

The Composition of the Copper Alloys used by the Greek, Etruscan and Roman Civilizations

3. The Origins and Early Use of Brass

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This is the third of a series of papers dealing with the composition of copper alloys used in the classical world.

Although a few isolated examples of prehistoric copper alloys containing several per cent of zinc are known, notably from Cyprus, it was not until the first millennium BC that the deliberate production of brass commenced, probably in Asia Minor. From the 7th century BC the Greeks commented upon brass, but always as an expensive, exotic metal not produced in Greece, and this is borne out by the absence of zinc in the great majority of Greek bronzes. Similarly, of the many Etruscan bronzes analysed, only two from the 5th and 3rd centuries BC respectively were of brass and these contained about 11% zinc with less than 3% tin (see below).

By the 1st century BC the Romans were using the cementation process for producing brass. Initially it seems to have been used for coinage, but rapidly became popular in other fields, especially decorative metalwork where it largely replaced bronze. During the 2nd and 3rd centuries AD the zinc content of the coinage fell, and brasses with a high zinc content ceased to be used, although brass continued to be as popular as ever accounting for about 30% of Roman copper alloys. By the 3rd century an alloy of copper with a few per cent each of lead, zinc and tin (modern "leaded gunmetal") was in regular use, and has remained so ever since.

From the time of the King James Bible of 1611 in which all copper alloys are called "brass" irrespective of composition, the early development and use of brass has been confused, and learned books, both ancient and modern have often tended to increase rather than decrease this confusion! The origins of both terms "Brass" and bronze are obscure, but it seems that in medieval times brass was applied to all copper alloys, and only from the Renaissance the term *bronz* was used in Italy to denote copper alloys specifically alloyed with tin. However the terms continued indiscriminately in use in England until the 19th century; Johnson defines bronze as brass in his Dictionary. However amongst the many works on the subject, those by Caley (1964) and Werner (1972) are very useful and shed much light on what is otherwise a rather dark area.

By combining the information in these books with the new analyses, particularly those of the Roman period to be published in subsequent parts of this work, a much more complete picture of the early history of brass from its inception until the end of the Roman Empire can be built up.

For the purposes of this review brass is taken to mean an alloy of copper to which zinc has been deliberately introduced. In pre-Roman brasses the zinc normally replaces tin, but in Roman brass the two metals are often both present in the alloy.

The Occurrence of Zinc in Copper

Zinc is usually found in nature as the sulphide (ZnS) *blende* or *sphalerite*; the carbonate ($ZnCO_3$) *calamine* or *smithsonite*, and *hermimorphite* ($2ZnO \cdot SiO_2 \cdot H_2O$) once called

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calamine as well. These ores are found in association with copper and lead ores (Catling, 1964); in fact sulphidic copper ores almost invariably contain *some* zinc (Key, 1963). It is, however, rare for prehistoric artifacts to contain more traces of zinc. The reason for this lies in the volatility of the zinc, causing it to be lost during the smelting of the copper rather than absorbed. If a sulphide ore is used then it must first be roasted in air to convert the sulphides to oxides, and in this process most of the zinc would be lost. Even if some zinc did survive the roasting or if an oxide or carbonate ore of copper was used the zinc would still be lost on smelting as it boils at 905°C, that is, 175°C below the melting point of copper. Before it could dissolve in the copper it would tend to oxidize and be lost, and thus no equilibrium between zinc vapour and the zinc in the copper could be established. Only in exceptional cases should any zinc be retained in the copper. Some examples are however known.

The earliest large group of copper artifacts containing zinc so far reported is from the Early Bronze Age site of Vounous Belapais, Cyprus (Stewart (1950), analysed by Desch).

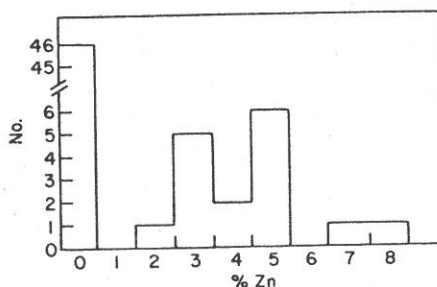


Figure 1. Zinc content of Vounous bronzes.

The 60 artifacts analysed were of arsenical copper or of tin bronze, but 16 artifacts also contained more than 1% zinc (Figure 1). This is the sort of random distribution and spread of results one would expect from the chance introduction of zinc into the copper, as a result of using zinc rich copper ores. The zinc content has no relation to the tin or arsenic content, suggesting that the metalsmiths were not aware of its presence. The Cypriot copper ores contain zinc; modern analyses of concentrates from the mines show that they contain about 32% copper and 1.5% zinc (Catling, 1964). Therefore if all the zinc was retained the resulting metal would contain about 5 or 6% zinc, which compares well with the higher contents reported from Vounous Belapais. The Early Bronze Age smiths are believed to have used only oxide or carbonate ores (Coghlan *et al.*, 1963). These were smelted directly with charcoal under reducing conditions, so that under favourable circumstances, that is, in a strongly reducing furnace, much of the zinc could enter the copper. In contrast later copper from Cyprus only contains traces of zinc, this is probably because by the Late Bronze Age the deeper sulphide ores were being mined (Giles & Kuypers, 1974) and any zinc present would be removed either on the initial roasting of the ore or during the smelting of the roasted ore. Tylecote *et al.* at Newcastle have been working on smelting oxide and sulphide copper ores under primitive conditions and their work suggests much more of the zinc may be lost in the smelting process using a higher temperature furnace such as was used in the Late Bronze Age.

The analyses published by Renfrew (1967) of Early Cycladic metalwork showed the copper to contain either tin or arsenic, with the exception of one dagger which also contains 5.1% zinc. Masson & Sarianidi (1972) mention that a Middle Bronze Age axe

from the excavation at Namaga-Depe was of brass. An axe from Beth-Shan was reported as having 6.5% zinc with the tin (Orens, 1971). In these cases the presence of zinc is again almost certainly accidental.

