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Appendix: Analysis of Caucasian Metalwork – The Use of Antimonal, Arsenical and Tin Bronze in the Late Bronze Age

Abstract

The British Museum's collection of Central Caucasian and Transcaucasian metalwork was characterized, qualitatively using X-ray fluorescence, and quantitatively by inductively coupled plasma atomic emission spectroscopy.[54] The results indicate the use of antimonal copper, arsenical copper and tin bronze. The use of antimony in copper alloys was probably deliberate (rather than through the fortuitous use of polymetallic ores) either by the addition of metallic antimony to copper, or the co-smelting of antimony and copper ores. The reliance on antimony and arsenic in copper rather than tin may have been due to the lack of tin in this area.

Introduction

This study characterizes the composition of Late Bronze Age (LBA) and Early Iron Age (EIA) Caucasian metalwork qualitatively and, where appropriate, quantitatively and briefly explores the differences, and hence developments (either cultural, technological or geographical) from the preceding periods. Analytical studies of this material in the West have been limited, and although laboratories such as the Institute of History of the Academy of Sciences at Baku, Azerbaijan, have been undertaking analyses by arc emission spectroscopy for several decades (Selimkhanov 1982), few results have been published outside the former Soviet Union.

In the present study a number of specific areas have been explored within a LBA/EIA Caucasian perspective, including the nature of alloying practices and 'deliberate' versus 'accidental' alloying of copper. Although this debate usually centres around the inception of copper metallurgy it has implications in all periods for the understanding of ancient metallurgical knowledge and technology, and the degree of specialisation, if any, in metal production. While this study can only touch on these questions, especially given the lack of archaeological and contextual information on the objects in the collection, the qualitative and quantitative characterisation of the metalwork can provide a starting point for an understanding of LBA/EIA metallurgy in this area.

A Brief History of Caucasian Metallurgy

Although the majority of the artefacts analysed are from the LBA period (mid-2nd–1st millennium BC), to place them in context, a brief review of the metallurgical history of preceding periods is given below.

The Copper Age: c. 5th to mid-4th millennium BC

The majority of metal finds from this period come from the southern, Transcaucasian region of the Caucasus. They have been associated with later levels of the Shulaveri-Shomutepe culture, although are relatively rare. Metal awls and knives occur, although stone, bone and horn tools predominate and the majority of copper finds are small bead-like ornaments made from rolled up copper sheet. Analysis has shown most objects are relatively pure copper, although in one or two cases arsenic is seen up to about 1% (Chernykh 1992: 35). It is uncertain whether this indicates the deliberate addition of arsenic in some way or the fortuitous use of arsenical copper ores and there is some debate as to whether the early metal age of the Caucasus should be subdivided into copper and arsenical copper ages (e.g. Selimkhanov 1982).

The Early and Middle Bronze Ages: mid-4th to mid-2nd millennium BC

With the onset of the EBA, the use of arsenical copper increases dramatically throughout the Caucasian region. The Kuro-Araks culture spread through eastern Transcaucasia, typically evidenced by small settlements of circular or sub-rectangular houses, but with a settlement density that indicates a dramatic increase in population. Copper alloyed with up to 7% arsenic seems to be universally recorded, and 'pure' copper objects are exceedingly rare, although it is difficult to attribute with certainty all but a few of the objects to the Kura-Araks culture. Unusually, analyses of some objects have shown a comparatively high zinc content (1–2%), and a small group with high nickel (0.04–1%). The high nickel alloys are similar in composition to those found in Anatolia, Mesopotamia and Iran, and the metal for these objects may not be of local origin (Chernykh 1992: 58–67).

