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Trace Element Fingerprinting of Ancient Copper: A Guide to Technology or Provenance?

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The hypothesis that trace element concentrations should be a guide to the provenance of ancient metals has been around for more than a hundred years. Although very large analytical programs for ancient metal objects have been based on this concept, its validity is still in dispute with opinions that range from complete rejection to virtual acceptance. However, the apparent dichotomy expressed in the title is a false one. There are a number of elements whose concentrations are predominantly governed by ore mineralogy/composition and could thus, in principle, be used for provenance determinations. Other elements, found in ancient copper metal artefacts, are more closely related to the smelting process and so are of little use in provenance studies.

The relationships between copper ore and metal, as deduced from physico-chemical considerations and data; smelting experiments in the laboratory; and well-defined archaeological case studies such as the ancient copper production centres of Timna and Feinan in the Near East, are reviewed and principles governing these relationships are established. The usefulness of these principles and the conclusions drawn from them are shown in a large-scale investigation of Chalcolithic copper production and distribution in southeastern Europe; a study that included both trace element and lead isotope measurements. Long standing questions such as the possible use of native copper for the manufacture of heavy implements and the role in the early metallurgy of the Balkans of the, as yet earliest known, copper mines at Rudna Glava and Ai Bunar are discussed.

Keywords: Trace Element Fingerprinting; Provenance Studies; Chalcolithic Copper Production.

Introduction

The hypothesis that trace element concentrations can be a guide to the provenance of ancient metals was formulated more than hundred years ago. One early example is Göbel (1842) with an extended title that reads like an abstract. In (my own) translation it reads: “On the impact of chemistry on the tracing of prehistoric peoples, or results of the chemical investigations of ancient metal objects, especially of those from the Baltic region, to determine the peoples from whom they derive.” He drew his conclusions from the geographical distribution of about 120 analysed objects and ascribed them to seemingly well-defined ethnic groups as was normal in those days. It should be remembered that the three period system had been proposed only a few years before, by Thomsen in 1836, and that an additional motivation for the analyses was the desire to date metal objects based on their compositions. It was discovered that minor elements were useful in determining the nature of the ore from which the metal came and perhaps even its geographical origin (von Fellenberg 1860-66; von Bibra 1869). Furthermore it was found that compositional differences between copper metal were to be expected when native copper, oxide or sulfide ores were used for smelting (Wibel 1865), an idea repeated almost exactly hundred years later by Friedman *et al.* (1966).

Very large analytical programs for ancient metal objects were performed along these lines but their results are still in dispute and the conclusions that can be drawn from them seem unclear. Opinions range from complete rejection to close to acceptance. The largest and most heavily criticized project was that undertaken by the Württembergisches Landesmuseum in Stuttgart (Junghans *et al.* 1960; 1968; 1974) with more than 20000 analyses of prehistoric metal objects from all over Europe. They were classified according to their chemical composition and the distribution of these metal groups was studied in time and space. Obviously, the classification scheme (based on a frequency analysis of the concentration of As, Sb, Ag, Ni, and Bi) was not understood, because the most strident critics of this work achieved almost the same result when they used a small subset of the data (Waterbolk & Butler 1965). Another point of concern was the choice of elements. These were based on an earlier work (Otto & Witter 1952) which assumed that, of all elements analysed, this set (As, Sb, Ag, Ni and Bi) would best characterize the original ore.

With the application of lead isotope analysis to copper-based alloys (Gale & Stos-Gale 1982) chemical analysis of ancient metal objects seems to have become obsolete. Indeed, it is constantly said that chemical analyses alone will not allow copper-alloy artefacts to be matched to their parent copper ores. Although this is often correct, there are cases where the trace element pattern may be more indicative of an ore source than lead isotope ratios. At Feinan, Jordan, for example, the ore deposit is chemically homogeneous but shows wide variations in its lead isotope ratios (Hauptmann *et al.* 1992). In addition, lead isotope ratios are strongly correlated so that only a small part of the theoretically possible, three-dimensional space is occupied resulting in a tendency for different ore deposits to overlap. In such a situation it is common sense that a combination of both sets of data - lead isotope ratios and trace element concentrations - will provide better discrimination between different sources. This approach was adopted by the Heidelberg/ Mainz group from the very outset (Pernicka *et al.* 1984).