Perhaps the most famous and widely quoted example of the alleged occurrence of early brasses are those from Gezer, an Early Bronze Age city of Palestine, excavated by Macalister (1912). The site was occupied until Hellenistic times, and samples of metalwork taken from all periods contained zinc including one pin with 23.4% zinc. The samples, analysed by J. E. Purvis were described by Macalister as "small corroded worthless pins". However no reference numbers were given, the method of analysis was not published, and no comment was made on the high zinc content of the samples. If valid these are the earliest brasses in the world, and are often quoted as such by Needham, Partington, Caley, Forbes etc. These results are strange as no other Palestinian metalwork contains more than traces of zinc (Buchholz, 1967; and Branigan *et al.*, 1976). Thus it would seem that this city alone possessed the secret of brass manufacture and used it independently for nearly 2000 years. Unfortunately it is impossible to check the validity of the results quoted by Macalister. However, recently a dagger from an Early-Middle Bronze Age (1500 BC) burial at Gezer, analysed by Hughes (1973), was found to consist of copper with 4% arsenic, and only slight traces of zinc, suggesting that far from being innovators the smiths of Gezer were rather conservative; therefore the claim for early deliberate brass from Gezer must be treated with caution.

Moorey (1964, 1967) has published the analyses of 102 bronzes from Luristan of the Late Bronze Age-Early Iron Age, and found two of brass, with only small amounts of tin. Because of the absence of tin these are definitely deliberately produced brasses, but since they were acquired from dealers and not direct from excavations, there is no information about their provenance. Because of their importance in the history of brass it was decided to examine them carefully in the British Museum Research Laboratory. The patina of both pieces was found to be just stuck to the totally uncorroded metal beneath and therefore was not ancient. This evidence together with the unusual nature of the alloy and the lack of provenance strongly suggest that the two pieces are modern.

Amongst the 1300 analyses performed by Otto & Witter (1952) on European Bronze Age material, 30 were found to contain zinc as a component of the alloy, in some cases replacing tin. The 30 are in no way associated chronologically or geographically, all they have in common being the presence of more than trace amounts of zinc in the alloy. They are once again not direct from excavations but chance finds or acquired from collections, and a strong possibility exists that they are more recent copies of ancient artifacts. No European group of Bronze Age metalwork from a hoard, or excavated from a barrow, for example, has shown more than a small amount of zinc; this suggests that the few deliberately produced pieces of brass reported by Otto & Witter are not of the Bronze Age.

The Earliest Deliberate Production of Brass

So far we have looked at brasses which were either accidentally produced, or are of dubious antiquity and we must now examine the evidence for the earliest alloys in which zinc replaces other metals as the main constituent with the copper. From a variety of sources attention is drawn to Asia Minor in the 1st millennium BC. Fibulae of the 8-7th century BC (Muscorella, 1967), excavated by Young (1958) at Gordion, the ancient capital of Phrygia in Asia Minor, were analysed for Arthur Steinberg (to whom I am grateful for this personal communication) by the Oxford Research Laboratory for Archaeology and the History of Art and found to be of copper with about 10% zinc and little tin or lead. Subsequent X-ray fluorescence analysis of other Gordion fibulae has shown that they are of the same alloy, and other Phrygian and East Greek material

has also been shown to contain zinc. Unfortunately as yet very few quantitative analyses have been performed on Anatolian bronzes of this date. Surface analyses may be misleading due to the phenomena known as "Dezincification" whereby the zinc may be totally lost from the surface of a brass (Butts, 1954). A Urartian bull's head examined by Gettens (Hanfmann, 1956) was described as being of bronze, with horns of brass.

From Ithaca, Greece, Benton (1934/5) excavated a Geometric cauldron handle which was analysed by O. Davies and found to contain 69.18% copper, 1.07% tin, no lead and 6.56% zinc. Unfortunately the handle was badly corroded which explains the low analytical total, and limits the usefulness of the analysis; however since corroded metal normally contains more tin and less zinc than the original uncorroded metal, it is difficult to avoid the conclusion that this handle was deliberately made of brass, the earliest yet found in Greece itself. The copper ores of the Eastern Mediterranean are rich in zinc, and so the source of zinc presents no problem. From this general area several unusual alloys not previously encountered are met with. In the early part of the 1st millennium BC copper was alloyed with antimony or even silver (Craddock, 1976), and zinc may represent another, ultimately more successful experiment in replacing tin. The disorders following the collapse of the Mycenaean trading Empire must have made tin scarce and encouraged experimentation with other metals.

Of the hundreds of pre-Hellenistic Greek Bronzes analysed in this project, only three have more than 1% zinc and then only 1.1, 1.7 and 2.3%. Caley (1939) found no zinc in the Greek coins he analysed, and reported that Von Bibra had only twice found more than 1% in the coins he analysed, namely 2.3 and 3.7%. All of these levels are low enough to be accidental inclusions as they do not replace the tin. However, Picon *et al.* (1968) found 6% zinc replacing the tin, in a 6th century BC statuette of Apollo. Until the Hellenistic period the production of brass was probably confined to Asia Minor, but after Alexander's campaigns knowledge of the process could well have been disseminated throughout the Eastern Mediterranean. The late Hellenistic statuette group of Hermes leading a lady of the 1st century BC from Egypt analysed as part of this project contained 26% zinc [cat. no. 260, 261 (Craddock, 1974)]. However, few pre-Roman Hellenistic brasses have yet been discovered. This is partly due to the difficulty in formally ascribing bronzes to the Hellenistic, rather than to the Roman period. For example, the small statuettes of dwarfs and grotesque figures which are typical of the Hellenistic period known as "Alexandrian" may indeed have been manufactured in Alexandria (Havelock, 1973) but production of these continued with very little stylistic change well into the Roman period. Picon *et al.* (1967) analysed 21 of these figures and found 14 of them to contain between 2 and 16% zinc. These they initially published as being of the 3rd-2nd century BC. However in a later paper (1973) they have had to admit that the figures could just as easily be Roman of the 1st and 2nd centuries AD.

The problem of dating does not apply with the Etruscans as their distinctive metalwork ceased manufacture entirely during the 2nd century BC following their conquest by the Romans. Amongst the vessels analysed by Van Boersted & Hoekstra (1965) were two handles from a vessel of the Late Etruscan period. They each contained 2.7% zinc and 5% tin; thus in these pieces the zinc is probably an accidental inclusion.

However, the statuette of a naked youth (Figure 2) from the British Museum (cat. no. 686), dated to the 3rd or 2nd century BC and the base of the statuette of a boxer also from the British Museum (cat. no. 526) dated to the 5th century BC contain 11.8 and 11.5% zinc respectively with only 0.68 and 3.0% tin (see part 4 of this project, forthcoming). The composition suggests that the zinc had been deliberately added to the alloy to replace tin, and thus these are the first Etruscan brasses so far known. Stylistic and technical examination of the statuettes and the base has confirmed their authenticity beyond any reasonable doubt.

