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TECHNICAL STUDIES ON THE BRONZE AGE METAL ARTEFACTS FROM THE GRAVEYARD OF DEH DUMEN, SOUTH-WESTERN IRAN (THIRD MILLENNIUM BC)*

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During the excavations of the graveyard at the site of Deh Dumen in south-western Iran, 15 graves from the Early/Middle Bronze Age were uncovered that contained a variety of metallic artefacts. This paper reports on the analysis of nine metal artefacts, including eight broken vessels and a decorative strip that covered the handle of a dagger. The ICP–MS results showed that the bodies of the vessels are made of tin bronze alloy with variable amounts of tin, while the internal piece of the base of one vessel is made from an arsenical copper alloy. Further, the metallic strip is a thin sheet manufactured with partially pure silver. Microanalytical and microstructural information yielded by SEM–EDS revealed elongated Cu–S inclusions and lead globules as various phases formed in bronze solid solution. This study presents some information about the transition from arsenical copper to bronze metallurgy in the third millennium BC in south-western Iran.

KEYWORDS: BRONZE AGE, IRAN, DEH DUMEN, TIN BRONZE, ARSENICAL COPPER, SULPHIDIC INCLUSIONS, ICP–MS and FE-SEM–EDS

INTRODUCTION

The Iranian Plateau is one of the important regions for the development of metallurgy in the ancient world. The first evidence of the manufacture of metal artefacts in Iran is the small ornamental objects made by worked/annealed native copper, dated as early as the eighth to seventh millennium BC in western Iran (Smith 1967; Bernbeck 2004; Pernicka 2004; Pigott 2004; Oudbashi et al. 2012; Helwing 2013). By the fifth millennium BC, there is evidence for the casting of melted native copper and then the smelting of copper ores (Moorey 1969; Thornton et al. 2002; Thornton 2009; Oudbashi et al. 2012). The majority of the copper artefacts from these early periods contain significant amounts of arsenic (Pigott 2004; Thornton 2009). Objects made of tin bronze and dated to the late fourth to early third millennium BC, marking the start of the Bronze Age, have been found in western Iran (Dyson and Voigt 1989; Pigott 2004; Fleming et al. 2005; Thornton 2009;
The earliest evidence for the intentional production of bronze (Cu–Sn) has been identified in the Early Bronze Age Kalleh Nisar graveyard in Luristan, western Iran (Fleming et al. 2005).

In spite of these early tin bronze artefacts, the extensive use of tin and the manufacturing of tin bronze objects in Iran starts towards the end of the third millennium BC (Stech and Pigott 1986; Pigott et al. 2003; Thornton et al. 2005; Frame 2010). In fact, the appearance of copper–tin alloy in late Chalcolithic/Early Bronze Age contexts in western Iran (about 3200–2800 BC) is surprising because, in many cases, a complete lack of any amount of tin (even in minor content) is typical of many other sites on the Iranian Plateau before the end of the third millennium BC (Thornton 2009). Throughout the Late Bronze Age (2000–1500 BC) and the Iron Age (1500–550 BC), tin bronze was the predominant alloy used by Iranian metalworkers (Fleming et al. 2005, 2006; Frame 2010; Oudbashi et al. 2013).

The important Bronze Age assemblage in Iranian metallurgy has not been extensively analysed and thus very little is known about the alloys used to produce metallic artefacts. Especially, because of the transformation from accidental/intentional alloying of arsenical copper in the Chalcolithic/Early Bronze Age period (Weeks 2003; Thornton 2009; Rehren et al. 2012) to intentional copper alloy (tin bronze) in Iran during the third millennium BC (Thornton 2009; Oudbashi et al. 2012), the analysis of metal artefacts from Early/Middle Bronze Age sites can help us to reveal metallurgical events during this crucial period of transition.

In order to provide more evidence for this period, this paper presents the compositional analysis of the metallic artefacts of the Deh Dumen site in order to ascertain the types of alloys used, as well as to characterize the microstructure and phase determination in the metal samples, to identify the metalworking traditions in the Deh Dumen objects and to provide comparative data for contemporary metallurgical finds from western Iran.

