An antimony bead from Jerablus Tahtani

Andrew Shortland

ABSTRACT: This paper presents an analysis of a bead from third millennium BC levels of Jerablus Tahtani, near Carchemish in Syria. The bead was found to consist of almost pure metallic antimony, with small amounts of lead, arsenic, copper and tin. Antimony objects are very rare in the archaeological record and very few analyses have been carried out. Until this paper, no description of the microstructure of such beads has been published. The paper goes on to discuss the probable sources of the antimony metal and the possible provenance of the bead itself.

Introduction

Prof Peltenburg of the Dept of Archaeology, Edinburgh, submitted a fragment of a tube bead from the site of Jerablus Tahtani, near Carchemish in Syria, to the Research Laboratory for Archaeology for analysis. The bead, number JT1219, was uncovered in Tomb 787 which was found in Area IV, Level 4 of the site. Although disturbed, it had an assemblage of beads and pendants in layers thought to date to the same period as the Bead Level of Nineveh, that is to about 2300–2500 BC (Peltenburg *et al* 1996, 10 and Fig 10).

Analysis quickly showed that the bead was made of antimony. Objects of metallic antimony are very rare in the archaeological record. Very few analyses have been conducted and many of those that have are old, dating back to the 19th century. This paper presents one of the first analyses of an antimony bead using modern analytical equipment. It is also the only analysis yet published to give details of the microstructure of an antimony object, rather than just a bulk chemical composition. It goes on to suggest a how the object was made and discuss possible sources of the metal.

Experimental Method

A small piece of the bead was mounted in cross section in a resin block and polished for analysis in an SEM. The initial reconnaissance was carried out on a Cameca SU30 microprobe at the RLAHA, where the nature of the microstructure was explored. The analyses and elemental mapping were completed on the Jeol JXA 8800 multi-spectrometer machine in the Department of Materials, University of Oxford.

Results

Initially when the bead was submitted for analysis, it was thought that it was a ceramic bead coated in silver foil, but analysis quickly revealed that this was incorrect and the bead actually consisted mostly of antimony. Metallic antimony is an extremely brittle metal with a flaky, crystalline habit. It typically is bluish-white and has a metallic lustre, which tarnishes to black over time in air. The cross-section showed that the bead consisted of three main layers: an inner layer of ceramic, a middle layer of well-preserved metal and an outer layer of oxidized metal (see Figure 1).

Of greatest interest are the well-preserved metallic areas of the bead. The matrix of the bead (phase A) is 98.5% antimony with traces of arsenic, tin and lead (see Table 1)The clear microstructure is picked out by other phases that are concentrated in the grain boundaries of the matrix. The grainsize of the matrix is fine, usually around 20–30μm across, the edges of which are defined by a brighter, high-backscatter phase and a darker low-backscatter phase (phases B and C respectively, see Figure 2). In addition to these structures, there are circular masses in the matrix, some of which contain a single low-backscatter phase (phase D) and some of which contain a complex of two phases with dendritic intergrowths (phases E and F).

Analysis of the high-backscatter phase (phase B) shows that it is essentially almost pure lead, with trace amounts of copper and arsenic. Although analyses of phase B appear to indicate that it contains some antimony as well, this is probably due to the accidental incorporation of some of the antimony-rich matrix within the analytical area due to the small size of the phase. Phase B is therefore unlikely to contain more than trace amounts of antimony. The other phase found in the grain boundary areas (phase C) was analysed as 50.0% antimony and 45.4% copper, with significant amounts of arsenic and traces of lead. This phase is likely to be Cu_2Sb. Within the grains themselves, away from the boundaries, spherical and sub-spherical areas of another phase (phase D) are present. Analysis of several of these areas showed a consistent composition with 35-37.5% copper, 45-49% lead and 15-17% sulphur. This copper-lead-sulphide is as yet unidentified.