The behaviour of trace elements

In the first half of this century geochemists divided the elements into three groups. Siderophile elements that are concentrated in the iron core, chalcophile elements in the outer core and mantle, and lithophile elements concentrated in the crust (FIGURE 1). There is also a group of atmophile elements that are gaseous under normal conditions. Since this concept was partially derived from observing the distribution of elements during metal smelting, it is certainly a useful one in the context of the analysis of ancient metals.

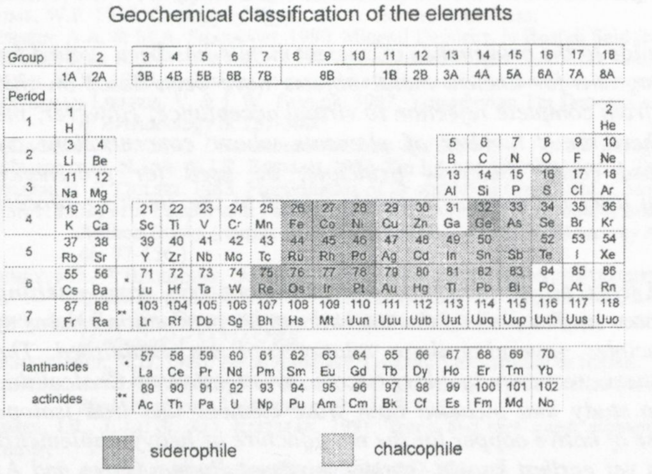

Figure 1: Geochemical classification of the elements. Elements not shaded are either lithophile or atmophile and of little use in provenance studies.

In provenance studies only those elements that follow copper during smelting are useful, which means that the element/copper ratio largely remains the same between the ore and the final smelted copper. Three major complications have to be considered at this point: Ores are generally inhomogeneous on all scales; they show zoning (Ixer this volume). The objection has been raised that this precludes any correlation between artefacts and ores but this need not be so as the prehistoric mining region of the Mitterberg in Salzburg, Austria shows. Here, trace element concentrations in chalcopyrite-rich ores vary over two orders of magnitude (FIGURE 2), yet this variation is not a random one. It is known, for example, that nickel occurs mainly in the form of Ni-As minerals such as gersdorffite (NiAsS) so that copper produced from Mitterberg ores is characterized by a combination of nickel and arsenic as major impurities with variable concentrations combined with relatively low amounts of antimony, silver and bismuth. In a recent study of some 800 Late Bronze Age copper artefacts from the adjacent area it was found that about 80% of the copper alloys conformed to this general pattern. Knowing that the peak production period at the Mitterberg was during the Late Bronze Age Urnfield Culture, it is only reasonable to assume that a correlation between ores and artefacts does exist.

It is essential that any ore deposit suspected of being a metal source in antiquity needs to be investigated, not only chemically but also geologically, to obtain as much information on its structure, mineral content and variability as is possible. The major disadvantage of this approach is that it needs a sizeable number of samples. In addition, it is often difficult to find equivalent samples to the rich ore that may have been used by ancient smelters because subsequent mining has removed all of the ores that were available in prehistory, as at Majdanpek, Serbia (Pernicka *et al.* 1993). Under such circumstances only very generalized conclusions can be drawn from the mineralization.

