Early brass in the ancient Near East

Christopher P. Thornton & Christine B. Ehlers

Abstract
Discussions of early brass production in the Near East have been, to date, inherently tenuous as they rely on isolated and questionable finds and analyses. It is a history lacking reliable data in support of the position that the production of pre-1st-millennium BC high-zinc copper alloys was part of an informed, deliberate process employed by metalsmiths. The results of analyses conducted on samples taken from excavated materials, now housed in museum collections, provide evidence for earlier and more widespread intentional brass-making than has been available heretofore. The data indicate that high-zinc copper-base alloys were used to fashion artefacts found in mid-2nd millennium BC contexts at the sites of Tepe Yahya and Nuzi. Perhaps more significantly, comparison with contemporary materials suggests that these brasses were the result of intentional choices made on the part of early metalsmiths.

Introduction
The history of copper-zinc alloys such as brass (Cu-Zn), gunmetal (Cu-Sn-Zn), and latten (Cu-Zn-Sn) is shrouded by poor excavation reporting, questionable analyses, and numerous misconceptions. Early claims of intentional brass (i.e. above 8 wt% Zn) from sites such as Early Bronze Age Gezer (Macalister 1912: 265) in Palestine and at Neolithic Jiangzhai and Jiaoxian (Rubin & Tsun 2000) in China have been rightly criticized, if not entirely discredited (see Craddock 1980 and Zhimin 2000, respectively). The reason for such skepticism is that high-zinc copper-base alloys are extremely difficult to make due to the volatility of zinc at temperatures above 906 °C; i.e. 177 °C below the melting point of copper (see Pollard & Heron 1996 or Craddock 1990 for more detailed descriptions of copper-zinc production). Although zinc ores (e.g. sphalerite, ZnS) are often found in association with copper and lead ores, and could easily have found their way into a smelt accidentally, the majority of zinc present in the ores would vaporize leaving only a trace (up to 1 wt%) in the resulting copper metal unless deliberate measures were taken to prevent the loss of zinc by reintroduction of the vapor back into the smelt. In rare instances, such as under extreme reducing conditions, copper-zinc alloys with up to 8 weight percent zinc could be produced by mixing copper and zinc ores in a furnace. This has been used to explain low-zinc copper-base artefacts such as an Early Bronze Age dagger from the Cyclades (5.1 wt% Zn), two slightly later axes from Namazga-Depe in Turkmenistan (unknown) and Beth-Shan in the Levant (6.5 wt% Zn as well as Sn) (see Craddock 1978: 2-3), numerous finds from the 3rd millennium graves of Umm an-Nar in the Persian Gulf (4.1-10 wt% Zn; Frifelt 1991: 100) and possibly a few copper-zinc alloys from the MBA site of Trianda on Rhodes (S. Stos, personal communication).

These isolated finds are generally agreed to be accidentally produced copper-zinc alloys, the implication being that early metalsmiths were not aware of the zinc content until much later in history or were not in possession of the technical knowledge to control it. Dating to the 1st millennium BC, three gunmetal fibulae from Gordion in Anatolia with roughly 15 weight percent tin and above 10 weight percent zinc (see Young 1981: 287-290), as well as scattered examples with 10 to 20 weight percent zinc found throughout the eastern Mediterranean world are widely accepted as being the first deliberately-produced copper-zinc alloys (Craddock 1988: 320; Pollard & Heron 1996: 201). The method presumed to have been used to produce these early brasses is known as cementation (a.k.a. the calamine process), whereby smithsonite (ZnCO3; zinc spar) is heated with copper metal in a closed crucible. Once the temperature rises above 906 °C, the zinc vaporizes and is absorbed into the solid copper solution. Experimentation has shown that the upper limit of zinc uptake by the cementation process is roughly 28 to 30 weight percent zinc, although up to 10 weight percent zinc can be lost through subsequent melting (Pollard & Heron 1996: 199; Ponting 1999: 1315). The smithsonite used in the cementation process can either be found as a natural ore or can result from sphalerite roasting and sublimation in a special furnace to collect the zinc vapour in the form of zinc oxide (Ponting 1999). The use of these two alternative methods is usually distinguishable based on chemical analysis of the resulting metal; significant levels of manganese and iron in finished alloys suggest the utilization of natural smithsonite with the absorption of manganese and iron into the smelt, while the iron and manganese in sphalerite will not vaporize with the zinc during the roasting and sublimation process and result in finished alloys containing notable zinc levels, but lacking significant levels of manganese and iron (Ponting & Segal 1998: 117).