The final phases of interest are restricted entirely to other spherical areas, this time polyphase in nature. These spherical inclusions have a matrix of dark-backscatter contrast (phase E) which is intergrown with a brighter, dendritic phase (F). All these phases are small (less than 5μm across) and the surrounding material inevitably contaminates the analyses obtained on them. Element mapping of the fine detail of these polyphase areas helped to clarify which phases contain which elements. Both phases are free of antimony but contain sulphur, phase E being also rich in lead and free of copper, whereas phase F is rich in copper with some iron, but free of lead. With this information it is possible to remove the antimony and, in the case of Phase E, the copper and a proportion of sulphur and renormalize the Phase E analysis (see Table 1). Carrying this out shows that phase E is about 86% lead and 14% sulphur, strongly suggesting that it is PbS (galena). Similarly the antimony, lead and a proportion of sulphur equivalent to the Pb:S ratio in galena can be removed from the Phase F analysis and this renormalized. While Phase F is more difficult to identify, when the galena and antimony contamination are taken away, the remaining composition is 74.2% Cu, 1.6% Fe and 23.9% S, suggesting Cu_8S_5 (geerite), though the related copper sulphides digenite and anilite are other possibilities.

Discussion

The small granular microstructure of the bead strongly suggests that the bead cooled from a molten state, the antimony grains (phase A) solidifying first with the lead- and copper-rich phases (B and C) remaining molten longer and eventually solidifying along the boundaries

Figure 1: Low magnification backscattered SEM image of the cross section of the bead, showing fresh unweathered metallic antimony areas (light grey), the oxidized outer surface (mid grey) and remnant ceramic core (speckled dark grey).

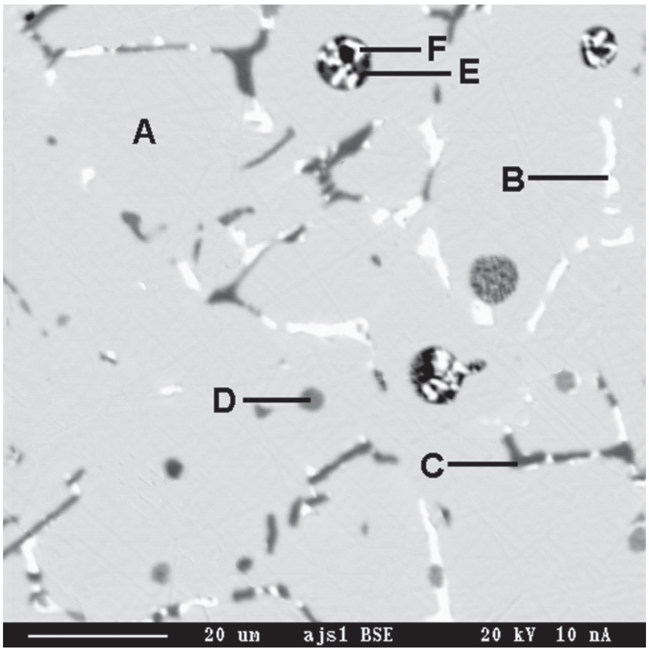

Figure 2: High magnification backscattered SEM image of the well preserved metallic antimony areas showing the microstructure present. A to E indicate the phases A to E as mentioned in the text.

Table 1: WDS analyses for the different phases in the antimony bead.