THE DEH DUMEN ARCHAEOLOGICAL SITE

The graveyard of Deh Dumen (or Deh Paein) is located at latitude 31°9´13˝ N and longitude 51°6´14˝ E, on mountain slopes about 100 m south-west of Deh Dumen village, a suburb of Dena Township, and about 70 km north-west of the city of Yasuj, the capital of Kohgiluyeh and Boyer-Ahmad province, in the south-west of Iran (Fig. 1). The recent archaeological excavations carried out at the site in winter 2013, under the supervision of R. Naseri, were part of the emergency archaeological excavations for archaeological sites at risk due to the dam project over the Khersan River. The Deh Dumen graveyard is located on a natural hill that is formed from river rubble stones. In the 2013 archaeological excavations, a 20 m ×30 m trench was excavated, revealing 15 large graves constructed with stones (Fig. 2). Two specific grave forms can be observed at Deh Dumen: graves with a smooth and flat roof (box-shaped graves) and graves with a herringbone (or peaked) roof (mound graves). Besides the stone graves, two large burial jars containing skeletons were found (Fig. 2, J3 and J4). Furthermore, remnants of the bases of three jars were also found that could not be recognized as burial jars (Fig. 2, J1, J2 and J5). Many objects were placed in the graves close to skeletons. They included different styles of pottery, also different metallic artefacts such as vessels and weapons, as well as stone vessels and arrowheads (Naseri 2013).

Most of the potteries from the graves have a red to brown slipped fabric and includes jars with impressed decorative bands on the body and base, as well as jars with parallel grooved and jagged decorations on the body (Fig. 3). These pottery types are comparable with examples found at Bani Surmeh (Haerinck and Overlaet 2006, 23, Fig. 7, 26, 27) and Susa D (Carter 1979, 452),
belonging to the second half of third millennium BC. Painted pottery is rare in the Deh Dumen graves; nevertheless, some monochrome painted vessels from the graves find comparisons at Bani Surmah (Fig. 3) (Haerinck and Overlaet 2006, 26, Fig. 10, A13-1). The most common types of metallic vessel found in the Deh Dumen graves include simple vases with a broad neck and mouth, and a sharp carination at the shoulder or in the middle of the body (Figs. 4 (a) and 4 (b)). These are very similar to bronze vases discovered at the Bronze Age graveyard of Bani Surmeh (Haerinck and Overlaet 2006, 42, Fig. 20, Al-7 and Al-4-54) that are dated to the Early Bronze Age III of Pusht-i Kuh of Luristan, generally equated to the Early Dynastic III period in Mesopotamia. Similar vessels are also known from Susa and assigned to the Susa D stage (Le Breton 1957, 118, Fig. 40, 32 and 33). In addition to plain metal vessels, a small number of the metallic vessels found in the Deh Dumen graves were decorated. Two decorated vessels were discovered in grave no. 15 (Fig. 4 (b)). One vase (D.P.287) is elaborated with three rows of different geometric and zoometric patterns. The upper decorative row includes triangles surrounding the vase; two other rows consist of circles and fish that are separated by horizontal projecting lines encircling the vase. Some analogous examples for comparison with this vase are available, such as a vessel found in the Susa D stage (Le Breton 1957, 118) as well as vessels in the Louvre museum.
(Begemann et al. 2008, 60; Engel 2008, 68) and the Preussicher Kulturbesitz museum (Engel 2008, 68). These are all dated to the middle or the second half of the third millennium BC (Figs. 4 (c) – 4 (e)). Another vessel from grave no. 15 (D.P.283) is a small vessel similarity elaborated with a row of triangles, circles and fish (Fig. 4 (b)).

Although metallic weapons are rare in the Deh Dumen graves, two daggers were found in graves no. 3 and no. 15 (Figs. 5 (a) and 5 (b)). These are comparable to daggers of the Susa D stage, dated to the second half of the third millennium BC (Le Breton 1957, 118, Fig. 40, 19 and Fig. 41, 16). Further, a shaft-hole axe from grave no. 15 (Fig. 5 (c)) may also be dated to the second half of the third millennium BC, in comparison with examples found at Susa D and Bani Surmeh (Le Breton 1957, 118, Fig. 41, 6; Haerinck and Overlaet 2006, 36, Fig. 16, B15-1). Based on the structure of the graves and the different metal and pottery finds, the site is dated to the Early/Middle Bronze Age (third millennium BC). The graves and

Figure 2. (a) A plan of the excavated area of Deh Dumen and 15 Bronze Age graves. (b) One of the Bronze Age graves from Deh Dumen (no. 1). (c) The design of the same grave.
Figure 3  (a) A pottery jar (D.P.121) from grave no. 4. (b) A pottery jar (D.P.254) discovered in grave no. 15. (c) Monochrome painted pottery (D.P.309) from grave no. 7.
burial goods found at Deh Dumen find many comparisons with Early/Middle Bronze Age graveyards excavated at Pusht-i Kuh in Luristan, western Iran, such as Bani Surmeh (Haerinck and Overlaet 2006).