Although generally attributed to the first millennium BC, the invention of the cementation process is probably related to the invention of co-smelting and other mixed-ore smelting techniques in the Chalcolithic of the Near East, documented as early as the fourth millennium BC (see Rapp 1986). Indeed, the development of co- and mixed-ore smelting methods was likely responsible for the explosion of copper-base alloying in the third millennium BC to include copper-arsenic, lead, nickel, antimony, and tin. Despite the ubiquity of zinc ores that naturally occur in association with copper ores, there is little evidence of widespread copper-zinc alloying before the first millennium BC.

A few notable exceptions that have been published but not often remarked upon in the context of early brass involve the corpus of metal objects from Thermi on the Greek island of Lesbos, a site that spans most of the Aegean Early Bronze Age (circa 3000-2500 BC). This collection is most famous for having some of the earliest tin bronzes in the Aegean (a pin from Thermi I) as well as the oldest example of tin metal (a bangle from Thermi IV) (Begemann et al. 1992). For this reason, two major lead isotope provenance studies, Stos-Gale (1992) and Begemann et al. (1992), have been carried out on this material in order to address questions about the early sources of tin in the Aegean, with little attention having been paid to the alloying and production technologies used to fashion these artefacts. Given that copper-zinc alloys occur alongside the copper-tin alloys from levels I-V at Thermi, a more comprehensive compositional and metallographic examination of objects from this collection could help to place these objects in a more informed context in the development of brass and tin bronze technology. Table 1 documents the numerous copper-zinc alloys (above 8 wt% Zn) at this site in relation to other early examples.

Begemann et al. (1992: 219) wrote of the early copper-zinc alloys from Thermi, “We consider this to be a chance occurrence, not the beginning of intentional brass technology,” a sentiment shared by Stos-Gale (1992: 160). The assertion that
these early copper-zinc alloys were accidental is founded on an implicit assumption that can now be re-evaluated in light of recent findings. The interpretation of these alloys as accidental or unintentional implies that ancient metalworkers were somehow unaware or not technologically capable of managing the materials of their own craft. Alternatively, we suggest that these early examples of copper-zinc alloying attest to a more widespread and earlier working knowledge and use of brass production in the Near East than is commonly accepted.

In recent years, two separate archaeometallurgical projects on artefact collections from Harvard University museums were analysed at the Center for Materials Research in Archaeology and Ethnography (CMRAE), Massachusetts Institute of Technology, under the direction of Professor Heather Lechman, both of which uncovered evidence for intentional copper-zinc alloy production in the mid-second millennium BC. Although a millennium later than the Thermi objects, the artefacts from Nuzi, in northern Mesopotamia, and Tepe Yahya, in southeastern Iran, are synchronic with a single find from Ugarit (Ras Shamra) with 12 weight percent zinc (Schaeffer-Forrer et al. 1982, in Craddock 1988) and the much-contested pin from Ugarit (Ras Shamra) with 12 weight percent zinc (Schaeffer-Forrer et al. 1982).

Results and Discussion from Tepe Yahya
The three brass artefacts analysed from Tepe Yahya, housed in the Yahya collection of the Peabody Museum at Harvard University, were all excavated from the same archaeological context dated to the end of the Late Bronze Age period ‘IV A’ (circ. 1700 BC; see Thornton et al. 2002). They were found in an area of the site that exhibits more resemblance in material culture to the Bactrian Margiana Archaeological Complex (BMAC) of Central Asia than to the local material culture of the preceding Middle Bronze Age period (Period IVB: 2400-2000 BC). This distinctive material culture, which is found throughout Iran at this time, has been discussed by Hiebert and Lamberg-Karlovsky (1992), and interpreted as an actual movement of people and not just a result of trade or cultural adoption. Within the metals collection from Tepe Yahya, there is a dramatic difference in chemical composition and form between the objects found within the ‘Central Asian’ area of well-built domestic houses on the southern side of thetell site in Period IV A (including the three brasses presented here) and contemporary artefacts from the northern area of the site that are a
direct continuation of the Period IVB culture (see Thornton et al. in press). In addition to the copper-zinc alloys, ornaments in the ‘Central Asian’ area of the site were made of tin bronze, leaded tin bronze, and even ‘proto-pewter’ (Pb-Sn), while those from the local Period IVB areas of the site were predominantly arsenical copper.