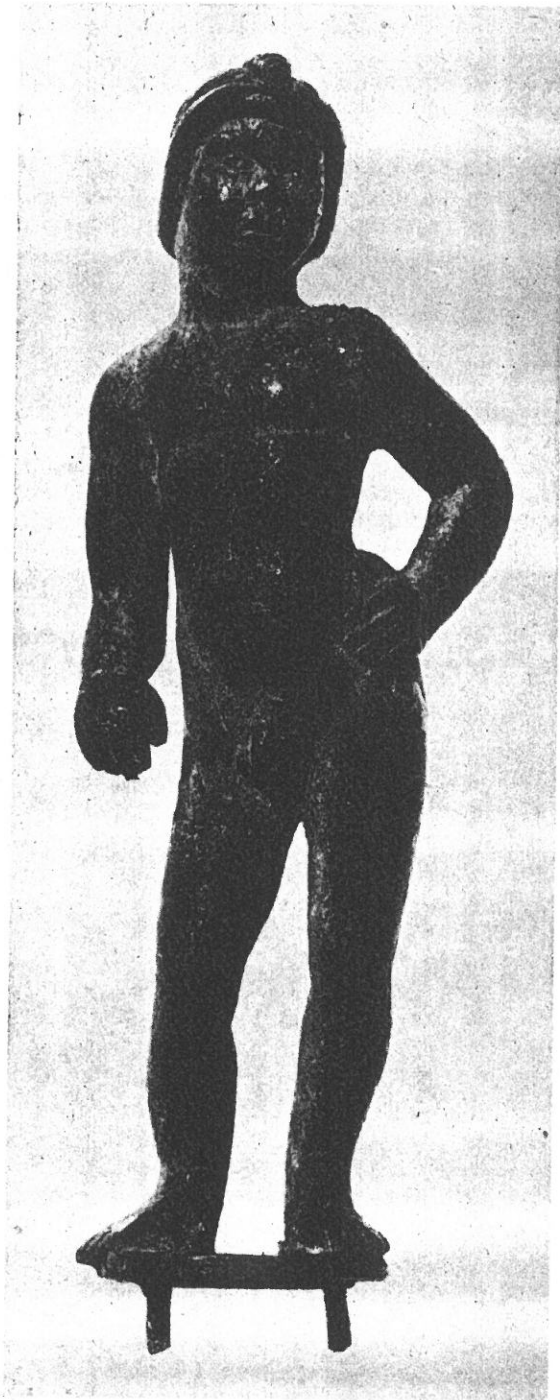


Figure 2. Etruscan statuette of brass (photo: Andrew Morris, British Museum Research Laboratory).

Although as we have seen brass was rare in pre-Roman Greece, references to a metal "*Oreichalkos*" (i.e. "mountain copper") which is distinct from "chalkos" (i.e. ordinary bronze or copper) appear in Greek literature from the 7th century BC onwards. The identity of the metal has been the subject of much discussion. Most authors, such as Caley (1964) and Partington (1935) believed the word to mean brass, but recently the possibility that it might refer to arsenical copper as first suggested, but rejected, by Caley, has been revived by Eaton & McKerrell (1976).

The word *Oreichalkos* continued to be used through the Roman period by such technical authors as Dioscorides and there can be no doubt that the word then meant brass. But before the 1st century BC brass was a rare metal and its identification with *oreichalkos* is less certain. Fortunately the context of the word in pre-Roman literature gives us many clues as to its identity.

The earliest reference to *oreichalkos* occurs in an anonymous poem "*Shield of Herakles*" probably written by a Boeotian follower of Hesiod in the 7th century BC. The reference occurs in lines 121–122, which are translated: "so he spoke and placed about his legs his greaves of shining *oreichalkos*, the glorious gift of Hephaistos" (Evelyn White, 1965). Slightly later than this, *oreichalkos* is mentioned in one of the Homeric Hymns to Aphrodite where it is said that: "the Hours attached to the ears of the Goddess an ornament of precious gold and *oreichalkos*".

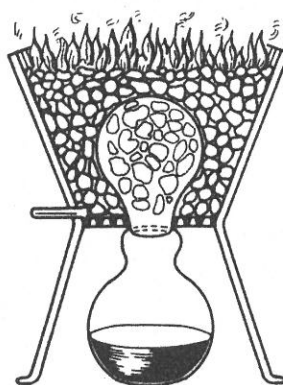


Figure 3. The apparatus used by the Hindu metallurgist for the manufacture of zinc (taken from Forbes' *Studies in Ancient Technology* Vol. VIII, 1971, p. 281).

Both these early texts suggest that *oreichalkos* was very rare and expensive. Even in the 4th century BC Plato in the *Critias* refers to the metal as being a rarity and of great value. Describing the walls around the capital of Atlantis he says that "They covered the inside wall with fused tin, but the wall around the acropolis itself with *oreichalkos*, which had a fiery resplendence". He relates that the interior of the principal temple was covered with ivory, variegated with gold, silver and *oreichalkos*, and states that gold was the most precious, but *oreichalkos* the second most precious metal known to the inhabitants of Atlantis.

Perhaps the most important reference to the early production of brass is contained in the *Philippica* of Theopompus, written in the 4th century BC. The original work is lost but substantial quotations were made from it by Strabo in his "Geography" and by Stephen of Byzantium in his *Geographical Lexicon*. The text of the relevant quotation from Strabo reads as follows: "There is a stone near Andeira [a town in north-west Asia

Minor] which yields iron when burnt. After being treated in a furnace with a certain earth it yields droplets of false silver. This, added to copper, forms the so called mixture, which some call 'oreichalkos'." The "droplets of false silver" which added to copper to give *oreichalkos* can be interpreted as metallic zinc. If the certain earth was a reducing agent, then smelting the Andeirian Stone with it in a furnace could have produced zinc metal which would have boiled at 905°C. Providing the atmosphere was kept reducing then droplets of zinc would have condensed on the walls of the cooler parts of the furnace. However most of the zinc would be converted to zinc oxide and lost, so although this is a feasible way of making brass it would have been too expensive for everyday use.

