>Instances of x</li> <li>BM Reg. No.</li> </ul>	very high ir. Weight	n content Table 3 Cu	in copper, i Compositi	reported el: on (%) o	sewhere ( , , , , , , , , , , , , , , , , , ,	not detect cco hars j Ag	ed; blank from the 1 Sb	implies not Departmer Ni	reported). 11 of Coin Au	s and Me Co	dals, Bri As	tish Mus Cd	r una	õ	u.X	WW
74.7-14.101 74.7-14.104 74.7-14.104 74.7-14.105 74.7-14.105 74.7-14.106	2247 829 815 665 665	67.0 75.0 71.5 71.5 72.5 78.0	231.3 231.3 26.4 20.3 20.3	0.300 0.080 0.800 0.120 0.700	0.200 0.100 0.100	0.060 0.065 0.060 0.080 0.050	0.200 0.280 0.040 0.300	0.030 0.024 0.040 0.040 0.040	0.008 0.007 0.008	0.001 0.060 0.060 0.060	006.0 001.0 009.0 009.0 009.0	00.0		010	0.300 0.600 0.300 0.300 0.300 0.300 0.300	100.0
74.7-14.102 rumo secro bar from Bocca Lorenza Vicenza, Italy (Matteoli and Storti	1410 1 1982)	62.8	35.7 (	0.002	0.009	0.5	0.001	0.032		0.110			0.0	002	0.00	0.014

194

# P. T. Craddock and N. D. Meeks



Figure 3 Large fragments of two ramo secco bars from Italy sixth-third century B.C.: left, BM Reg. 74.7-14.104; right, BM Reg. 74.7-14.101.

typical of unrefined copper. Usually the iron was substantially reduced by refining, but scattered throughout the literature are reports of copper-based artefacts with much higher iron contents, typically between 20% and 40% (tables 2 and 3). It seems that in these cases the iron content has not just been tolerated but actively encouraged. Significantly all the examples occur in metal which had been used as some form of currency, where weight was the primary consideration, and where in the volume production of the currency a given weight of copper ore would have produced 20–40% 'extra' metal straight from the furnace. Although quite widespread most are isolated examples. However, there is one reasonably well-documented group which regularly have a high iron content. These are the *ramo secco* bars found throughout Italy usually in contexts dated between the sixth and third centuries B.C. (figure 3) (Burnett and Craddock 1986). A bar found at Bitalemi near Gela in Sicily was found with pottery of the mid-sixth century B.C., but other bars have been found in Roman coin hoards dated as late as the third century B.C. The bars are often found with coinage and they are generally considered to be primitive precursors of the Roman *bar aes*.

Although these bars were made to no fixed weight standard, they all have the same general appearance, about 30–50 mm thick, 75–95 mm wide and of varying length. Their most distinctive feature is their cross section with its distinctive flanges, and very often the bars are more or less wedge shaped and bear prominent mould marks showing that they have been cast into a simple two piece ingot mould. The name *ramo secco* is taken from the design of a branch which usually occurs on one or both sides of the bar. Analyses given in table 3 show that they are of highly ferruginous copper. Another bar, from the Bocca Lorenza cave near Santorso Cuicenze, was recently analysed by Matteoli and Storti (1982), and found to contain 35.73% iron. This bar was mistakenly identified as being Late



Figure 4 Typical example of dendritic iron-rich alpha phase in copper-rich epsilon phase matrix, from one of Merkel's experimental furnaces. Mid-grey inclusions are copper iron sulphides, and fayalite slag shows as the dark inclusions (magnification,  $\times 200$ ).

Neolithic on the grounds that it was found by a farmer *near* where four copper axes of undoubted Late Neolithic date had been found in a cave. Significantly their average iron content was 0.015%. The bar had the distinctive wedge shape and mould marks of a *ramo secco* bar.

Because the iron content is regularly much higher than that expected from ordinary copper smelting, even before refining, it seems possible that the iron was deliberately encouraged to enter the copper. This poses a number of questions: (a) what is the metallographic structure of these highly unusual alloys? (b) how were they made? (c) what was the function of such an intractable and apparently useless metal?

# Metailographic structure of the ramo secco bars and comparative material

Two metallographic sections were cut from *ramo secco* bars and two from copper produced by Merkel using a reconstruction of a Late Bronze Age furnace from Timna, Israel (Merkel 1982) The ore used in these experimental smelts was malachite from Timna itself, which can however contain significant quantities of sulphur.