	Element (wt%)													
	As	Fe	Sn	Sb	Co	Pb	Ag	Ni	Bi	Cu	S	Zn	Au	Total
Phase A	0.44	0.01	0.48	98.52	0.01	0.43	0.02	0.00	0.02	0.03	0.00	0.01	0.01	99.48
Phase B	0.36	0.00	0.01	9.23	0.01	89.66	0.00	0.02	0.00	0.44	0.03	0.03	0.08	99.87
Phase C	2.83	0.02	0.17	50.65	0.02	0.79	0.02	0.71	0.09	45.91	0.00	0.00	0.01	101.20
Phase D	0.05	0.22	0.00	1.79	0.00	46.44	0.00	0.00	0.00	35.68	15.83	0.00	0.00	99.08
Phase E	0.05	0.00	0.02	5.53	0.00	75.28	0.00	0.00	0.00	5.34	13.78	0.00	0.00	98.45
Phase F	0.12	1.13	0.03	4.62	0.00	21.39	0.00	0.07	0.00	52.45	20.18	0.00	0.00	102.70
Galena (PbS)						86.60					13.40			
Geerite (Cu$_8$S$_5$)										76.00	24.00			
Phase E, as analysed	0.05	0.00	0.02	5.53	0.00	75.28	0.00	0.00	0.00	5.34	13.78	0.00	0.00	100.00
calculated contamination				5.53						5.34	1.69			12.56
contamination subtracted	0.05	0.00	0.02	0.00	0.00	75.28	0.00	0.00	0.00	0.00	12.10	0.00	0.00	87.44
re-normalized	0.05	0.00	0.02	0.00	0.00	86.09	0.00	0.00	0.00	0.00	13.83	0.00	0.00	100.00
Phase F, as analysed	0.12	1.13	0.03	4.62	0.00	21.39	0.00	0.07	0.00	52.45	20.18	0.00	0.00	100.00
calculated contamination				4.62		21.39					3.31			29.32
contamination subtracted	0.12	1.13	0.03	0.00	0.00	0.00	0.00	0.07	0.00	52.45	16.87	0.00	0.00	70.68
re-normalized	0.17	1.60	0.04	0.00	0.00	0.00	0.00	0.10	0.00	74.21	23.86	0.00	0.00	100.00

Note: The right-hand column shows the original total given by WDS analysis; the data given for phases A-F have been normalized to 100% for ease of comparison.

of the growing antimony grains. The spherical areas of phase D and phases E and F solidified last of all. The fact that the microstructure indicates solidification from a melt shows that the bead was cast, the fine size of the grains suggesting rapid cooling. The ceramic core of the bead is a remnant of part of the mould that was used. The casting metal was over 95% antimony, with trace levels of other elements, primarily lead, arsenic, and copper, but also tin and iron in lower quantities.

The question of most interest is the source of the antimony, both whether it is derived from native antimony or smelted stibnite and where that source might be located. Moorey (1994) has argued that: ‘it is unlikely that the preparation of metallic antimony from stibnite was a process practised in antiquity’ and therefore believes that native antimony is the source for the few Mesopotamian antimony objects that he lists (discussed below). However, there are archaeological indications that antimony smelting has occurred in rare spots where stibnite ores are particularly common. An example of this is the Caucasus, where in a Late Bronze Age context, ‘traces of antimony smelting have been found near the Zopkhito ore body’ (Chernykh 1992, 276). The analysis of the bead presented in this paper shows that within the microstructure several sulphide phases were preserved. While it possible that these sulphides were included accidentally with native antimony when the bead was made, it is more likely that they are the remains of the sulphides left over from an inefficient smelting of a primarily stibnite ore that contained traces of other lead, arsenic and copper sulphides.

Comparative material

When considering where the source of antimony that makes up the Jerablus Tahtani bead might be, two sorts of comparative material must be considered: other objects of metallic antimony and objects of antimonial bronze. The other antimony objects known are listed and discussed in Lucas and Harris (1962) and Moorey (1994). They can be split into two groups: those found in the Caucasus and those from areas south of this region. Selimkhanov (1975) analysed twelve objects of antimony from the LBA tombs of Redkin Lager in Transcaucasia. He states that the majority of the antimony objects found in Transcaucasia come from Redkin Lager. He lists eight further objects as having been excavated from another necropolis just across the River Akstafa from Redkin Lager. Selimkhanov mentions other antimony objects from a Koban tomb near Tblissi, a 3rd millennium tomb in Velikent, Daguestan and a 2nd millennium tomb in Mamai-

Koutan, also in Daguestan. All these objects are small beads, buttons and pendants. Chernykh (1992, 290) states that at sites like Kayakent (LBA, near the coast of the Caspian Sea), 'large number[s] of small antimony ornaments (pendants and beads)' are present. Objects of antimony are therefore reasonably common, at least on some sites, in the 2nd and 3rd millennium of the Caucasus.