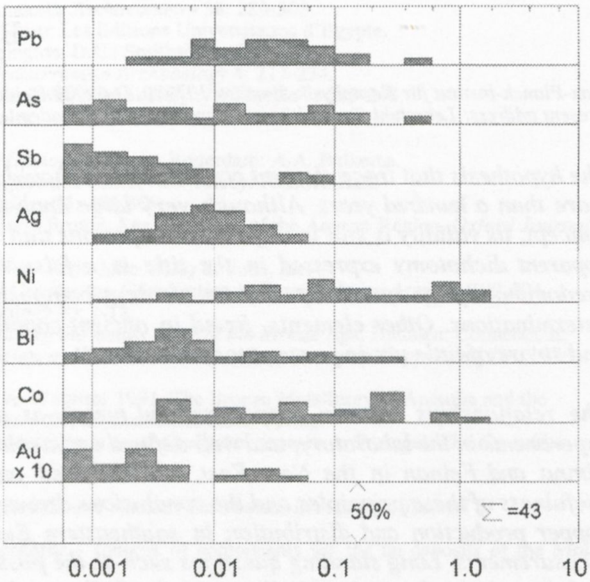

Figure 2: Variation of elements with possible reference to provenance studies in chalcopyrite concentrates from the Mitterburg area (after Pernicka 1987). The histogram is drawn in the style of Waterbolk & Butler (1965) for a better comparison with artefact analyses. The raw data have been recalculated so that the sum of copper and the plotted elements total 100%.

A second complication arises from the smelting process, as this will differ depending on the type of ore being used. Reduction of oxide ores is quite straightforward compared with the processing of sulfide ores. Although it cannot be expected that reduction happened under chemical equilibrium conditions, it is possible to use thermodynamic data for equilibrium reactions to predict the general behaviour of certain trace elements during smelting (Pernicka 1987). From these data it can be deduced that the concentration of some elements, notably nickel and arsenic, strongly depends on the smelting temperature and that copper, with or without nickel, could be produced from the same ore (Pollard *et al.* 1991; Budd *et al.* 1992). This is, however, very theoretical and needs the assumption that high and low impurity coppers were being produced intermittently due to different smelting temperatures. It is hard to imagine that ancient smelters did not know what they were doing and so sometimes smelted with low efficiency and without slag formation below the melting point of copper and at other times at very high temperatures above 1200°C. It is far more likely that people who were able to cast copper and thus achieve temperatures above 1100°C would strive to smelt at the maximum temperature obtainable with charcoal (between 1200 and 1300°C). Under these circumstances both slag and metal are liquid and the smelting process is easier to control and much more efficient. Consequently, it is most likely that the reduction smelting of ores containing nickel and arsenic would produce copper rich in both elements.

On the other hand, sulfide ores cannot be reduced directly but must be oxidized (roasted) before reduction. This is usually accomplished at around 700°C, well below the melting point of copper and most ore minerals. Nevertheless, it has been suggested that volatile elements like zinc, arsenic antimony and, presumably, selenium and tellurium, are partly lost during roasting (Tylecote *et al.* 1977). This may need more investigation, as was demonstrated by the experimental smelting of fahlerz from Cabrières in southern France. Here several Chalcolithic mines have been discovered (Ambert 1990/91; Ambert & Barge-Mahieu 1991) and copper mainly occurs in the form of tetrahedrite, a complex Cu-Sb sulfosalt. It is interesting to note that fahlerz-type copper dominates southern France during the late Chalcolithic. FIGURE 3 shows the concentrations of major impurity elements in the ore, the roasted ore and the raw copper metal. For comparison, all concentrations were recalculated so that the sum of the analysed elements and copper is 100%. This is equivalent to the assumption that all three elements (arsenic, antimony and silver) pass without loss from the ore into the metal. From FIGURE 3 it is evident that this assumption does not hold for antimony, whose concentration is reproducibly reduced by a factor of ten, while silver stays at the same level as expected. Interestingly, the arsenic content is far less reduced, although arsenic is more volatile than antimony. This is almost certainly due to the much lower concentrations of arsenic in the ore, for it seems that under these conditions volatilization of arsenic is reduced.

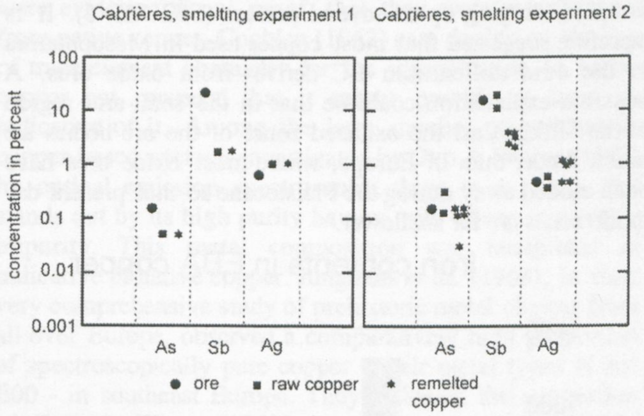

Figure 3: Results of smelting experiments of copper ores with high antimony concentrations (fahlerz) from Cabrières in southern France. For comparison the ore data have been recalculated according to the same method as in Fig.2.