In all four samples the iron is concentrated in iron-rich alpha phase dendrites in a matrix of the copper-rich epsilon phase (figures 2 and 4–6). (At the freezing temperature of 1100 °C the iron-rich gamma phase of the dendrites contains about 8% copper but after further cooling this transforms to the alpha iron phase containing only 1.4% copper in solid solution. The remaining 6.6% copper within the dendrites precipitates out as the epsilon phase with 98% copper. 2% iron, as can be clearly seen in figure 7.) In both the *ramo secco* bars there are macroscopic globules of both copper–iron sulphides (presumably surviving unreduced from the original pyrites ore) and slag.



Figure 5 Partition zone between copper (bottom right), containing fine precipitated iron-rich alpha phase, and fayalite slag (top left). Note the iron-precipitate depleted zone adjacent to the slag (magnification,  $\times$  2000; Merkel sample).



Figure 6 Ramo secco bar showing dendritic iron-rich alpha phase, round inclusions of copper/iron sulphides and a large globule of fayalite slag (black) within a large sulphide inclusion (magnification,  $\times 32$ ).



Figure "Iron-rich dendrites containing precipitated copper-rich epsilon phase are seen with interdendritic copperrich epsilon phase matrix (magnification,  $\times 800$ ) in ramo secco bar.

Iron has a limited solubility in copper just above the melting temperature (2.8% at 1100 C rising gradually to 20% at 1400 °C, then increasingly sharply to 70% solubility by 1450 °C). If however sulphur, as copper sulphide or as copper-iron sulphide is present in significant quantities ( $\ge 2\%$ ) then the situation changes drastically, for example 20% iron can be accommodated in solution at only 1200 °C with 2% sulphur, and if 3% sulphur is present then the system can accommodate up to 40% iron at about 1300 °C (Rosenqvist 1983 p. 326). Our analyses of the bulk sulphur content of the four samples sectioned are ambivalent, two, the *ramo secco* bar 74.7-14.104, and Merkel's copper from smelt No. 21 contained about 2% sulphur, but bar 74.7-14.101 and Merkel's smelt No. 29 contained less than 0.2% sulphur overall, although a few isolated pyrites inclusions were observed.

In all samples the sulphur was concentrated entirely in small globules of copper-iron sulphide with the stoichiometric composition equivalent to  $CuFeS_2$ , which has a melting point of about 950 °C, and thus would be the last phase to solidify, hence its appearance as dispersed globules. However, as well as these small inclusions there are also much larger globules which seem never to have been in solution, possibly because there had been insufficient time for that particular piece of ore or matte to dissolve before the metal was tapped: clearly the system was not in equilibrium, and thus the published copper-iron diagram cannot be applied too rigorously. Even so it is very likely that the two sulphur-rich metals could have accommodated their iron in solution, rather below 1400 °C, but with the other two pieces with low sulphur, the presence of the iron-rich phase in a dendritic form indicates that the iron was once all in solution and that the temperature in the furnace was apparently in excess of 1400 °C which is much higher than is usually accepted for early furnaces. Thus special attention was paid to the possibility that much of the iron was

present as discrete particles in the copper and not in solution so removing the problem of the high temperature required. Merkel's practice was to bring the furnace up to full operating conditions before any ore was charged and then to add the iron oxide flux before the copper ore. This procedure could have produced conditions more akin to those in a bloomery furnace for producing iron and solid particles of iron could easily have been produced by direct reduction and incorporated later as inclusions in the forming copper metal. This was suggested by Clough (pers. com.) who had observed some particles of iron which had clearly never been in solution in Merkel's copper. Further, if the iron contains a small amount of carbon then the melting point drops dramatically (iron with 4% carbon melts at 1147 °C, compared with 1550 °C for pure iron). A large but isolated inclusion of molten or cast iron was observed in one of Merkel's samples examined by us (No. 21, see figure 8). This contained about 3% carbon, i.e. it had a cast iron structure and would have melted at about 1300 °C. A similar globule of cast iron has been observed previously in an ancient piece of copper (Tylecote et al. 1983). This was in a fragment of a Late Bronze Age copper ingot from Sardinia, found in the Nuragic settlement of Sa Sedda'E Sos Carros at Oliena, near Nuoro.

However, no solid particulate or cast iron was observed by us in either of the *ramo secco* bars examined and only the one small globule of cast iron in Merkel's copper. Clearly particulate inclusions of iron, be they solid or molten, cannot account for much of the iron which in total forms around 30% of the weight and even more of the volume of the metal. Thus, there is no escaping the conclusion that the bulk of the iron was once in solution in the copper.