In EBA north Caucasus, focused around the River Kuban, the Maikop culture is represented by rich 'kurgan' burials containing large numbers of copper-based and precious metal artefacts. Unusually, the evidence for metal from settlement sites is sparse, and there seems to have been a reliance on stone tools. Chernykh (1992) writes that a similarity between the composition of Maikop and the Transcaucasian Kura-Araks copper based objects, and the lack of evidence for Maikop mining activity, suggests that the metal for these artefacts may also have come from outside the region, e.g. from Anatolia, Mesopotamia or Iran. Selimkhanov (1962) gives the results of 27 analyses of Maikop artefacts. Almost universally arsenical copper is being used, with 1–10% arsenic. A quarter have a high nickel content (up to 4%), which provides a link with the metal of the Kuro-Araks culture. However, Ravich and Ryndina (1995) report work by V.A. Galibin (1991) who suggests the undated mines in this area, containing copper with a nickel and arsenic impurity, were in fact in use in the Early Bronze Age. This would give a local source for the high-nickel copper rather than a source outside the Caucasus.

By the MBA the focus of rich burials seems to have moved southward to eastern Transcaucasia with the kurgans of the Bedeni and Sachkere culture that replace the Kuro-Araks. Rich funeral assemblages have been found, containing bronze tools and precious metals. Although copper with up to 15% arsenic predominates, we begin to see the appearance of tin bronze, and the early signs of complex arsenic- antimony and arsenic-tin bronzes. Chernykh (1992) suggests the Sachkere culture continued to use the ore sources of the Kuro-Araks culture, but there are almost no objects with a high nickel content. This may imply that the supply of metal from Anatolia and other areas ceases. In many objects, antimony (1–2%) is present, which Chernykh suggests is a deliberate addition. Selimkhanov (1975) gives analyses of metallic antimony objects, one of which dates from the end of the third millennium. This suggests that antimony is being smelted, and it is not unreasonable that it was deliberately added to copper.

By the MBA of the northern Caucasus, the rich kurgan burials of the Maikop culture have declined and have been largely replaced by burials in pits or small cists. Chernykh (1992) sees two distinct foci, the Terek River in the east and the Kuban River in the west. In both areas, arsenical copper is most prevalent, particularly arsenic-antimony alloys. Towards the end of the MBA, tin bronze makes an appearance, but in general its adoption is slower than in Transcaucasia. Chernykh argues that the general composition of the alloys does not fit with the compositions of northern Caucasian ore deposits and the source of the metal may have been south of the Caucasus mountain range.

In general, the MBA represents an explosive growth in metallurgy, with an estimated order of magnitude increase in the number of metal objects being produced (Chernykh 1992: 166), but there is a sharp decline towards the end of this period.

The Late Bronze Age: mid-2nd to 1st millennium BC

The LBA and Early Iron Age saw an increase in the metallurgical activity in these areas which to some extent was in decline towards the end of the MBA. Chernykh (1992) suggests this is associated with the growing exploitation of copper and polymetallic deposits associated with primary (sulfidic) copper minerals. He sees the deposits of the Little (or southern) Caucasus as the main focus for this new surge in mining activity. Pyritic copper mines have been identified in the main Caucasus range, and over a hundred are known from the Gornaya Racha region of Transcaucasia which also produced antimony and arsenical ores (Chernykh 1992: 276).

Many of the objects in the British Museum's collection are typical of LBA metal production. Perhaps under-represented in the collection are the highly decorated incised axes with stylized zoomorphic designs. The typology of these and other tools are the basis for the division of the Caucasian metallurgical province into two regions: the western Koban-Colchidic zone and the eastern Caucasian-Caspian zone. According to Chernykh (1992: 283, 290) there are differences in metallurgical development in the two zones. In general tin bronze predominates but there are significant numbers of arsenical coppers and complex alloys which shows a certain continuity and development from the MBA period. The Koban region, however, remains backward, producing fewer tin bronzes than arsenical coppers. The eastern zone shows a similar range of complex copper-tin-antimony or tin-arsenic-antimony alloys, but arsenical copper without the addition of other impurities is rare.

The initial use of iron from the 11th century BC does not seem to be reflected in a decline in the use of bronze, and it was not until the 9th–8th centuries BC that the use of iron became dominant.