Eaton & McKerrell translate the quotation slightly differently, that is, "then when heated in a furnace with a kind of earth it drips down mocksilver". Now Eaton & McKerrell state that if the mocksilver was zinc it should have gone up the flue of the furnace and most certainly not drip down. However, the earliest known zinc distillation furnaces from medieval India, did just this (Figure 3). Calamine and resins were heated in a vessel with its neck inverted into the top of another vessel and drops of zinc metal were collected in the water below. The origins of this technique of *destillatio per descensum* are very ancient, and this oblique reference in Strabo may refer to it. Unfortunately in the absence of actual physical remains of one of these pieces of apparatus it is dangerous to read too much into secondhand literary references; but actual examples of zinc metal have been found in archaeological contexts (see below).

Eaton & McKerrell following Forbes (1971) suggest that the droplets of "false silver" so produced were of arsenical copper.

There are two objections to this. Firstly, there is no reason why the arsenical copper should form itself into droplets implying condensation (in fact Leaf (1923) translates it as "distills"), as the arsenical copper clearly could not condense from a vapour, only solidify from a liquid. Secondly, and more important, this quotation was used by Strabo in his Geography at a time when the meaning of "*Oreichalkos*" was quite clearly brass. Thus Strabo obviously intended the reader to believe that the droplets of "false silver" were going to produce brass, and thus they *must* be zinc. If an alloy of copper whitened by the addition of arsenic compounds had been intended then the word *Asem* is more likely to have been used. Various methods of preparing *Asem* are described in the Leyden Papyrus X (Caley, 1926), a work of the 4th century AD, but echoing fragments of much earlier works. *Asem* seems to have been used as a counterfeit silver or gold. At least one of the various recipes for making *Asem* involves using *Oreichalkos* with an arsenic compound, *Sandarack* described as being the sort which whitens, in order to manufacture *Asem*. The important point to note is that *Asem* denoting a whitened copper, usually achieved by additions of arsenic, and *Oreichalkos* are mentioned in the same sentence and are clearly different; *Oreichalkos* is the starting material for *Asem*.

There is some evidence for the existence of zinc metal in Hellenistic times. In the course of the excavation of the Agora in Athens a roll of sheet zinc was found in a sealed deposit dating from the 3rd or 2nd century BC (Farnsworth *et al.*, 1949). The metal was 6.5 × 4 cm and about 0.05 cm thick after cleaning. Analysis showed it to be nearly pure zinc with just 1.3% of lead, 0.06% cadmium, 0.016% iron, and 0.005% copper with traces of manganese, magnesium, tin, silver and antimony. Although this is not the normal composition of modern zinc, some doubt has been expressed about this piece, not archaeologically, but because it is apparently a unique survival. However a Hellenistic statuette also from the Agora, but from a mixed deposit, has also been shown to contain more than 99% zinc (T. Wheeler, University of Pennsylvania, personal communication).

It is often thought that the production of zinc metal would have been impossible for the ancients, yet this idea does not stand close examination. The problem is to solidify the zinc vapour before it oxidizes. The medieval Indian process was simply to smelt the

calamine ores with charcoal in a closed vessel, the neck of which led into a vessel containing water, where the zinc metal condensed. Thus the technology should not have been beyond the Greeks as quite complex distillation apparatus is known from the 4th millennium BC (Levey, 1959). It must also be remembered that zinc metal has occasionally occurred in the flues of medieval lead smelters (Day, 1973), something the Greek workers must also have noted. The available evidence does not therefore support Forbes (1971) in his claim that the ancients could not have produced zinc on a commercial scale. However it is true that zinc metal was exceedingly scarce, even allowing for lack of survival, or recognition. Why if zinc was known did it not become popular in Antiquity? It must be borne in mind that when Champion introduced zinc smelting into Europe it took over 100 years, and his own bankruptcy, before the cementation process of brass production was superseded. The latter is a direct single stage process, whereas making the zinc metal first involves a two stage process for the production of brass, both stages of which need time and fuel and lose considerable quantities of zinc.

Two other important passages in Greek literature refer to copper alloys that do not contain tin, both being from the pseudo-Aristotelian work "On Marvellous Things Heard", which is a rather dubious work compiled by followers of the great philosopher probably in late Hellenistic and Roman times. Amongst the many and varied statements is the following: "They also say that amongst the Indians the bronze is so bright, clean and free from corrosion that it is indistinguishable from gold, but that amongst the cups of Darius there is a considerable number that could not be distinguished from gold or bronze except by odour". Now the Phrygian brass fibulae, the Geometric Handle, and the two Etruscan brasses all seem to contain, or to have originally contained, about 10-12% zinc. This alloy with copper is very golden in colour, and is not easily distinguished from gold or bronze. The characteristic greenish-yellow colour of brass appears only with zinc contents above 20%.

The reference to the odour is interesting; the metal is claimed to give off an unpleasant, "metallic" smell after it has been handled, especially with sweaty hands. Brasses are also claimed to have a bitter metallic *taste* not encountered with bronze or gold.

The second quotation is "they say that the bronze of the Mossynoeci is very shiny and light in colour though tin is not mixed with the copper but a certain earth which occurs there is smelted with it". The Mossynoeci lived in Asia Minor near where both zinc and arsenic ores abound. This could therefore be a reference to the use of a form of cementation process for making brass containing enough zinc to significantly lighten it. Alternatively it could refer to the use of arsenic ores smelted with copper to lighten it. Caley (1964) believed the former was more likely but it is impossible to be sure.

In conclusion the literary sources and the analytical data both indicate that brass was very uncommon and only occasionally used prior to the Romans. The earliest regular use of brass seems to have been amongst the Phrygians in Asia Minor. Similarly the Greek writers through the centuries refer to *oreichalkos* as a rare, exotic, expensive material, and where a place of manufacture is mentioned this is always in Asia Minor. The process for the manufacture of brass is not clear. The reference to the Mossynoeci suggests a form of cementation, but it is not clear that zinc oxide is necessarily involved in the process described. In contrast the reference to the stone of Andeira, and the finds of ancient zinc, suggest that brass may have been made by directly mixing the two metals, copper and zinc.

Brass in the East

The possibility that the earliest brasses should be looked for in the Far East has also been investigated and examined both from ancient texts (Needham, 1974) and analytically (Werner, 1972). Both authorities conclude that brass was not widely used in the

Far East prior to the 1st century AD and, was probably introduced *from* the west. Gettens *et al.* (1969), working on the Freer Bronzes, Wang Chin (1923) and Barnard (1961) all showed that Chinese alloys from the Han period (200 BC–AD 200) rarely contained more than traces of zinc and that brass was not really an established alloy until after the Han period. Wang Chin believed it was not deliberately produced until the 7th century AD. Although this is almost certainly too late, his suggestion that the zinc may originally have been added to the alloy accidentally in with the lead is important, as lead and zinc often occur together and frequently the metals contaminate each other unless deliberately separated.