MATERIALS AND METHODS

For this study, eight broken vessels or parts of broken vessels excavated from different graves (Fig. 6) as well as a metallic strip covering the handle of a dagger were examined (Fig. 5 (b)). Two vessels (D.P.190 and D.P.287) have a metal piece that has formed the vessel’s base, and
the sheet metal of vessel has been used to cover it to shape the form of the base. It was possible to sample from the base of vessel D.P.190 because it was broken into many pieces; thus two samples were selected from this object, one from the metal sheet and the other from the internal base piece (Figs. 6 (e) and 6 (f)). Finally, 10 metal samples were selected and prepared from nine metallic artefacts.

For the compositional analysis, 0.5 g from the metallic bulk of each sample was cut and all of the corrosion layers were removed. Each sample was dissolved in aqua regia in preparation for chemical analysis. Another small piece of each sample was mounted in epoxy resin, ground with abrasive paper (from 180 to 3000 grit) and then polished with 3 and 0.5 μm diamond pastes, respectively, to prepare cross-sections.

The prepared solutions were analysed using the quantitative inductively coupled plasma – mass spectrometry (ICP–MS) method, in order to identify the major, minor and trace elements present in the samples. The ICP–MS analyses were performed on a HP 4500 ICP–MS system produced by GMI. The microstructural observations and microanalyses were done using the method of scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM–EDS). The polished cross-sections were analysed using field emission SEM (FE-SEM) equipment (model MIRA3, from TESCAN) coupled with an EDS analyser.

Figure 5  (a) A dagger (D.P.108) from grave no. 3. (b) A dagger with decorative strips (D.P.302) from grave no. 15. (c) A shaft-hole axe (D.P.270) from grave no. 15.
RESULTS AND DISCUSSION

The results of the ICP–MS analysis for identifying the chemical compositions of 10 metallic samples from Deh Dumen are presented in Table 1. The major (>1%), minor (1% > 0.1%) and trace (<0.1%) elements in the composition of samples are shown in weight per cent (wt%) values. The ICP–MS analysis indicated that the bodies of eight metallic vessels were made from tin bronze alloy, with differing amounts of Sn (Table 1). The Sn content varies between 5.72% and 10.11%. In the sample from the internal metallic piece of the vessel’s base (sample D.P.190/1), tin was detected only as a trace element (0.02 wt%), while arsenic was measured as the main alloying component, at 1.83%. Arsenic is present in eight of the bronze samples as a minor element. Other important minor/trace elements detected in the composition of the nine copper alloy samples are silver, bismuth, iron, nickel, lead, sulphur, antimony, selenium and zinc. The amounts of Ag, Fe, Ni and Pb are variable in the different samples. Sulphur and antimony were detected at less than 0.1%, as traces, and bismuth and selenium were only detected at the 0.01% level in some samples, while zinc was measured in similar amounts in almost all of the samples.

Figure 7 shows a comparison between the analysed Deh Dumen copper alloy objects and previously published results for some other tin bronze objects from the Kalleh Nisar and Bani Surmeh Bronze Age sites (Begemann et al. 2008) and the Old Elamite site of Malyan...
Table 1  The results of ICP–MS analysis on 10 metallic samples from Deh Dumen: the type of samples are shown and the elements detected in all the samples are presented in weight per cent (wt%)