Analytical Methods

All the copper-based metal objects in the collection were first qualitatively analysed using X-ray fluorescence (XRF). Drilled samples were then taken from 39 selected objects, and analysed quantitatively using inductively coupled plasma atomic emission spectrometry (ICP-AES).[55]

X-ray fluorescence

The qualitative metal analyses were performed using energy-dispersive XRF employing a molybdenum target tube operating at 45 kV. The X-ray beam was collimated to a spot about 1.5 mm in diameter on the artefact. The spectra collected were calibrated by reference to standards of known composition (e.g. Cowell: 1998).

XRF is a surface analysis method, and since little or no surface preparation was carried out before analysis, the analyses represent the composition of the surface metal, including any overlying patina or corrosion. Because of surface enrichment/depletion effects or the preferential corrosion of different phases of an alloy, the composition of the unabraded surface metal is unlikely to be quantitatively representative of the whole object. Thus, these analyses are qualitative (or at best semi-quantitative), that is, they are only an indication of the metal or alloy types.

Qualitative analyses involve the identification of the presence/absence of particular elements, or in this case the presence of a sufficient concentration of a particular element to conclude that it has a significant effect on the properties of the alloy and is not just a 'background' impurity. An element was considered significant if it was present at the surface at a concentration of more than about 1% (for tin, antimony and arsenic) and 2% for lead. Each object was assigned to one of the following categories:

Bronze (Cu + Sn)
Leaded bronze (Cu + Sn + Pb)
Antimonal copper (Cu + Sb)
Arsenical copper (Cu + As)
Brass (Cu + Zn with or without Pb)
Gunmetal (Cu + Zn + Sn with or without Pb)
Tin
Iron
Complex alloys (These are described in full, e.g. an alloy of copper, tin, lead and arsenic)

The reliability of assigning objects to these categories using surface analyses was tested retrospectively by a comparison of the XRF data with the subsequent quantitative ICP-AES results (see below). Of 39 cases 33 were assigned to the same category in both cases. Of the six that were misassigned three proved to be borderline, i.e just slightly less that 1% of the significant metals. Of the three badly misassigned, one was identified by XRF as a gunmetal, but proved to have had a zinc based pigment applied to its surface, and the other two were very badly corroded. This level of error is considered unavoidable without surface preparation, but it is within an acceptable limit given that the alloy types of about 90% of the objects were correctly identified.

Inductively-coupled plasma atomic emission spectroscopy

A small sample was removed (*c.* 10–20 mg) from the selected objects using a hand drill with 0.6–0.8 mm high speed steel bits. The drillings from any corrosion/patina and from the first 0.5mm of surface metal were discarded to avoid problems with surface enrichment and contamination. The drillings were weighed and then dissolved in aqua regia, heating gently on a hot plate. The solution was then diluted with distilled water to 20 ml (Hughes *et al.* 1976).

The analyses were performed on an ARL 3410 sequential spectrometer, and 15 elements were quantified with reference to prepared standard solutions, and solutions of dissolved standard metals (see Hook 1998). The precision of the technique is about ±1–2% for copper; ±5% for major elements (i.e. those present at levels >10%); ±10% for minor elements (present at 1–10%) deteriorating to about ±50% at the detection limit.

One element, bismuth, is not easily measured in copper-based solutions by ICP-AES and this was determined by atomic absorption spectroscopy (AAS) using the solution remaining after ICP-AES analyses, following the method of Hughes *et al.* (1976).

Results

The qualitative XRF results are given in **Table 1**. As mentioned above, some heavily corroded objects may be misassigned, but this seems unavoidable without surface preparation.

Table 2 gives the quantitative ICP-AES and AAS results. The most likely sources of error in these results are from the effects of corrosion that has penetrated into the heart of the object. In these cases inaccuracies will occur because the sample includes corrosion rather than pure metal. Elements such as oxygen, chlorine and carbon that have not been analysed are present from carbonates, chlorides and other compounds that make up the corrosion. In general, these inaccuracies can be seen as a total of significantly less than 100% after allowing for overall precision, i.e. less than 97%. Only a few artefacts exhibit totals low enough to indicate significant amounts of corrosion; these include two belt plaques (**cat. nos. 136, 141**), and an openwork pommel (**cat. no. 129**).