Werner concluded that brass was probably exported to the Far East from Asia Minor and the Middle East via such trading cities as Taxila in the Punjab from about 200 BC and somewhat before brass manufacture started there in the 1st century AD.

Production of Brass in the Roman Period

By the middle of the 1st century BC at the latest the large scale production of brass had been started by the Romans. This can be dated with reasonable accuracy because coins were amongst the earliest objects to be made of brass (Caley, 1964).

Apart from the information to be inferred from the brasses themselves, and the rather oblique references to brass made by Pliny and Dioscorides, not much is known of the actual techniques of Roman brass production.

Large scale Roman brass works are believed to have been operating in North Gaul near present day Aachen and Stolberg, and excavations have revealed evidence of Roman calamine mining (Willers, 1907), but in general excavation has not produced evidence of brass making.

Pliny mentions that of the various kinds of copper, *Mariam* absorbs *cadmea* (zinc oxide or carbonate) most readily and reproduces the colour of *Aurichalcum* (= *oreichalkos*) in making *sestertii* and *dupondii* (coins of brass). This statement of copper absorbing zinc oxide strongly suggests that the cementation process (described below) was being used for making brass. Further evidence for this is provided by the analytical data to follow which is discussed below. Dioscorides describes the fine white smoke produced during the production of brass, and this must be zinc oxide, which suggests that since the zinc was escaping, the apparatus used by the Romans was not very efficient. Pliny mentions the various kinds of zinc oxide, or "furnace calamine" adhering to the walls and roof of the furnaces together with their use as medicinal ointments, this also suggests that much of the zinc was being lost from the cementation crucibles.

The Production of Brass by the Cementation Process

In this process fragments of copper were packed in a sealed crucible with charcoal and zinc oxide and heated to a temperature of between 900 and 1000 °C; that is, hot enough for the zinc to have been vaporized but not so hot that the copper melted and ran to the bottom of the vessel. The zinc vapour in the sealed vessel readily dissolved in the widely dispersed copper and brass was formed. At the end of the process the temperature was raised and the then molten brass was stirred to form a uniform alloy.

Werner (1970) has performed experiments with Haedecke to determine the likely composition of brass produced in this manner and these are briefly described below.

First copper filings were placed in a boat in a sealed tube with a mixture of zinc oxide and charcoal and heated for two hours at 1000 °C (Figure 4). On subsequent analysis the metal in the boat was found to contain between 23 and 28% zinc. The same apparatus was then set up and with a brass containing 42% zinc being substituted for the copper and was heated as before. In this case it was found that the zinc content of the brass

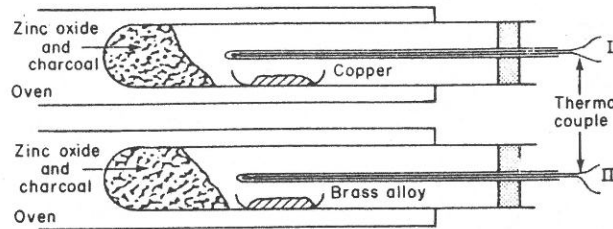


Figure 4. Sketch of apparatus used by Haedecke to determine maximum zinc content of brass prepared by the cementation process.

had decreased to 28%. Thus in the presence of zinc oxide, charcoal and copper an equilibrium reaction must be set up. This was expressed by Werner as follows: $2\text{ZnO} + 2\text{C} + \text{Cu} \rightleftharpoons \text{Zn} + \text{CuZn} + 2\text{CO}$, although this is an oversimplification. When higher temperatures were used in the laboratory experiments, more zinc was absorbed. However if the temperature went much over 1000 °C then the forming brass would melt and run to the bottom of the crucible thus only maintaining a relatively small surface in contact with the zinc vapour, making the process much less efficient. Thus brass produced by the cementation process should contain between 22 and 28% zinc. These figures are closely confirmed by the composition of the brass made in the early 18th century at the Baptist works, Bristol (Day, 1973). A maximum zinc content of 28% in the brass was achieved using broken up copper distributed in the crucible and employing temperatures just below the melting point of the brass, i.e. similar to the Roman process.

However by experiment Champion, using granulated metal formed by pouring molten copper into water, obtained a maximum zinc concentration of 33.3%. Why did the Romans not achieve this? Ultimately the answer lies in the attitude to experimentation. The Baptist works even had its own laboratory, something unthinkable in a Roman works with the Romans' negative attitude to technical innovation.

The analytical data for Roman brasses (to be published as Part 5) shows that they regularly contain up to a maximum of 28% zinc, with little or no tin or lead being present. These data therefore confirm that they were made by the cementation process. Copper metal would have had to have been used in the crucible since, if bronze containing more than 5% tin had been used, the metal would have melted before the zinc vaporized

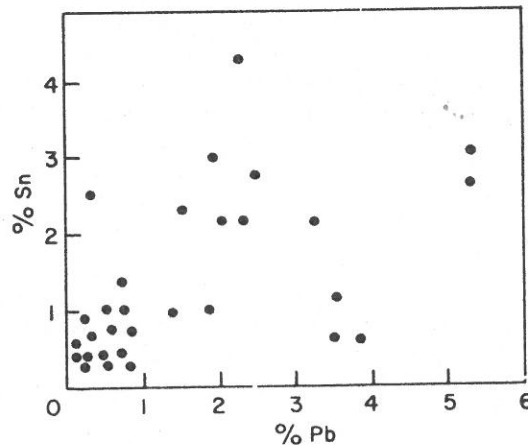


Figure 5. Lead and tin content of Roman brass containing more than 22% zinc.

at 918 °C. This deduction is confirmed by the analytical data of Caley (1964), Boersted (1965) and my own forthcoming analysis which shows that none of the 32 brasses containing more than 22% zinc contain more than 5% tin and lead and most contain much less (Figure 5).