This creates a major problem, for if the bars and Merkel's copper with low sulphur



Figure 8 Merkel's sample No. 21 is shown where white cast iron, at the top, is interfaced to copper at the bottom by way of dendritic, pearlitic iron (magnification,  $\times$  440).

content did once contain more than 20% iron in solution in equilibrium conditions the temperature should have been over 1400 °C which is substantially higher than furnaces are believed to have attained in antiquity. This problem must now be considered.

## Production of the iron-copper alloy

There are only two possibilities: either the copper was melted and iron added and dissolved, or else iron was encouraged to enter the copper during smelting.

The first possibility requires that the copper was melted in some form of crucible to a temperature of 1400 °C by some external source of heat, and thus the crucible must have also been at this temperature. No ancient refractories are known, from the Western World at least, which could have withstood such temperatures (Freestone *et al.* 1987). Second, the presence of large globules of slag and of copper–iron sulphides (surely the unreduced ore), is suggestive. All except the most microscopic inclusions of slag are almost unknown in copper alloys of any period since even the most perfunctory remelting will remove them. It would seem, therefore, that the copper had been run straight from the furnace into the mould and that no one was too concerned if a little slag and dross ran in as well.

It does seem therefore that the second possibility (i.e. that the iron entered the copper during smelting) is more likely and that the high temperatures can be reconciled with our present understanding of ancient smelting.

First, all of the temperature estimates for ancient furnaces have necessarily been made on the surviving fragments of the wall, and the thermocouples in Merkel's furnace were also mainly towards the edge. In the actual reaction zone immediately beyond the tuyere, the temperature could easily have been several hundred degrees higher. (On several occasions, Merkel's furnace *approached* 1400 °C *near* the reaction zone, and once burnt out a chromelalumel thermocouple that should have withstood temperatures well in excess of 1400 °C.) The furnace charge and slag act to insulate the furnace wall to some degree, and thus the higher temperatures were not encountered there.

It must also be stressed that conditions in the reaction zone of an ancient furnace where the iron and copper were being produced simultaneously in an atomic state, were decidedly non-equilibrium. The newly-formed iron could easily have entered into a supersaturated solution in the copper only to be shed as dendrites when the metal moved to a somewhat cooler more stable region below.

Having established that the iron-rich copper of the *ramo secco* bars is likely to have been formed directly in the smelting furnace, it does seem that conditions necessary to produce such a high iron content are markedly different from those that usually prevailed in ancient furnaces. Reconstructing the smelting furnaces has been enormously helped by the opportunity to work with Merkel on his smelting experiments and to examine some of the metal that he produced. The similarity in composition and metallographic structure of the *ramo secco* bars and Merkel's copper suggest the smelting conditions must have also been similar.

Merkel used a small clay furnace approximately cylindrical with a diameter of 30 cm and a height of approximately 100 cm which was believed to be very close in shape to those used in the Mediterranean area during the first millennium B.C. Throughout the experiments Merkel continually made minor changes to the ratios of fuel/ore/flux, and to the airflow rate through the tuyeres. Typically, however, the fuel to ore ratio was around 1:1, and the flux to ore ratio was around 4:1. The airflow was around 3501 per min and usually delivered through 3 tuyeres. Merkel himself recognized that the copper thus produced was much more ferruginous than ancient raw copper straight from the furnace, and suggested that this was because the furnace conditions were made too reducing by an excess of charcoal and possibly because there was an excess of iron oxide flux.

Merkel quotes the illuminating example given by Peters (1907), who was present at the blowing-in of a simple copper smelting blast furnace. This began to go disastrously wrong with the slag not flowing and the tuyeres beginning to block. Too much coke in the charge had created over-reducing conditions and large amounts of metallic iron had rendered the slag immovable. The local furnace men suggested yet more fuel in a desperate attempt to melt out the obstructions, but Peters stepped in as he said 'to save the furnace from total destruction', and told them to charge much *less* coke. After a while the furnace began to operate normally but the first copper tapped from it had 32% iron, similar to the *ramo secco* bars. Thus creating over-reducing conditions primarily by an excess of fuel had led to a high iron content.

The presence of large slag globules in the *ramo secco* copper suggests that no subsequent refining took place and that they are as cast from the furnace. Thus the highly ferruginous copper bars were probably made by charging excessive amounts of charcoal with the iron-rich ore to the furnaces, and running the resultant metal straight from the furnace to the mould. The presence of pyrites or other sulphur-rich ores in the furnace could have promoted the dissolution of the iron but its erratic content in the samples examined here both from the *ramo secco* bars and from Merkel's copper suggests it is not the primary explanation of the high iron content in solution.