| Sample | Type       | Grave no. | Ag  | Al  | As  | Bi  | Ca  | Cu  | Fe  | K   | Mg  | Mn  | Na  | Ni  | P   | Pb  | S   | Sb  | Se  | Si  | Sn  | Zn  | Yb |
|--------|------------|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| D.P.NON | Body of vessel | 9         | 0.01| n.d.| 0.11| 0.01| n.d.| 91.08| 0.07| n.d.| n.d.| n.d.| 0.16| n.d.| 0.11| 0.01| 0.01| n.d.| 8.41| 0.12| n.d.|
| D.P.102 | Body of vessel | 3         | 0.01| n.d.| 0.10| 0.01| n.d.| 91.15| 0.06| n.d.| n.d.| n.d.| 0.16| n.d.| 0.11| 0.01| 0.01| n.d.| 8.35| 0.12| n.d.|
| D.P.144 | Body of vessel | 3         | 0.01| n.d.| 0.11| 0.01| n.d.| 90.79| 0.09| n.d.| n.d.| n.d.| 0.16| n.d.| 0.12| 0.02| 0.00| 0.01| n.d.| 8.67| 0.12| n.d.|
| D.P.150 | Body of vessel | 1         | 0.24| n.d.| 0.23| n.d.| n.d.| 91.52| 0.17| n.d.| n.d.| n.d.| 0.02| n.d.| 0.02| 0.01| n.d.| 7.69| 0.12| n.d.|
| D.P.190/1 | Base of vessel | 6         | 0.21| n.d.| 1.83| 0.01| n.d.| 96.90| 0.47| n.d.| n.d.| n.d.| 0.22| n.d.| 0.15| 0.03| 0.09| 0.01| n.d.| 0.02| 0.13| n.d.|
| D.P.190/2 | Body of vessel | 6         | 0.03| n.d.| 0.24| n.d.| n.d.| 90.22| 0.09| n.d.| n.d.| n.d.| 0.02| n.d.| 0.04| 0.04| 0.02| n.d.| 9.32| 0.12| n.d.|
| D.P.222 | Body of vessel | 13        | 0.25| n.d.| 0.21| n.d.| n.d.| 90.96| 0.18| n.d.| n.d.| n.d.| 0.04| n.d.| 0.07| 0.02| 0.02| n.d.| 8.14| 0.12| n.d.|
| D.P.283 | Body of vessel | 15        | 0.10| n.d.| 0.39| n.d.| n.d.| 93.08| 0.22| n.d.| n.d.| n.d.| 0.16| n.d.| 0.09| 0.08| 0.05| n.d.| 5.72| 0.12| n.d.|
| D.P.287 | Body of vessel | 15        | 0.04| n.d.| 0.24| n.d.| n.d.| 89.26| 0.17| n.d.| n.d.| n.d.| 0.01| n.d.| 0.03| 0.01| n.d.| n.d.| 10.11| 0.16| n.d.|
| D.P.302 | Strip       | 15        | 97.01| 0.08| n.d.| n.d.| 0.51| 0.08| 0.04| 0.45| 0.14| 0.45| 0.27| n.d.| 0.04| 0.06| 0.41| 0.02| n.d.| n.d.| 0.06| n.d.| 0.02|

Figure 7  Scatter plots for comparison between the compositions of nine copper alloy objects from Deh Dumen and some tin bronze objects from three Bronze Age sites in Iran—Kalleh Nisar, Bani Surmeh and Malyan (Pigott et al. 2003; Begemann et al. 2008): (a) Sn versus As; (b) As versus Sb; (c) Ag versus Ni.

(Pigott et al. 2003). Only tin bronze objects from the three sites were selected for comparison with the Deh Dumen objects.

Figure 7 (a) shows a variation diagram of tin versus arsenic in the nine copper alloy samples from Deh Dumen, in comparison with the bronze composition at the three sites. Based on the diagram, eight samples from Deh Dumen are alloyed with tin, while arsenic is the main alloying element in one sample. The amount of tin is variable across all the samples. Based on the diagram, arsenic plays an important role in alloy composition in only one sample (D.P.190/1). All of the bodies of the vessels are made of tin bronze, while the internal metallic piece of the vessel’s base is made of arsenical copper. Arsenic plays a more significant role in bronze samples from other Early Bronze Age sites—Kalleh Nisar and Bani Surmeh—and when tin is detected, it is present in low amounts in these bronzes. On the other hand, Malyan and Deh Dumen bronzes contain higher amounts of Sn.

It has been suggested that the tin bronzes of the Early Bronze Age may have been produced accidentally, because while a tin-bearing copper ore was being smelted for the production of copper/arsenical copper, the naturally occurring presence of tin in ore caused tin bronze to be produced. In fact, the EBA metalworkers did not exploited cassiterite; but they were aware that the ore from some specific mines resulted in better-quality metal objects (Muhly 1985). However, it should be observed that there is no regular pattern in the tin content of bronzes from different sites and tin is clearly present in all bronzes, although the tin content does increase over time, from smaller amounts found at Kalleh Nisar and Bani Surmeh (first half of the third millennium BC) to greater amounts found in the metal objects from Malyan and Deh Dumen (second half of the third millennium BC).