The Use and Range of Roman Brass Alloys

Although initially restricted to coins, brass rapidly became widely used and during the 1st and 2nd centuries AD was extended to most other types of bronzework. Zinc is much more abundant than tin, which only Spain and Britain produced in the Roman Empire; zinc is nowadays approximately one-tenth of the price of tin, and only half the price of copper and this relative pricing was roughly the same in Roman times. Therefore for large scale metal production such as coinage, brass had the obvious advantages of cheapness once viable ways of manufacturing it had been found.

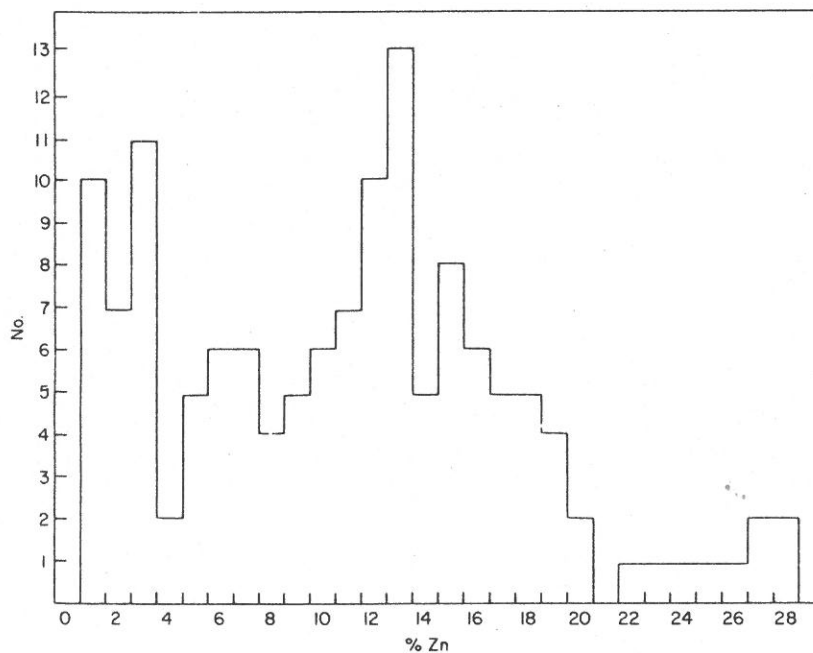


Figure 6. Zinc content of Roman copper alloys (containing above 1% zinc).

In addition, the bright golden colour already noted by the classical authors, made it especially attractive for such decorative metalwork as fibulae, rings, trappings, etc. In fact only about 20% of the ungolded Roman decorative metalwork to be reported here and in Part 5 contains less than 4% zinc, and the average zinc content is about 12%.

One particular advantage of brass demonstrated by Moss (1952) is that although niello will not adhere to bronze it will adhere to brass. Niello, a mixture of copper and silver sulphides, has a dense glossy black appearance, and was widely used by the Romans for inlaying silver, with which it contrasted well. During the 1st century AD large numbers of trappings were made of brass covered with silver foil, and with niello inlaid through the silver into the brass beneath (Craddock *et al.*, 1973). Thus there were good reasons, both economic and aesthetic, to explain the growing popularity of brass alloys.

From the histogram of the zinc content of all the Roman copper alloy objects containing more than 1% zinc (Figure 6) analysed in this project (Part 5, forthcoming) it can be seen that the zinc content falls into three groups. The first group contains less than 4% zinc, and the presence of zinc here almost certainly arises fortuitously from the use of scrap brass in the alloy. The second group contains between 4 and 20% zinc with an essentially normal distribution around 13%. It would seem that these alloys were made by mixing freshly made brass, containing 22 to 28% zinc with scrap bronze, and that an alloy containing about 13% of zinc was preferred. This is the approximate zinc content of modern pinchbeck or gilding metal, widely used now, as in Roman times, for decorative metal. Another possible reason for the popularity of brasses with this zinc content is that the simplest dilution process would be to mix equal amounts of scrap bronze and brass containing 22–28% zinc. This would produce a metal containing between 10 and 15% zinc (slightly lower than half since brass loses up to 10% of its zinc content each time it is melted). The third group contains between 22 and 28% zinc. These are clearly brasses straight from the smelter, without the addition of any scrap bronze or copper to reduce the overall zinc content.

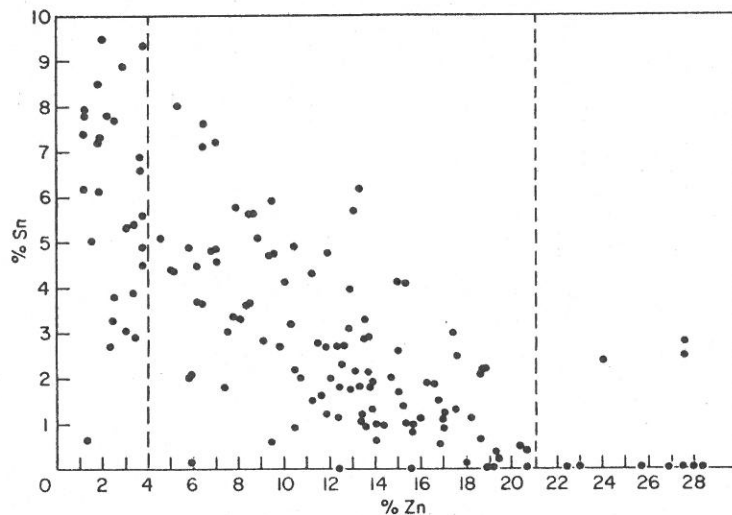


Figure 7. Plot of zinc against tin content for Roman copper alloys (containing above 1% zinc).

Confirmation of these three groups as real entities comes from an examination of the tin content of the brasses. Figure 7 is a plot of zinc versus tin content. Below 4% the zinc content bears no relation to the tin suggesting that the zinc is there unintentionally in the form of scrap. The zinc content in the 14–20% range tends to be inversely proportional to the tin content, that is as more scrap bronze is added, the zinc is progressively diluted. Above 22% zinc only two of the nine brasses have any tin at all, and in these brasses the small amount of tin could well have been in the original copper used in the cementation process. During the formation process metals such as tin or lead in the copper depress the amount of zinc absorbed. Metals soluble in the alpha-phase may replace zinc in the proportions expressed as the zinc equivalent for the metal in question—lead is 1, tin is 2 etc. Thus for example, a copper containing 3% tin would absorb 6% less zinc than it would otherwise have done. If the small amounts of tin present in the brasses had been present in the original metal used in the cementation process then one

would expect a range of brasses with from about 18 to 28% zinc and about 1-5% tin and/or lead, whereas in fact one does not get metal with this composition in the Roman period, demonstrating that tin and most of the lead were introduced from the scrap metal added to the original brass after manufacture.