The third complication arises from the treatment of the smelted copper to produce the finished object. Nowadays raw copper is generally refined to remove sulfur, iron and other impurities and this may also have been true in prehistoric times. This is an easy process because all it needs is to remelt the copper. Iron and other easily oxidized impurities are then removed as dross. It has been suggested that the refining of copper erases most of the characteristics that survived from the ore (Merkel 1983; 1990). However, using Merkel's experimental data it can be shown that this is not the case for elements like silver, nickel and antimony (FIGURE 4).

In a similar experiment to Merkel, Zwicker prepared a copper alloy with 2.02% Ni, covered it with charcoal and inserted it into a furnace at 600 °C. After 4 hours, when 1100°C was reached, the alloy began to melt; after 4.5 hours a temperature of 1150 °C was achieved and the alloy was completely molten but still covered with charcoal. Then the metal was partly poured out and chilled (sample 1). Charcoal was removed and the remaining metal left for further 15 minutes at 1150 °C in the furnace, then a further portion was poured out and chilled (sample 2). The remaining metal was left to cool in the crucible under a gentle airflow (sample 3). Chemical analysis showed 1.57% Ni for sample 1, 1.23% and 0.97% for samples 2 and 3, respectively. This demonstrates that, although some nickel is lost during simple re-melting, it is not so much as to make inferences impossible. It must be remembered that all processes, from ore formation to smelting and refining, depend on the distribution of the elements between various phases. Since the distribution laws are rational it is vital to compare ores and artefacts on a logarithmic scale, as shown in FIGURE 4. In such a diagram a loss of 25% nickel as in sample 1 does not appear dramatic, especially if considered alongside the range in concentrations seen in ores within a single deposit.

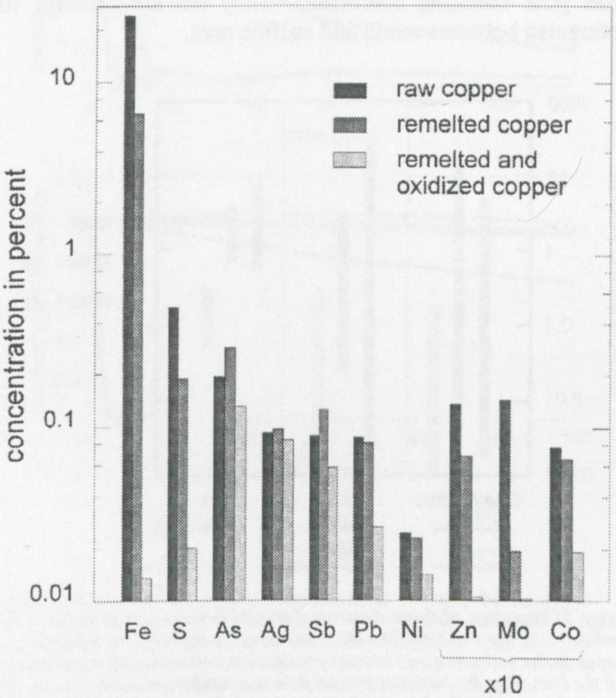

Figure 4: Summary of refining experiments performed by Merkel (1983;1990). It is evident that the concentrations of most elements relative to copper do not significantly change on simple remelting, except for Fe, S and Mo, all of which are irrelevant for provenance studies. It is unlikely that molten copper was regularly exposed to a blast of air for extended time as indicated in the third column (remelted and oxidized copper). But even then only Co, Ni and Pb are reduced by a factor of 2, which is of little significance when ores are compared with artefacts (after Pernicka 1987).