Figure 7 (b) shows a scatter plot of the As versus the Sb content in the composition of copper alloy samples from Deh Dumen and other sites. The plot shows the relationship between the amounts of As and Sb, indicating that as As increased, so did Sb. It is only in the high-arsenic copper sample that antimony has also been detected in high amounts, confirming the homogenous character of the Deh Dumen tin bronze materials. From a comparative point of view, there seems to be no apparent relationship between the composition of the Deh Dumen samples and other Bronze Age (third millennium BC) bronze objects based on the As and Sb contents. Figure 7 (c) shows a scatter plot of the Ag versus the Ni content in the composition of the copper alloy samples from Deh Dumen and other sites (Kalleh Nisar, Bani Surmeh and Malyan), which clearly indicates differences between these samples. It states that there is no apparent relationship between the Deh Dumen samples based on the Ag and Ni contents. On the other hand, the Ag versus Ni contents in bronzes from Deh Dumen and three other sites also shows no relationship between the composition of the Deh Dumen samples and other Bronze Age (third millennium BC) bronze objects.

The chemical composition of sample D.P.302 is completely different from that of the other samples. This is part of a thin metal strip that covered the handle of a metallic dagger. The ICP–MS analysis of this sample (Table 1) revealed that it was made from an almost pure piece of silver. The strip has 97.01% silver, and other elements such as Cu, Fe, P, Pb, S and Sb are measured as minor and trace amounts. Also, the Al, Ca, K, Mg, Mn, Na, Si and Yb detected as minor/trace contents in this sample may have come from the soil after long-term burial.

Observation of the microstructure of the copper alloy samples by FE-SEM showed many elongated dark inclusions scattered in the copper matrix (Fig. 8). These dark inclusions were elongated in the long direction of the cross-sections. EDS analysis on one of the dark elongated inclusions in sample D.P.190/1 showed its composition as follows: Cu, 54.27%; S, 18.43%; Pb, 12.85%; Fe, 9.70%; Se, 3.55%; Sn, 0.78%; and As, 0.42%. According to the composition, it is
Figure 8  FE-SEM–BSE micrographs of some samples from Deh Dumen: (a) D.P.102, showing some lead globules scattered in the microstructure; (b) a tin-rich α + δ eutectoid phase formed in a solid solution matrix; (c, d) elongated Cu–S inclusions in samples D.P.190/1 and D.P.190/2; (e, f) lead inclusions scattered in the microstructure, with intergranular and intragranular corrosion affecting the relevant grain microstructure in bronze samples showing twinning and slip lines, samples D.P. Non and D.P.150.
obvious that the dark elongated inclusions are copper sulphide phases with some impurities. Further, some bright globules are also visible in the high-magnification view of the bronze matrix. Analysis of these globules showed that they are Pb-rich phases with more than 80% of lead.

In addition, some metallic fine phases are visible in the FE-SEM micrographs (Fig. 8 (b)). Based on EDS analysis, these are some Cu-Sn, tin-rich phases with about 30% of tin, and they may be $\alpha + \delta$ eutectoid phases that have remained unchanged from the original casting microstructure of the bronze alloy. In some samples, internal corrosion attacks have caused the formation of intergranular and intragranular corrosion in the bronze matrix. These phenomena have created a grain microstructure in some samples (Figs. 8 (e) and 8 (f)). Accordingly, it is clear that the microstructure consists of worked and annealed grains containing twinning and slip lines. This proves that the original cast bronze ingots were changed by a cycle of cold-working and annealing to shape thin sheets that formed the bronze vessels. In some cases, the working and heat treatment was unable to remove all the segregations that occurred during the solidification of the molten alloy and some eutectoid phases may be observed in the microstructure (Scott 1991, 2014).