Outside the Caucasus, finds of antimony objects are very scattered. The most famous object is part of a 'vase' found at Telloh, also known as Girsu, in Southern Mesopotamia (Selimkhanov 1975; Moorey 1994, 241). It is by no means certain that the complete object was a vase and it may instead have been a fragment of jewellery. Selimkhanov (1975) completed an analysis of the object, revealing it to be over 99% antimony, with traces of calcium (0.2%), copper (0.072%), lead (0.05%), sodium (0.045%) and arsenic (0.02%). All the other objects are small and mostly unpublished. Moorey (1994, 241) lists a cast tube, perhaps a bead, from a 3rd millennium context at Tell Leilan, which was analysed to be 99.7% Sb, some antimony jewellery from Assur, dating to about 2000 BC, and some personal ornaments from the Iron Age at Hasanlu, in northwest Iran (Dyson 1964). The only metallic antimony objects known from Egypt are a series of beads from Lahun, excavated by Petrie (Petrie 1891) in the late 19th century and dating to the 22nd Dynasty (945–716 BC). Four more beads are listed as being found at Tell el-Farah, Israel and dated to the Iron Age, but these have been analysed to be 66% tin and 33% antimony (Dayton 1978, 450).

Antimonial bronze

When present at levels of several percent or more, antimony makes a copper alloy brittle and also lowers its melting point, reaching a eutectic of 645°C at 10.9% antimony. The viscosity of the melt is also reduced and, on cooling, the alloy expands slightly. All this makes a high antimony bronze ideal for casting, but of relatively little use for hot working. Antimony has been recognized as a trace element in ancient copper and bronze objects in Egypt (Lucas and Harris 1962), Mesopotamia (Moorey 1994) and elsewhere (Davies 1935). Since small amounts of antimony ores are often found in association with copper ores, when present in trace quantities the antimony is almost certainly a result of chance contamination.

Bronzes with more than trace levels of antimony are much rarer (Pike *et al* 1996), with notable occurrences limited to Velem St Vid in Hungary, Hasanlu in Iran, the Nahal Mishmar hoard in Israel and the Caucasus. In the case of the Nahal Mishmar hoard, the antimony is probably not added as a separate component, but included within a polymetallic *fahl* ore, albeit by deliberate selection (Shalev and Northover 1993). However, in the Koban Culture (LBA, starting in around the 12th century BC), of the Caucasus it has been argued that 'a relatively pure antimony mineral has been co-smelted with copper, or reduced to metallic antimony which was added to the copper' (Pike *et al* 1996). Similarly Chernykh, working on antimonial bronzes from the Ankhazian Megalithic cists of Western Transcaucasia (end of the MBA, about 1600 BC), has strongly argued that due to the high levels of antimony and arsenic in the alloys (15–20% combined), in this case too 'the addition of antimony was clearly deliberate' (Chernykh 1992).

Antimony sources

The main ore of antimony is stibnite (Sb_2S_3), which, while not uncommon in small traces within a lead-zinc sulphide ore body, is more unusual in larger quantities (Halse 1925, Tylecote 1987). There are three possible sources for the antimony of the Jerablus Tahtani bead: Iran, Anatolia and Caucasia. Iran and Anatolia have large modern antimony mines and Turkey in particular is a significant producer of antimony in the world today. However, there is no evidence that any of these mines were exploited in antiquity. Caucasia, as already mentioned, is a different matter. More ancient objects of antimony have been identified in the Caucasus than in the rest of the Near East combined. Large deposits of stibnite are known from both the Main Caucasus range and the Southern (Lesser) Caucasus. There were mines in both the Main and Southern Caucasus, but due to modern mining, the ancient mines of the Main Caucasus range are better preserved. Here, at heights of around 2,500-3,000 metres, many surface outcrops of pyritic copper ores show evidence of LBA working. Best studied are the mines of the Gornaya Racha region at the headwaters of the River Rioni in Transcaucasia, where about a hundred locations have been discovered where copper, arsenic and antimony ores were worked (Chernykh 1992, 113 and 276). The ancient workings include open surface quarries and shafts with sloping galleries, some stretching for 100–200m into the mountain. The largest copper mines at Gornaya Racha have been found in Chkornali and Chvesho, but the largest antimony mine is at Zopkhito and another is at Sagebi. Radiocarbon dates on charcoal from these antimony mines show that mining began in the 17th century BC, but large-scale exploitation began only in the LBA (from about 1500 BC). The source of the antimony before the 17th century BC is unknown, but it is reasonable to expect that it would have been in the area of these later mines. Caucasia is therefore the only area yet discovered with antimony mines that were active in the late Bronze Age and also a thriving metallurgical industry that fairly regularly used antimony both alone for small cast objects and combined with copper in antimonial bronzes.