These figures also show that it was usual for the metalworkers to dilute the brass with relatively cheap scrap bronze rather than with pure copper, the resulting mixed alloy being well suited to everyday purposes. The coin makers of the 1st and 2nd centuries AD on the other hand must have usually used copper to dilute the brass, since the coin analyses published by Caley (1964) show only six coins with more than traces of tin, although 15 of the coins have between 6 and 18% zinc. This result is paralleled by unpublished analyses carried out on hoards of Roman military trappings from Ribchester and Xanten where once again the zinc content of the brass lies between 12 and 19%, but only traces of tin were found. The overall picture that emerges is of the brass smelters producing a metal containing between 22 and 28% zinc, and the Imperial coiners and Legionary smiths mixing this with pure copper, but the small commercial producers seeming to have used brass mixed with scrap bronze for reasons of utility and economy.

Of the 444 Roman copper alloys analysed in part of this project, 108 contained 4% or more of zinc. This overall picture is however misleading since, for example, none of the 34 mirrors and their handles analysed here contain more than traces of zinc, and only two statues have more than 1% zinc, namely 1.15 and 2.4%. Thus zinc was never deliberately added to either mirrors or statuary bronze. This contrasts strongly with decorative metal. Of the 94 samples, 64 have more than 4% zinc, and of the remainder, 10 are of mercury gilded copper, leaving only 21 of bronze.

However, if one takes the 84 objects of everyday metalwork, i.e. lamps, hinges, spoons, chariot fittings etc., one has a more representative if smaller sample. Of the 84 such objects 26 have 4% or more of zinc and this would suggest that approximately one-third of Roman copper alloy objects deliberately contained zinc.

Chronology

Unfortunately most of the Roman material analysed in this project does not come from controlled excavation and therefore does not have a precise date, but much of the material, such as fibulae, can be stylistically dated to within a century at least. The *sestertii* and *dupondii* coins analysed by Caley (1964) are of course much more closely dated. Table 1 shows the change in the average zinc content over the period of the first four centuries of the Roman Empire, for coins, all other metalwork, and decorative metalwork. The most striking feature of the table is the relative stability of the zinc content of all brasses except coins compared with the rapid fall off in the zinc content of coins. For both groups the decrease in brass containing more than 22% zinc is especially noticeable. Thirteen of the 82 1st century brasses and coins have over 22%, but only two of the 94 2nd century, and none of the 32 3rd and 4th century Roman brasses have more than 22% zinc. Thus it would seem that brass straight from the smelter was not used much after the 1st century AD, but always mixed with copper or bronze. If one removes brasses containing more than 22% from the tables, then the fall in average zinc content becomes much less steep, especially for non-coinage brasses, where the fall from the 1st to the 4th century is only 3%.

Caley (1964) suggested on the basis of the coin analyses alone that the knowledge of brass smelting may have been lost after the 1st century, and remelted scrap brass provided the only source of metal for the later coins. These coins are diluted with scrap bronze, not copper as was the case earlier, and this might be taken as further evidence that controlled production had ceased. However, now that a large number of analyses

Table 1. Zinc content of Roman brasses

| Date | Overall zinc content (%) | | Zinc content in <i>sestertii</i> and <i>dupondii</i> (%) | | Zinc content in decorative metal work (%) | |
|----------------|--------------------------|------------|--|----------------|---|------------|
| | All >4% | 4-22% only | All >4% | 4-22% only | All >4% | 4-22% only |
| 1st century AD | 16.4 | 13.3 | 18.9 | 16.9 | 15.0 | 14.5 |
| 2nd century AD | 12.2 | 11.5 | 10.7 | 10.7 | 12.6 | 11.9 |
| 3rd century AD | 12.0 | 12.0 | 7.7 | 7.7 | 12.2 | 12.2 |
| 4th century AD | 10.0 | 10.0 | — ^a | — ^a | 8.6 | 8.6 |

^aNo longer minted. Other copper base coins have no zinc.

of metal other than coins is available it can be seen that the fall in the zinc content for the other metalwork is much less pronounced than for coins. Furthermore a table of the percentage of *sestertii* and *dupondii* coins, and of general metalwork containing more than 4% zinc (Table 2) shows clearly that whereas the coins drop dramatically from 100% to nil, the percentage for general metalwork *increases* from 25% to around 40%. It now becomes clear that whereas the use of zinc in base metal coins did decline, the use of zinc in Roman alloys generally flourished. However the average zinc content fell slightly, and the use of high zinc brasses ended, and the alternative alloy of copper with some tin, zinc and lead began and rapidly established itself. One must be careful not to think of this in terms of a debasement as suggested by Caley, but rather that a more suitable alloy for general purposes was being developed. The tin helps the strength of the alloy, the zinc acts as deoxidant, and the lead improves the casting properties and machinability of the resultant alloy. Today these alloys are known as leaded gun metals and are amongst the most widely used of all copper alloys and from the Roman Empire onwards alloys of copper with zinc, tin and lead have remained one of the most popular alloys used by the metalsmiths.

Table 2. Percentage of copper alloys containing more than 4% zinc

| Date | All metal work (%) | <i>sestertii</i> and <i>dupondii</i> (%) | Decorative metal work (%) |
|----------------|--------------------|--|---------------------------|
| 1st century AD | 25 | 100 | 76 |
| 2nd century AD | 25 | 90 | 88 |
| 3rd century AD | 30 | 64 | 50 ^a |
| 4th century AD | 40 | — | 50 ^a |

^aMost of the remaining 50% of decorated metal work is gilded copper.

References

- Barnard, N. (1961). *Bronze Castings and Bronze Alloys in Ancient China*. Monumenta Serica Monograph XIV, Canberra.
- Benton, S. (1934/5). Excavations in Ithaca III. *Annual of the British School at Athens* XXV, 73.
- Boersted, M. H. Van & Hoekstra, E. (1965). Spectrochemical Analyses of the bronze vessels in the Rijksmuseum, G. M. Kam at Nijmegen. *Oudeheidkundige Mededelingen uit het Rijksmuseum van Oudheden te Leiden*. N.R. 46.
- Branigan, K. (1974). *Aegean Metalwork of the Early and Middle Bronze Age*. London: O.U.S.
- Buchholz, H.-G. (1967). Analysen Prähistorischer Metallfunde aus Zypern und den Nachbarländern. *Berliner Jahrbuch* 7, 189-256.