The identification of the tin bronze in the Deh Dumen Bronze Age graveyard is significant for the development of copper archaeometallurgy on the Iranian Plateau. From the Neolithic up to the end of the Chalcolithic period, metalworkers used copper to make different artistic and functional artefacts. Many of these copper objects contain significant amounts of arsenic, especially in the Chalcolithic period (4500–3000 BC). The arsenical copper may initially have been an accidental alloy, created through the use of As-bearing copper ores for copper production (Pigott 2004; Thornton 2009, 2010; Thornton et al. 2009; Oudbashi et al. 2012). The emergence of deliberate alloying of copper may go back to the third millennium BC. The first evidence of tin bronze production in western Iran is from the AI and AII areas of the Kalleh Nisar Bronze Age graveyard in Luristan (late fourth to third millennium BC), from some other graveyards in Luristan (third millennium BC), in some bronze objects from Susa, in south-western Iran (late fourth to early third millennium BC), in one bronze object found at Tappeh Giyan in western Iran and in one bronze needle from Sialk, in central Iran (both from the third millennium BC) (Ghirshman 1938; Moorey 1982; Tallon 1987; Fleming et al. 2005; Nezafati 2006; Nezafati et al. 2006; Begemann et al. 2008; Haerinck and Overlaet 2008, 2010). Begemann et al. (2008) and Fleming et al. (2005) reported some analytical results on some metallic artefacts from the Kalleh Nisar graveyard from western Iran belonging to the Early Bronze Age (early third millennium BC). Most of these objects are made from tin bronze alloy containing a significant amount of tin (more than 2%), which shows that a deliberate alloying process was probably employed to make these objects (Fleming et al. 2005; Begemann et al. 2008; Haerinck and Overlaet 2008, 2010). On the other hand, 19 metal artefacts from Area C of Kalleh Nisar, dated to the Early Bronze Age II (EBA-II, 2900–2600 BC) were analysed and 15 objects were found to be made from tin bronzes containing variable amounts of Sn (Fleming et al. 2005; Haerinck and Overlaet 2008). Although some of the Kalleh Nisar graveyard’s tombs were reused in the Middle Bronze Age (the early second millennium BC), the analysed artefacts are dated to Phase I of the Early Bronze Age (EBA-I, late fourth to early third millennium BC) (Begemann et al. 2008; Haerinck and Overlaet 2008, 2010). According to the literature, the application of tin bronze at the beginning of third millennium BC is restricted to noted examples. On the other hand, in the second half of the third millennium BC, some limited evidence about tin bronze production has been found, such as the low-tin arsenical bronze from Tappeh Yahya, in southern Iran (Thornton and Lamberg-Karlovsky 2004; Thornton 2009), some bronze objects from Godin Tappeh, in western Iran (Frame 2010),

and some tin bronze objects from Malyan, in south-central Iran (Pigott 1990; Pigott et al. 2003). In fact, the development of bronze metallurgy in Iran occurred in the second millennium BC (Late Bronze Age and Iron Age). Although the Malyan and Susa sites are related to the Old Elamite period (2750–1500 BC), because of their proximity to Deh Dumen, they may be important in the bronze metallurgy of the third millennium BC in the west/south-west of Iran. On the other hand, some similarities can be observed between bronze objects from Deh Dumen and Susa D, as discussed earlier.

Based on the analytical results, the bronze vessels from the Early/Middle Bronze Age site of Deh Dumen are made from bronze alloys containing variable amounts of tin. The tin bronze artefacts containing considerable amounts of tin (4–10%) are an important find in the archaeometallurgy of Bronze Age Iran. Further, the absence among these same samples of a significant amount of arsenic in the composition of the copper/bronze objects is also important. Usually, in analysed bronzes from the Iranian Iron Age (about 1500–2000 years later than the Deh Dumen graves), arsenic is detected only as a minor/trace element and tin is measured as the main alloying component in different objects (Fleming et al. 2005; Fleming et al. 2006; Oudbashi et al. 2013). Also, other metallic elements such as lead are detected as a minor component. The composition of eight samples from the bodies of vessels apparently shows that the bronze alloy was made by means of an uncontrolled alloying process (Oudbashi and Davami 2014). The minor/trace elements detected in the Deh Dumen bronzes may reveal a metallurgical technology (mining/smelting/alloying) that resulted in the production of homogeneous tin bronze alloy (Puziewicz et al. 2014), although the tin content shows significant variation in different samples.