The three brass pieces analysed from Period IVA are a small fragment of cylindrical shape, a broken ‘bracelet’ fragment, and a piece of 1-2 mm thick ‘ribbon’ wire (not analysed metallographically). The bracelet fragment was covered by an even yellow-green patina, with one end having been more heavily corroded. X-radiography of this object showed that the modern corrosion surface does not mimic the original shape of the metal, which was of uniform thickness throughout (about 4 mm). A transverse section of the bracelet revealed a large stress fracture in the centre of the object that runs longitudinally through the length of the object. The metal itself, which contains roughly 19.4 weight percent zinc and 0.86 weight percent lead, has a bright golden hue and contains a number of inclusions determined by EMPA to be zinc sulphide and lead inclusions. Etching with alcoholic ferric chloride (FeCl₃) and potassium dichromate (K₂Cr₂O₇) revealed fairly equiaxed grains containing annealing twins, with smaller grains toward the outer edge and larger grains along the fracture and centre of the object (Fig. 1). This, along with the absence of strain lines, indicates the final step in production was an annealing episode. The fact that this object was not work-hardened as a final manufacture step suggests it was decorative rather than utilitarian, and likely a bracelet, as labelled by the excavators.

The cylindrical fragment had an even yellow-green patina similar to that found on the bracelet, with one end of the piece having been flattened into a finished edge. Although not x-rayed, a small stress fracture can be seen in the bottom centre of the transverse section. The metal, which contains roughly 16.9 weight percent zinc, 1.82 weight percent lead, and 0.78 weight percent tin, again had a golden hue, but slightly less lustrous in appearance due to decreased zinc and increased lead content.

Etching with ferric chloride and potassium dichromate again revealed equiaxed grains (although roughly half the size of the bracelet’s grains) with annealing twins, and no strain lines. This cylindrical fragment contains a higher number and concentration of zinc-sulfur and lead inclusions than are present in the microstructure of the bracelet, and the inclusions have been plastically deformed and elongated towards the V-shaped fissure on the edge of the object (Fig. 2). The presence of this fissure suggests that this object was initially cast with a rectangular cross-section, but through episodes of working and annealing of the exterior edges in opposite directions, the metal was plastically deformed and bent around into a circular shape leaving only the V-shaped fissure where the two edges met. The presence of distinct clusters of small grains on the edge of the bracelet fragment (not shown) may suggest that both objects began with rectangular transverse sections.
There are a number of intriguing questions that can be addressed using the results of chemical and metallographic analyses of these brasses from Tepe Yahya. First, and perhaps the most obvious, is how were they made? Cementation seems to be the most likely explanation. Although iron could not be detected using the ICP-MS due to isobaric interference with the argon carrier gas, the average manganese composition of the entire collection was 7 ppm with a maximum of 28.5 ppm, suggesting an anthropogenic zinc oxide was used in the process and not a natural ore. The second question that must be asked is where did this brass come from, as there is almost no indication of metalworking in any period at Tepe Yahya. Based on the archaeological context, one possible explanation is that brass, tin bronze, and other alloys came to Yahya along with the material culture (if not the people) from the BMAC (see Thornton et al. in press). Finally, why were the fragment and the bracelet worked in such different ways if we presume that both were intended to have a circular cross-section? Is this indicative of two different metalworkers (perhaps a product of the ‘cottage’ industry suggested by Heskel (1982) for the earlier periods at Yahya) or simply the same metalworker with a different goal for each object? These questions may be far more difficult to answer.

Results and Discussion from Nuzi, Iraq

The artefacts reported here form part of the Nuzi collection housed at the Semitic Museum at Harvard University, excavated from 1927-1931 by a joint project of Harvard University and the American School of Oriental Research, Baghdad. Two finger rings were recovered from Stratum II occupation levels in the temple complex on the main mound. Stratum II, the most extensive Bronze Age occupation at the site, is identified as Mitannian, Nuzi Ware having been identified in a number of contexts (Starr 1939; Shoemaker 1996). The Stratum II occupation was destroyed and abandoned and much of the Mitanni occupation was sealed by this destruction layer, dated to c. 1350 BC, which clearly marks the end of a Mitanni presence at Nuzi (James Armstrong, personal communication).

A small ring in the shape of a flat band was recovered from the main courtyard of the Stratum II temple (Temple A). Identified by excavators as having been part of the store of temple offerings and furnishings, this piece survived the sack of Nuzi and was found in the occupation layer just below the destruction level. A second ring with ridged surface decoration was recovered from an open area just outside the northern entrance to Temple A, sealed in a context below the destruction layer. The small finds excavated from this area are thought to have been part of the Temple A furnishings. The objects appear to have been scattered as a result of the looting and destruction of the Temple during the sack of Nuzi.

Chemical analysis identified the band as a copper (77.6 wt%), zinc (12.2 wt%), tin (6.3 wt%), lead (3.35 wt%) alloy. Metallographic analysis revealed a solid matrix of copper, zinc, and tin metal alloy with inclusions of lead that precipitated out of the molten metal along the grain boundaries during the initial casting and cooling of the metal (Fig. 3). Features of the microstructure reveal that the original cast blank, a rod or bar, was worked along both the interior and exterior surfaces, compressing and bending the metal into shape. The deformed and aligned lead inclusions along with the presence of equiaxed grains and annealing twins indicate that a number of working and annealing episodes occurred during the production of the ring (Fig. 3).