Discussion

The proportions of the various alloy types are shown summarized as a histogram in **Figure 48**. To enable a comparison between Koban and Transcaucasian artefacts, the percentage of objects in each alloy category has been calculated. The metals used include pure copper, tin bronze, antimonal copper, arsenical copper and complex mixtures with various amounts of tin, antimony and arsenic. The qualitative data suggest an emphasis on complex alloys, usually antimony or arsenic with tin. However, the quantitative data reveal that in most cases the primary alloying component is present in much greater concentrations than any secondary component. Thus, **Figure 49**, an orthogonal plot of the quantitative data for tin, antimony and arsenic, shows that most objects fall within the well defined categories of antimonal copper, arsenical copper and tin bronze.

It is clear from **Figure 48** that the use of antimonal copper, and other alloys containing antimony, is more prevalent in the Koban artefacts than the Transcaucasian objects which are more often of arsenical copper or tin bronze. This, however, may simply reflect the bias of the collection, rather than Koban manufacturing traditions, since there is an obvious relationship between alloy type and object function. For example, antimonal copper and alloys containing antimony were used mainly for the small cast pendants (e.g. the animal-bird pendant **cat. no. 19**) where they would improve the casting properties and possibly give a silver colour to the metal, whereas arsenical copper is used more for dagger blades where it would give a harder cutting edge. Chernykh (1992: 150) notes a dramatic change in emphasis of production from tools and weapons to ornaments from the EBA to the MBA in the northern Caucasus and we might anticipate that this trend continues into the LBA. The reverse is true for Transcaucasia where the emphasis moves from ornaments to tools and weapons. The differences in metal use may reflect more the emphasis on tool or ornament production than traditions of metal production in the two regions.

However, the difference in alloy use is still clear when only ornamental objects are considered. Thus, only 26% of Transcaucasian ornamental objects contain a significant amount of antimony whereas for Koban artefacts it is 83%. Arsenical copper is also more prevalent in Transcaucasian artefacts, and almost non-existent among the Koban objects. Although bronze seems to have been used in the same proportions in both regions, the four Koban 'tools' (i.e. axes and blades) are all bronze. Of the ten Transcaucasian tools, half are bronze, the rest being arsenical or complex arsenical alloys.

One dagger (**cat. no. 123**) has a blade of arsenical copper and a sleeve of copper alloyed with lead and antimony, showing the choice of different alloys for different fabrication techniques. Such instances add weight to the argument that arsenic and antimony are present from deliberate introduction, rather than the fortuitous use of polymetallic ores (see below). There are, however, inconsistencies in the use of alloys in some objects. The four Transcaucasian daggers (**nos. 122–5**), while seemingly of a similar type, have blades of leaded bronze, arsenical copper, bronze and arsenical copper respectively. This may reflect regional or temporal differences, or simply the availability of local materials. It is difficult, however, to assess the relationship between the function of an object and its alloy type since the majority of objects in the collection are likely to be from funerary contexts, and it is not known whether all the tools and weapons from such contexts were meant to be fully functional.

Arsenical copper
The presence of arsenic in copper increases the hardness of the metal, and also acts as an antioxidant which reduces gas porosity forming during casting. At higher levels it can impart a silver colour to the metal through the phenomenon of inverse segregation (see below). The arsenic content of the objects varies from none detected to 5.5%, with a mean of about 2.5%. Most of the alloys that contain more than 1% arsenic lie within the range 1–2%. This is below the 'ideal' according to Ravich and Ryndina (1995: fig. 5) who suggest an arsenic content between 4–5% gives the best compromise between hardness and ductility. However, they also find that the majority of arsenical copper objects fall well below 4%, with the majority having an arsenic content of 1–3%. Arsenic is rapidly removed from arsenical copper on heating in an oxidizing environment. This would include melting to cast a blank, and any subsequent hot-working of that blank (e.g. see experiments by McKerrell and Tylecote 1972). This makes it difficult to conclude, solely from the analytical data, whether the arsenic was being introduced deliberately with the intention of producing an 'ideal' 4–5% arsenic content (e.g. by co-smelting copper and arsenic-rich ores) and the arsenic content has been reduced by working, or whether the low arsenic content implies no deliberate control over the composition and is simply the accidental use of arsenic-containing copper. An additional problem in relating the property of an arsenical copper artefact to its bulk arsenic composition is that as much as 25% of the total arsenic in the object may be in the form of arsenic mineral inclusions (e.g. As_2O_3), and not contributing to the properties of the alloy (Northover 1989).