The varying tin content in the samples might be the result of several different smelting/alloying processes: (1) the co-smelting of copper and tin ores (Pigott 2004; Valério et al. 2013); (2) cementation of metallic copper with cassiterite (Murillo-Barroso et al. 2010; Valério et al. 2013); (3) the use of a complex Sn-bearing copper ore for the smelting of copper (Nezafati 2006); and (4) metal recycling (Figueiredo et al. 2010). Each of these could produce bronze alloys having different amounts of tin in each instance of the smelting/alloying process. Co-smelting of copper and tin ores may create different bronze alloys because the addition of cassiterite to copper ores decreases the melting point of the mixture and the smelting time. The second method has also been attested to in the ancient world, although it required covering the cassiterite and the molten copper with charcoal (Pigott et al. 2003). In the third method, the tin content of the bronze artefacts is strongly related to the tin content found in copper Sn-bearing ore, and many of the copper ores in Iran have no significant tin content (Cleuziou and Berthoud 1982). It should be noted, however, that a recent examination of ore from the ancient mine at Deh Hosein showed that copper and tin occur in the same mineralization (Nezafati 2006). Nevertheless, a high amount of tin in many Iranian archaeological bronzes is probably the result of deliberate alloying processes. The application of a recycling process to make new bronze artefacts has been a common method in bronze technology in the ancient world (Henderson 2000; Drewett 2001; Price and Burton 2011). The bronzes manufactured with this method usually have a low tin content because of the preferential oxidation of tin during the recycling (melting) operation, which produces low-content tin bronze or even copper with a small tin content (Figueiredo et al. 2010; Valério et al. 2010). Another way to produce bronze alloy is to add metallic copper to metallic tin. Although the ancient metalworkers could smelt metallic tin from cassiterite (SnO₂) and produce objects with metallic tin (Muhly 1985; Pulak 2000; Hauptmann et al. 2002), there is no evidence from tin smelting in the Early/Middle Bronze Age in the ancient world.
Thus with regard to significant amounts of tin in the composition, processes (1) and (2) above are more probable for the bronze alloy production in the Deh Dumen metal artefacts.

To judge from the other minor and trace elements, the bronze samples from Deh Dumen can be considered as similar composition metals. As noted above, the amounts of minor/trace elements in the metal objects are comparable. Nevertheless, there are some variations between the amounts of nickel and silver in all samples. Further, the arsenical copper sample shows different proportions between As and Sb in its composition, while there is no apparent variation between the As versus the Sb content in eight bronze samples. Of course, some minor/trace elements, such as Ni, Sb and As, may have been removed or transferred during the melting process at different temperatures but, in general, considering the minor/trace elements is a useful tool for the study of similarities or the provenance of archaeological metals (Pernicka 2014; Pollard and Bray 2014).

Sample D.P.190/1 is the internal piece of a vessel’s base and its compositional analysis showed that it was made from an arsenical copper alloy. As noted above, the application of arsenical copper during the Chalcolithic period was transformed into tin bronze production in the middle of the Bronze Age and continued until the Iron Age. Results of different studies on prehistoric copper metallurgy show that Chalcolithic and Bronze Age copper objects from the Iranian Plateau have significant amounts of arsenic, while Bronze and Iron Age tin bronzes contain arsenic as a minor or trace element (for more detailed results, see Pigott et al. 2003; Fleming et al. 2005, 2006; Begemann et al. 2008; Frame 2010). The Deh Dumen metal objects (and other third millennium BC copper and bronze objects) could be considered as the stage of transition from arsenical copper to tin bronze on the Iranian Plateau. This is visible due to the use of arsenical copper and tin bronze in the manufacture of a single bronze vessel. Interesting examples of the transition from arsenical copper to tin bronze may be observed in the copper metallurgy of western Iran, where the manufacture of different metals with arsenical copper in the Chalcolithic was changed to low tin bronze production alongside arsenical copper in the Early and Middle Bronze Age, and continued with tin bronze objects in the Bronze Age, as well as the Iron Age from different sites in Luristan and Godin Tappeh (Begemann et al. 2008; Frame 2007, 2010).

Of course, regarding the limited amount of metal finds from Deh Dumen and some limitations for sampling from unbroken objects, any conclusions from the present data about arsenical copper and bronze alloy at this site should be limited to the examined samples, and developing the results further requires more analyses of samples from this site. The amounts of minor/trace elements in the composition of the arsenical copper sample are partially different compared with the tin bronze samples. This may be due to different ore sources used for copper production. In fact, its base may have been produced from an As-rich copper ore from a region different from the source used for the other bronze objects.