A final consideration is that some elements were deliberately alloyed with copper. In antiquity these were mainly tin, lead and - starting with the late Hellenistic period - zinc. Thus TABLE 1 gives a summary of the information provided by various elements that, in principle, can be found in ancient copper. There are few elements that are solely indicators of provenance. However, in earlier times when it can be assumed that deliberate alloying did not occur, a whole suite of elements are available that can be useful in helping to determine provenance (columns 2 and 3).

See Table + Caption at end of paper.

Trace elements and technology

Most copper ores contain iron and sulfur as major elements. Indeed, the principle task of smelting is the separation of copper from these two elements. Accordingly, their concentrations in copper alloys reflect how efficiently this separation was accomplished, hence they provide information about the smelting and purification processes. Friedman *et al.* (1966) suggested that an increasing iron content could distinguish copper produced from the three essentially different ore types (native copper, oxide, and sulfide ores). By contrast, Tylecote *et al.* (1977) found in smelting experiments that copper produced from oxide ores tended to contain higher concentrations of iron than from sulfide ores. On the other hand, Craddock & Meeks (1987) found that the iron contents of copper artefacts tend to increase from very early to later and technologically more advanced times. They suggest that, in the early periods, only very high grade copper ores with more than 60% copper were smelted at relatively low temperatures and under poor reducing conditions. They did not attempt to distinguish between oxide and sulfide ores.

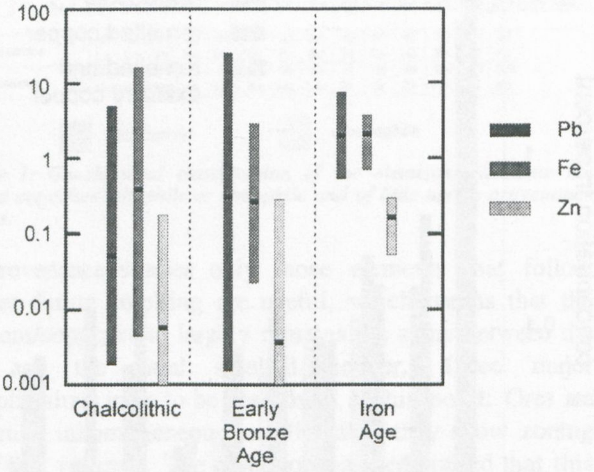

Figure 5: Variation of three elements that may be sensitive to redox conditions during smelting. The diagram shows that there was a major change in the technology of copper production between earlier periods and the Iron Age. In the latter period furnace conditions were presumably more reducing and better controlled as is indicated by the much smaller variations in Fe, Pb and Zn in copper prills extracted from slags (after Hauptmann et al. 1992).

The smelting of sulfide ores always includes the formation of matte; a mixture of copper and iron sulfides of variable composition that, together with the slag, takes up most of the iron. The matte can then be dead roasted and afterwards reduced like an oxide ore (an unfavourable process because of high fuel consumption) or it can be partly oxidized, in an open crucible, whereupon it yields quite pure copper. When oxide ores are reduced, then the iron content of the raw copper is bound to increase with increasing efficiency of the smelting conditions, namely with more reducing conditions. This is nicely demonstrated at Feinan (Hauptmann *et al.* 1992) where the copper ore is mainly present as oxides and where there is a clear increase in the iron content of copper metal between the Early Bronze Age and the Iron Age (FIGURE 5) by about an order of magnitude. This increase is accompanied by an increase in other elements that are sensitive to redox conditions in the furnace like lead, zinc, and cobalt (not shown in FIGURE 5). Although part of this change may be due to the exploitation of different ore charges, field evidence shows that considerable changes in the basic features of furnace construction occurred during this period. Presumably, these changes resulted in generally better controlled, more reducing furnace conditions, as is suggested by the decrease in variability in the contents of these elements in Iron Age copper. This conclusion is supported by the observation that if iron occurs in Chalcolithic copper prills at Feinan then it is always in an oxide form, magnetite or iron-rich slag, whilst in the Iron Age iron in copper occurs mainly as metallic iron or as carbon-containing iron phosphides (Hauptmann *et al.* 1992).