Arsenical copper was used for many of the dagger blades, but it was also found in one or two cast objects, e.g. an openwork pommel (**cat. no. 127**) where it may have been added as a colourant. Arsenical coppers with 1–3% arsenic are red in colour, gold-coloured with 4–12% arsenic and silver or grey with 12–18% (Ravich and Ryndina 1995). The cast arsenical copper objects have higher arsenic contents (3–5%) than the worked arsenical copper dagger blades. This may be because the working of the blades has removed arsenic, as mentioned above, or a high arsenic alloy may have been selected as a colourant for cast objects. Although a homogeneous 3–5% arsenic content will not create a silver colour in bulk, the phenomenon of inverse segregation, where the lower melting-point arsenic-rich phase (eutectic) is forced to the surface, can give the appearance of a silver colour. In theory this does not occur until the arsenic content is in excess of 7% (McKerrell and Tylecote 1972). However, they suggest that under practical non-equilibrium conditions alloys with as low as 3% arsenic may show this effect. Metallographic examination would be needed to investigate this. Some examples of arsenical copper from the MBA Maikop culture proved to contain between 18–21% arsenic and Ravich and Ryndina (1995) suggest this was deliberate in order to produce a silver colour. The microstructure of these objects is of a chill-cast (rapidly cooled) metal which they suggest is a deliberate casting technique to reduce the volatization of arsenous oxide from the moulten metal and maintain the silver colour.

The arsenical copper alloys with more than 1.5% arsenic are otherwise relatively pure, in most cases having low nickel, silver and antimony contents. This suggests that the source of arsenical copper may have been the co-smelting of copper and relatively pure arsenic minerals rather than the use of enriched sulfide ores (see below).

Antimonal copper
Many of the cast objects contain a significant amount of antimony. The quantitative analyses show 1–10% antimony, with the majority of antimonal alloys containing between 5–10%, often in conjunction with 1–2% tin. The colour of antimonal copper ranges from golden at about 10% to silver at about 20% antimony (P. Maclean, pers. comm.).

In other cases of high antimony copper alloys, for example the Nahal Mishmar hoard (Shalev and Northover 1993) and four LBA artefacts analysed by Craddock (1979), the antimony is accompanied by high nickel, arsenic and silver contents. This has been seen as indicative of the use of secondary enriched sulfide ores (grey ores or fahlerz). In many cases, groups of arsenical or antimonal copper artefacts show a correlation between these elements. For example, regression analysis of data published by McKerrell and Tylecote (1972) for British Bronze Age rivets has shown a strong correlation between silver and arsenic. This relationship probably reflects the composition of the ore body, and any attempt to deliberately modify the arsenic content during the finishing of the artefact (e.g. by oxidative working as McKerrell and Tylecote suggest) would disrupt this relationship. A similar regression analysis also shows a correlation between silver and antimony in the Nahal Mishmar hoard analyses. In these cases, it is probable that the control the smelter and metalworker exercised was simply over the selection of a particular ore for a particular task and a particular metal for a particular manufacturing process. Experimental smelting of polymetallic ores found on archaeological sites has shown that similar alloys to those in contemporary artefacts can be produced simply by smelting, without 'deliberate' (complex) processing, mixing or alteration of the furnace charge (Delibes *et al*. 1991). Some of the ores found at Norşuntepe in the river valley of the Upper Euphrates, dating from 3500 BC, also produced alloys containing high levels of antimony and arsenic (Zwicker 1980).