Determination of the tin sources in ancient Iran is one of the main problems concerning of the beginning of bronze metallurgy in the Early Bronze Age (Pigott 2004). There have been extensive discussions about tin sources due to the huge amount of tin bronze production on the Iranian Plateau from the Early Bronze Age to the end of the Iron Age (Moorey 1969, 1982; Coghaln 1975; Maddin et al. 1977; Muhly 1985; Pigott et al. 2003).

Some different tin sources for bronze metallurgy on the Iranian Plateau have been suggested by scholars. One of the most likely sources of tin for Iran in ancient time was Afghanistan, with which Iran had a long-standing interaction during prehistoric times (Muhly 1985; Pigott et al. 2003; Fleming et al. 2005). Moorey (1982) suggests two potential tin sources on the Iranian Plateau itself: the Central Lut (an extant desert in central Iran), for which there is minimal evidence, and in the west or north-west of Iran (maybe in Azerbaijan), for which there is still no hard evidence. On the other hand, Nezafati et al. (2006) have suggested that the mining region

of Deh Hosein in central Zagros was a source of tin for bronze production in the Bronze Age, based on results of analytical studies. Nevertheless, the identification of the copper and tin resources used for tin bronze production from the Early Bronze Age of Iran needs much more analytical and isotopic study, to establish the relationship between alloy composition and any particular metallic ores from different regions of Iran.

Another interesting finding at Deh Dumen is the use of silver for the decoration of copper alloy objects. Silver production and the use of silver to make various objects is well documented in the Chalcolithic and Bronze Ages of Iran at Arisman (central Iran) (Pernicka 2004; Vatandoust 2004) and Tappeh Hissar (northern Iran) (Dyson and Voigt 1989).

The presence of copper sulphide inclusions in the bronze matrix may be due to the use of sulphidic, a mixture of oxidic/sulphidic copper ores or even a complex sulphidic copper–tin ore (such as stannite) for smelting/alloying processes (Coghlan 1975; Wertime 1978; Rostoker et al. 1989). The Cu–S inclusions are common microstructural events in ancient copper alloy objects and have been observed in the microstructure of bronze objects. The morphology of these inclusions (elongated, circular) is strongly dependent on the shaping procedure applied to manufacture bronze objects in antiquity (see, e.g., Oudbashi and Davami 2014). The smelting of copper sulphide ores was a common method in ancient metallurgy to extract metallic copper (Coghlan 1975; Bachmann 1982; Hauptmann 2014; Killick 2014) and has been practised in Iran from the Chalcolithic period (Thornton 2009; Oudbashi et al. 2012). These copper sulphide inclusions may belong to unchanged original copper sulphide compounds or by-product copper sulphide compounds that are formed during the smelting process, but that have remained in the bronze microstructure—similar to products of matte production in the process of copper smelting (Craddock 2010; Valério et al. 2013).

CONCLUSION

Recently excavated metal objects from Bronze Age graves at Deh Dumen were studied by means of chemical analysis and microanalysis methods. The results established the use of tin bronze and arsenical copper in the production of different vessels; it has been observed that the thin sheet forming the body of the vessels was made from bronze with a variable tin content, while the internal piece of the base of one of the vessels was made from arsenical copper. The bronze metalworking in the Deh Dumen metal finds is very interesting because this site is dated to the Early/Middle Bronze Age (based on the graves, pottery and metal objects). Bronze production has taken place in Iran since the beginning of the Bronze Age (the late fourth to early third millennium BC), but the development of bronze metallurgy has previously been situated at the end of the third and into the second millennium BC on the Iranian Plateau. The Deh Dumen bronze objects reveal the development of bronze production and alloying in the third millennium BC in south-western Iran. Further, the use of arsenical copper and tin bronze together in a single vessel marks the phase of transition from an accidental/deliberate Cu–As alloy/alloying to deliberate Cu–Sn alloying in the Bronze Age of south-western Iran. The smelting of copper sulphide ores to produce copper alloy objects is another significant aspect of the results of these analyses. The Deh Dumen metals show the continuing application of sulphidic ores in the copper metallurgy of Iran in ancient times. The study of other metallic samples from the Bronze Age of south-western Iran and comparison of the results can help us to gain a better understanding of copper/bronze metalworking in this important period of archaeometallurgy in Iran.

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