Dyson (1964), provides evidence of contact between Caucasia and Northern Mesopotamia in the ninth century BC. He states that 'bronze weapons—maces and daggers—also suggest contact' between Hasanlu and Caucasia. Selimkhanov (1975) and Chernykh (1992) have also speculated that there was contact between Caucasia and Mesopotamia on stylistic and other grounds. Selimkhanov believes that the most likely source of the antimony of the Tello vase is Transcaucasia and Dyson gives the same source for the scatter of antimony objects found in Hasanlu. The most likely source for the Jerablus Tahtani bead would therefore probably also be Caucasia or Transcaucasia.

Conclusion

The antimony bead from Jerablus Tahtani is one of the earliest objects of pure antimony known, along with a very similar sounding 'cast tube' from a 3rd millennium context at Tell Leilan. An examination of the microstructure of the bead shows that it too has been cast, and the presence of impurities suggests that it was made of smelted stibnite rather than native antimony. Although no antimony mines are known anywhere dating from the 3rd millennium BC, from the 2nd millennium onwards cast antimony objects and antimonial bronze were fairly common in Caucasia, and mine workings are also known. These LBA technologies were descendants of earlier MBA industries, which had the same range of complex copper-arsenic and copper-arsenic-antimony alloys. Caucasia is therefore the most likely source of the antimony, as it is for most if not all of the antimony objects from the Near East of this period.

Acknowledgements

The author would like to thank Prof E Peltenburg for allowing analysis of the bead, and Mr Chris Salter and Dr Norman Charnley for their help in the analysis and the interpretation of the results.

References

Chernykh E 1992, *Ancient metallurgy in the USSR* (Cambridge).

Davies O 1935, 'Antimony bronze in Central Europe', *Man* 9, 86–89.

Dayton J E 1978, *Minerals, metals, glazing and man*, (London).

Dyson R 1964, 'Sciences meet at ancient Hasanlu', *Natural History* 73, 16–25.

Halse E 1925, *Antimony ores* (London).

Lucas A and Harris J R 1962, *Ancient Egyptian materials and industries* (London).

Moorey P R S 1994, *Ancient Mesopotamian materials and industries* (Oxford).

Peltenburg E, Bolger D, Campbell S, Murray M and Tipping R 1995, 'Jerablus Tahtani, Syria 1995: Preliminary Report', *Levant* 28, 10.

Petrie W M F 1891, *Illahun, Kahun and Gurob* (London).

Pike, A W G, Cowell M and Curtiss J E 1996, 'The use of antimony bronze in the Koban Culture', *Historical Metallurgy* 30, 11–16.

Selimkhanov I R 1975, 'Sur l'étude du fragment de vase de Tello appartenant au Musée du Louvre et le problème de l'utilisation de l'antimone dans l'antiquité', *Annales du Laboratoire de Recherche des Musées de France* 1975, 45–52.

Shalev S and Northover J P 1993, 'The metallurgy of the Nahal Mishmar hoard reconsidered', *Archaeometry* 35, 35–47.

Tylecote R F 1987, *The early history of metallurgy in Europe* (London).

The author

Andrew Shortland is Research Fellow in Vitreous Materials. Whilst maintaining a wide interest in all vitreous materials, his main research focuses on glass and glazes in the 2nd millennium BC, and the cultural, political and technological interactions that led to the numerous technological innovations that originate in this period. He read for a first degree in geology before taking a higher degree in prehistoric archaeology and a doctorate in Egyptology, all at the University of Oxford.
Address: Research Laboratory for Archaeology and the History of Art, University of Oxford, 6 Keble Road, Oxford OX1 3QJ.
e-mail: andrew.shortland@rlaha.ox.ac.uk