However, the high antimony alloys (>5%) analysed here do not show significant nickel, silver, cobalt or bismuth contents and differ from the antimonal alloys discussed above. The arsenic content is relatively low (<0.5%) in all but one case. Unless a relatively pure Cu-Sb mineral was widely available, the two most likely explanations for the compositions seen are the co-smelting of copper minerals with a relatively pure antimony mineral (e.g. stibnite, Sb_2S_3), or the addition of metallic antimony to copper. Either of these two options should certainly be seen as 'deliberate' alloying. There is evidence for antimony mining in the Gornaya Racha region (Chernykh 1992: 276), and a few relatively pure antimony objects have been found dating from the 3rd millennium in the northern Caucasus. Antimony from Redkin in Transcaucasia had arsenic as its major impurity, but never more than 1.2% (Selimkhanov 1975). If metallic antimony was being produced, there is no reason why it could not have been added to molten copper. This would produce a purer and more controlled alloy than the smelting of enriched sulfide ores. According to the literature, no antimonal ingots have been found, but this should not be taken to mean none were produced: consider the case for tin where tin-bronze was being produced in great quantities but finds of tin ingots are very scarce.

Another argument against the use of fahlerz for the production of these artefacts is that the arsenical copper alloys with more than 1.5% arsenic are also relatively pure (see above). These could have been produced by the co-smelting of copper ores with minerals such as orpiment (As_2S_3) or realgar (As_2S_2), or the smelting of enargite (Cu_3AsS_4, although Sb can substitute for As in this mineral). Analyses of MBA arsenical coppers by Selimkhanov (1968) also suggests many are too pure to be from the secondary enriched sulfide ores containing the tetrahedrite-tennanite series of minerals.

Tin bronze

The tin content of the tin bronze objects (not the complex alloys) ranges from 3–12%. The mean content is about 7%, although the mode (i.e. the most common value) is between 3–5%. This is low compared to European bronzes of this period (e.g. Bourhis and Briard 1979; Craddock 1980). Tin as an alloying element for copper has a similar effect to arsenic. It increases hardness and the effect of work-hardening, and lowers the melting point of copper. Its advantage over arsenic is that it is not volatile, and can be smelted to a metal, and thus more control over the composition of the alloy can be exercised. As noted above, the co-smelting of copper and arsenic minerals will produce an arsenic content dependent on the furnace charge and smelting conditions. Also, arsenic loss will occur on remelting or working of the metal (McKerrell and Tylecote 1972), and it would thus have been difficult to maintain a consistent level of arsenic. By contrast, making tin bronze may have been as easy as melting metallic tin and copper together in a crucible. Ravich and Ryndina (1995) see these advantages as prompting the adoption of tin and the decline of arsenic as an alloy for copper. There is also the toxicity of arsenic vapour as a possible reason. The relatively low tin content of these objects may be a result of a difficulty in obtaining supplies of tin in the Caucasus. Selimkhanov (1978) gives analyses of first and second millennium objects of near pure tin, and lead-tin 'pewter', mostly from Transcaucasia, yet he states that no tin deposits have been found in the Caucasus, as supported by recent geological surveys (e.g. Smirnov 1989). Tin may have been a rare commodity, to be used sparingly. Alternatively, in the case of objects from burials, the mechanical properties of the alloy may not have been important and thus less tin was used since the practical function of the object may have been limited.

The tin content in the complex alloys rarely exceeds 4% and this is usually seen in conjunction with up to 10% antimony or 5% arsenic. Craddock (1979: 380) gives the analyses of three LBA artefacts which contain both antimony and tin. The tin content is lower than the pure tin bronze artefacts, and he suggests that the smith was aware of the presence of antimony in the copper and therefore used less tin to make a satisfactory alloy. The associated high nickel and silver contents suggest that the antimony content originated fortuitously from the use of fahlerz. In the objects analysed here, it is more likely that the antimony is the deliberate alloy, and tin is present fortuitously. Rapp (1986) suggests that copper with a low tin content could be produced by smelting tin-rich copper deposits, such as are found in Cornwall, but the preferable explanation is that low tin contents are from the recycling of scrap bronze.