- Butts, A. (1954). *Copper*. American Chemical Society Monograph, New York, pp. 383-389.
- Caley, E. R. (1926). Leyden Papyrus X. *Journal of Chemical Education* 3, 1140-1166.
- Caley, E. R. (1939). *The Composition of Ancient Greek Bronze Coins*. Philadelphia: The American Philosophical Society.
- Caley, E. R. (1964). *Orichalcum and Related Ancient Alloys*. New York: American Numismatic Society, No. 151.
- Catling, H. W. (1964). *Cypriot Bronzework in the Mycenaean World*. London: Oxford University Press, pp. 11-12.
- Coghlan, H. W., Butler, J. R. & Parker, G. (1963). *Ores and Metals*. Royal Anthropological Institute Occasional Paper No. 17, London.
- Craddock, P. T. (1976). The composition of the copper alloys used by the Greek, Etruscan and Roman civilizations. 1. The Greeks before the Archaic period. *Journal of Archaeological Science* 3, 93-113.
- Craddock, P. T. (1977). The composition of copper alloys used by the Greek, Etruscan and Roman civilizations. 2. The Archaic, Classical and Hellenistic Greeks. *Journal of Archaeological Science* 4, 103-123.
- Craddock, P. T., Lang, J. & Painter, K. S. (1973). Roman horse-trappings from Fremington Hagg, Reeth, Yorkshire, N.R. *The British Museum Quarterly* 37, 9-18.
- Day, J. (1973). *Bristol Brass: The History of the Industry*. Newton Abbot: David and Charles, esp. pp. 48-72.
- Dioscorides. *Materia Medica*. Book V, ch. 84-85.
- Eaton, E. R. & McKerrell, H. (1976). Near Eastern alloying and some textual evidence for the early use of arsenical copper. *World Archaeology* 8, 169-192.
- Evelyn White, H. G. (1965, translated). *Hesiod and the Homeric Hymns*. Loeb Classical Library. London: Heinemann.
- Farnsworth, M., Smith, C. S. & Rodda, J. L. (1949). Metallographic examination of a sample of metallic zinc from ancient Athens. *Hesperia*, Supplement 8, 126-129.
- Forbes, R. J. (1971). *Studies in Ancient Technology* Vol. VIII. Leyden: E. J. Brill, esp. p. 272.
- Gettens, R. J., FitzHugh, E. W., Bene IV & Chase, W. T. (1969). *The Freer Chinese Bronzes*. Vol. 2. *Technical Studies*. Washington.
- Giles, P. L. & Kuypers, E. P. (1974). Stratiform copper deposits. North Anatolia, Turkey, Evidence for E.B.I. (2800 BC) mining activity. *Science* 186, 823-825.
- Hanfman, G. M. A. (1956). "Four Urartian Bulls' heads". *Anatolian Studies* 6, 203-213.
- Havelock, C. M. (1973). *Hellenistic Art*. London: Phaidon, pp. 120-121, 142, 143.
- Hughes, M. J. (1973). In "Notes & News". *Palestine Exploration Fund Quarterly* 106, 5-6.
- Key, C. A. (1963). Notes on the Trace Element Content of the Artifacts of the Kfar Monash Hoard. *Israel Exploration Journal* 13, 289-290.
- Leaf, W. (1923). *Strabo on the Troad*. Cambridge: Cambridge University Press, pp. 284-289.
- Levey, M. (1959). *Chemistry and Chemical Technology in Ancient Mesopotamia*. Amsterdam: Elsevier, pp. 31-41.
- Macalister, R. A. S. (1912). *The Excavation of Gezer*. Vol. II. London: Macmillan, pp. 264-265.
- Masson, V. M. & Sarianidi, V. I. (1972). *Central Asia*. London: Thames and Hudson.
- Mills, J. & Gillespie, M. (1969). *Studio Bronze Casting—Lost Wax*. London: Maclaren.
- Moorey, P. R. S. (1964). An interim report on some analyses of Luristan Bronzes. *Archaeometry* 6, 72-81.
- Moorey, P. R. S. (1971). *Catalogue of the Ancient Persian Bronzes in the Ashmolean Museum*. Oxford.
- Moss, A. A. (1952). Niello. *Studies in Conservation* 1, 49-63.
- Muscarella, O. W. (1967). *Phrygian Fibulae from Gordion*. London: Colt Archaeological Institute.
- Needham, J. (1974). *Science and Civilization in China*. Vol. V, part 2. Cambridge: Cambridge University Press.
- Oren, E. D. (1971). A middle Bronze Age warrior tomb at Beth-Shan. *Zeitschrift des Deutschen Palästina-Vereins* 87, 109-139.
- Otto, H. & Witter, W. (1952). *Handbuch der Alttesten vorgeschichtlichen Metallurgie in Mitteleuropa*. Leipzig, pp. 210-211.

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- Partington, J. R. (1935). *Origins and Development of Applied Chemistry*. London: Longmans, p. 73.
- Picon, M., Condamin, J. & Boucher, S. (1967, 1968 and 1973). Recherches Techniques sur des Bronzes de Gaule Romaine. II-IV. *Gallia* **25**, 165-168; **26**, 245-278; **31**, 157-178.
- Pliny, the Elder. *The Natural History*. Book XXXIV, ch. 4.
- Renfrew, C. (1967). Cycladic metallurgy in the Aegean Early Bronze Age. *American Journal of Archaeology* **71**, 1-20.
- Stewart, E. & Stewart, J. (1950). *Vounous Belapais 1937/8*. Lund.
- Wang Chin (1923). The composition of Wu-Chu coinage and the examination of Ancient Pewter. *Ko' Hsueh* **8**, 839-851.
- Werner, O. (1970). *Über das Vorkommen von Zink und Messing in Altertum und im Mittelalter*. *Erzmetall* **23**, 259-269.
- Werner, O. (1972). *Spektralanalytische und Metallurgische Untersuchungen an Indischen Bronzen*. Leiden: Brill.
- Willers, H. W. (1907). *Neue Untersuchungen über die Römische Bronze Industrie von Capua und von Niedergernariem*. Leipzig.
- Young, R. S. (1958). *The Gordion Tomb*. Bulletin of the University Museum of the University of Pennsylvania, pp. 3-13.