## Why was the alloy made?

Having established the metallographic structure and how these highly unusual pieces were made, it remains to suggest why they were made. With its high sulphide and slag content in addition to the iron, the metal was almost impossible to cast satisfactorily to any useful shape and quite impossible to work. It was in fact useless for any utilitarian purpose.

Instead, the most probable role of the bars was one of currency and, significantly, many have been found in hoards together with coins. In this context the presence of the iron is just an adulterant to lower the cost of production. The conditions of the copper smelting process were so fixed to maximise the yield of metal from the ore irrespective of its quality. Many contemporary and later coins are of unrefined copper often adulterated with large amounts of lead. Thus the Roman bar *Aes*, which succeed the *ramo secco* bars regularly contain between 20% and 25% lead (Burnett, Craddock and Meeks 1986), and much of the Late Etruscan coinage was regularly adulterated with massive amounts of lead. It is perhaps significant that the introduction of copper coins adulterated with lead coincided with the introduction of silver coinage in Italy and the availability of lead to the coin makers. The use of lead seems to have superseded the practice of making highly ferruginous copper.

Two other examples of currency using this ferruginous copper alloy are known to the authors. Firstly, there are coins of the seventh century A.D. from India analysed by Hegde (1975) which contain between 20% and 40% iron and which presumably were made by a similar process to that described above. Secondly, there are the very base silver coins of the Late Iron Age from Britain containing between 55% and 83% copper, and 7% and 29% iron (8% and 35% relative to the copper) (Sutherland 1955). Also, in the Classical world, coins were very occasionally made of iron itself. For example, a Greek coin of the fifth century B.C. from the British Museum (Coins and Medals Registration No. 1925.3-1.1)

which was examined by us had a structure typical of wrought iron, although there was some copper in the surface. The copper probably came from prolonged contact with corroding copper, possibly in the form of other coins.

A part from currency, instances of the deliberate production of ferruginous copper are very rare. From China there is an ingot of Eastern Zhou period (eighth-third century B.C.) (Zhang Jingguo *et al.* 1984) with 34% iron, and from Greece, there is copper from Macedonia of the Geometric period (eighth-seventh century B.C.) which apparently contained 18% iron, although the metal was corroded and the analyses only totalled 74% (Heurtley and Davies 1927).

Finally, there is one literary reference: Pliny (*Natural history*, Book 34, Chapter 40) describes a statue of Athamas in Rhodes by Aristonides who worked in the second century B.C. Aristonides is said to have 'made a blend of copper and iron, in order that the blush of shame should be represented by the rust of iron shining through the brilliant surface of the copper'.

### CONCLUSION

A study of large numbers of copper alloys from a wide range of cultures and locations show that the earlier, more primitive metalwork has a much smaller trace of iron than is found in the late metalwork. Iron enters copper during the smelting process and the change in iron content is indicative of a change in smelting practice. Very early copper smelting was probably a short, simple but inefficient process using very rich ores. Later more sophisticated processes successfully smelted lower grade ores which were either often rich in iron or to which iron minerals were often added as slag former. Thus the rise in the iron content of the resulting copper in any area may be taken as indicative of the adoption of the more sophisticated process. The examples given here suggest that the more advanced process was already in use in Egypt by the early third millennium B.C., but in Western Europe the primitive processes were still in use well into the first millennium B.C.

This change in smelting technology may also be reflected in the surviving field evidence of metal production. Throughout the Middle East and Mediterranean area early mines and slag heaps abound, whereas in Western Europe many early mines have been identified but slag heaps are notably absent until at least the Iron Age. The apparent association between low iron content in the bronzes and absence of slag heaps near the mines which produced the copper is suggestive. Perhaps the early slag heaps have not been located in Western Europe simply because they never existed. This scenario may be developed further since, in the absence of surviving smelting debris from Western Europe, attempts to reconstruct the local Bronze Age smelting processes have been based on evidence from the Middle East where furnace remains lie relatively well preserved under the slag heaps. If the interpretation of the iron content of the copper given here is correct, this may be a very misleading analogy.

I con readily enters copper during smelting and it is not difficult to co-smelt ores of the two metals to give copper containing 20% to 40% iron especially if more than 2% sulphur is present in the system. This alloy has occasionally been identified in ancient copper used for currency where weight was all important, but in Italy at least, this extremely intractable material was superseded by heavily leaded copper or bronze for the same function.

The regularity of the iron content in the *ramo secco* bars show the smiths were able to produce carefully controlled variation within the furnaces.

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