Trace element content: iron, nickel and silver

It is notable that most of the objects analysed have a low iron content. The composition ranges between 0–0.5% with most objects having less than 0.1% iron. There is a noticeable difference between the iron content of Transcaucasian (mean 0.08%) and Koban (mean 0.02%) objects, although with the small sample size this difference is not statistically significant. Craddock and Meeks (1987) show a trend of increasing iron contents in copper alloys as furnace and smelting technology progresses. They suggest that the appearance of a high iron content in copper (>*c*.0.2%) is indicative of the introduction of a deliberate slagging process, requiring a more reducing environment than non-slagging processes. The conditions required to produce a tappable slag could also reduce iron minerals to metallic iron which could be incorporated into the copper. However, this could be reduced by refining. Experimental work by Pollard *et al*. (1991) has shown that the incorporation of trace elements, especially nickel, from the ore into the metal is temperature dependent. Any nickel present in the ore will not be incorporated below temperatures of about 1000°C, whereas this does not apply to arsenic, silver and antimony. The lack of nickel in the Caucasian objects, however, does not necessarily mean low temperature smelting, but rather a lack of nickel in the ore. It is difficult to envisage the use of low-temperature smelting in the Caucasus at the beginning of the iron age. The archaeological evidence suggests the well developed large scale production of copper (Chernykh 1992: 276), not small scale low-temperature 'bonfire' smelting as the iron and nickel contents may suggest.

The general lack of these elements is also a supportive indication that the arsenic and antimony were added as separate, relatively pure minerals or perhaps in the case of antimony as a metal, rather than coming from polymetallic minerals. Although, perhaps, a non-ferrous flux (e.g. manganese) was used, or the copper was well refined. Hook *et al*. (1987; 1991) conclude from the analyses of artefacts, slag and crucible fragments from Bronze Age sites in south-east Spain that the majority of arsenical copper objects were made from metal smelted from a mixture of copper and arsenic minerals. The nickel, silver and iron content of the objects was also generally low, even though it is estimated that the smelting crucibles were held at a temperature in excess of 1100°C for at least two hours. It would be unwise however to speculate too much on the nature of the smelting technology, on the basis of the trace element composition of the alloys, without reference to archaeological evidence (e.g. furnaces, the presence or absence of slags, etc.).

Summary
These analyses suggest a metallurgical technology beyond the accidental production of copper alloys by the fortuitous smelting of polymetallic ores. The analyses do not show the characteristic impurities of many other antimonal and arsenical copper alloys that are generally thought to be from the smelting of fahl ores. Antimonal copper and possibly arsenical copper were probably being produced by careful selection and co-smelting of ores, or by the addition of metallic antimony. The use of antimony had its origin in the MBA, but was most prevalent in the LBA. In particular, the artefacts of the Koban culture show an emphasis on antimony-based alloys, and to some extent this differentiates them from those of preceding periods.

An appreciation of the properties of such alloys is demonstrated by the use of particular alloys for specific tasks: arsenical copper and tin bronze was used more for blades and tools, antimonal copper for cast objects. It is probable that antimony, and to a lesser extent arsenic, were used both to improve the casting and work-hardening properties of the alloy, and also as a colourant.

The low tin contents in the bronze of this period may be the result of difficulty in obtaining tin. It may also partly be explained by the emphasis on cast ornamental objects where the superior properties of tin bronze need not necessarily be exploited, although even many of the tools have a low tin content.

The overall picture of Caucasian metallurgy in the LBA is not one of stagnation in the arsenical copper-age when most of Europe and the Mediterranean were producing tin bronze. Rather, there is evidence that sophisticated smelting of antimony, antimonal copper and arsenical copper developed in a way that has few parallels elsewhere. Antimony and arsenic minerals were mined specifically, and metallic antimony was produced. Such alloys must have been appreciated as alloys, rather that harder versions of copper that could be fortuitously produced by smelting particular ores. To some extent, the lack of tin may have prompted this.