The results of chemical analysis reveal that the decorated ring was made from a leaded-brass alloy, 79.8 weight percent copper, 14.4 weight percent zinc, and 4.73 weight percent lead. The bright yellow-orange solid microstructure of the copper-zinc (brass) alloy also contains lead inclusions that precipitated out of the molten metal along the solidifying copper-zinc grain boundaries during the initial cast and cooling of the metal (Fig. 4). Metallographic examination of this piece reveals that it was also shaped from a cast blank; the small size and equiaxed
shape of grains along with the presence of annealing twins indicate that a number of alternating working and heating episodes were used to shape the original cast rod into a ring.

The production technique of shaping a cast blank into an object through sequences of hammering and annealing is well-attested in the Near East by the time of Nuzi. The striking and unexpected results of these analyses are the chemical compositions of the rings. The zinc content in these pieces, 12.2 weight percent and 14.4 weight percent, would have been sufficient to alter the appearance of the copper alloys. Even at low levels (relative to later ‘true’ brasses of 30 to 32 wt% Zn), the presence of zinc in copper alloys renders the metal a noticeably more golden colour than copper-tin or copper-arsenic brass (Craddock 1995: 293). The golden colour of the brasses used to fashion these rings would have made them distinct from contemporary bronze alloys.

The link between the selection of materials, the choices made during production, and the appearance of a finished product is documented elsewhere in the archaeological record (e.g. Hosler 1994; Lechtman 1996). The occurrence at Nuzi of two pieces of jewellery made from an alloy that would have resulted in a finished product with a distinctive colour and appearance is significant. In addition to these brass rings, six other artefacts from the Nuzi Collection were analyzed, all recovered from contemporary Nuzi contexts. The results of analysis of three arrowheads (C. Dixon, analyst) and three stick-pins/fasteners from the site reveal that metalsmiths were using different alloys for different kinds of objects. The arrowheads were made from copper containing small amounts of arsenic or tin along with trace amounts of other components. Two of the stick pins/fasteners were also made from copper with low levels of arsenic (less than 1 wt%); the third fashioned from a copper-tin bronze (Sn 6.37 wt%) distinct in composition from the brass rings. The materials used to fashion the arrowheads and two of the stick pins have been termed ‘dirty’ copper alloys, and interpreted as having been the result of smiths using poly-metallic ores or recycled metals rather than having been deliberate combination of metals to produce intentional alloys (Bedore Ehlers & Dixon 1998; Heather Lechtman, personal communication). It is possible that the production methods used to retain or introduce zinc in certain alloys were employed discerningly, with specific results in mind; it is intriguing that objects of personal adornment were made from golden-coloured brass while objects made for more functional purposes were fashioned from copper and copper alloys, notably lacking zinc.

Conclusions

The characteristics of zinc are such that its extraction and retention in an alloy require particular, refined processes during production. It seems unlikely that sites such as Thermi, Tepe Yahya, or Nuzi were centers of great metallurgical innovation, yet all three managed to acquire one of the most elusive alloys of the Bronze Age. Does this suggest that copper-zinc alloys were not as rare as previously thought, or could the lack of examples from the Bronze Age be a result of non-random sampling of metal collections - e.g., analysing large tools and weapons over small jewellery and personal ornaments? Future research has the potential to add much to this discussion, particularly on the relationship between zinc and tin, which are found both alloyed together and in association with one another at all three sites.

Requiring specific processing techniques and a deliberate investment of time and labour, the production of copper-zinc alloys indicates a high level of working knowledge of materials and material processing on the part of metalsmiths. Perhaps, as in the Medieval period of Europe, zinc was added to copper-tin alloys as a form of cheap bronze. Alternatively, copper-zinc alloys may have been highly valued due to their golden colour, distinct from bronze alloys, and thus their resemblance to objects fashioned from gold. Ultimately, evidence of brass production and the reconstruction of the components and production processes used in the manufacture of copper-zinc alloys indicates something about the methods used and the decisions and choices metalsmiths were making to result in the desired finished product.

The results of these recent studies provide evidence that copper-zinc alloys existed almost two thousand years before the date generally accepted for the development of the cementation process, suggesting that the history of brass is longer and more complex than is generally believed. Our role as archaeologists interested in metallurgy is to figure out how and why. Answers regarding the origins and development of early copper-zinc alloys in the Ancient Near East may be as elusive today as they were twenty years ago, but at least now we know to look for them.

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References