The Stuttgart analyses (Junghans *et al.* 1960, 1968; 1974) established that a major change in the metal composition occurred between the European Late Chalcolithic and the Early Bronze Age. The most abundant metal groups are chemically similar to the composition of fahlerz, so that it has been suggested that this may reflect the change from oxide to sulfide/sulfosalt ores. In this case rather low concentrations of iron would be expected, which is indeed observed in some 2500 Early Bronze Age copper-based artefacts from eastern Germany (FIGURE 6). Analyses were performed with an energy-dispersive X-ray spectrometer on drill samples (Lutz & Pernicka 1996) and in roughly half of the objects the iron content was below the detection limit of about 0.03%. Similar numbers of Early Bronze Age artefacts from Mesopotamia, analysed by the same method, exhibit a clearly different distribution of iron that was above the detection limit in almost all samples, ranging up to several percent (FIGURE 6). It is therefore suggested that most copper used in Mesopotamia in the third millennium BC derives from oxide ores. A possible explanation could be that in the semi-arid region of the Middle East the oxidized zones of the ore bodies are much deeper than in Europe, where most oxide ores have been eroded away during the Pleistocene so that present day oxide zones are far shallower.

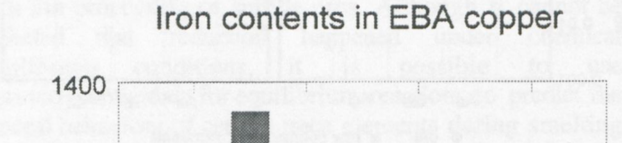

Figure 6: Iron contents in Early Bronze Age copper-based artefacts from eastern Germany and from Mesopotamia. Analyses were performed with energy-dispersive X-ray fluorescence on drill shavings.

Native copper is a special case. Its identification in artefacts is highly desirable, because it is generally held that the working of metals began with the use of native copper (Muhly 1989). The most straightforward method for its identification is investigation of its metallographic structure in polished section. This only works, however, if the native copper object has not been cast but been formed simply by hammering, and possibly tempering. Since it is more likely to find native copper in very early periods and because these early artefacts are usually very rare and small, e.g., beads or small tools, permission to take a large sample for metallographic study is extremely difficult to obtain. Often it is possible only to take a small sample by drilling or rubbing that is only suitable for chemical analysis. It would, therefore, be desirable to identify native copper by its chemical composition but this method is contentious. Native copper is usually very pure but it has been suggested that copper smelted from pure malachite or chalcopyrite could be just as free from impurities as native copper (Maddin *et al.* 1980).

Wibel (1865) proposed that high purity Neolithic and Chalcolithic copper artefacts from southeastern Europe were evidence, if not proof, that they were manufactured from native copper. Coghlan (1962) cast doubts on the use of trace element chemistry for the identification of native copper but conceded that it might provide at least an indication of it. Among the large number of prehistoric, copper-based artefacts investigated by Otto & Witter (1952) by optical emission spectroscopy, there is a group that stands out by its high purity having only silver as a major impurity. This metal composition was interpreted as indicative of native copper. Junghans *et al.* (1968), in their very comprehensive study of prehistoric metal objects from all over Europe, observed a comparatively high proportion of spectroscopically pure copper - their metal types N and E00 - in southeast Europe. They followed the suggestion of Otto & Witter (1952) that this was most probably native copper. Charles (1969) suggested that two Chalcolithic axe-adzes from Hungary and the former Yugoslavia were made of native copper, again on the basis of their purity.

One aspect seems to have been overlooked in this discussion, namely that the presence of volatile metals such as mercury could provide unequivocal chemical evidence for the presence of native copper. This was first suggested by Pernicka *et al.* (1993) after it had been found that many samples of native copper contain a few ppm of mercury. Contrary to common expectations mercury is not easily volatilized from copper, even at temperatures of several hundred degrees centigrade (FIGURE 7). Thus it could easily survive the tempering of native copper that seems to have been applied from the very earliest periods onwards (Maddin *et al.* 1991; Yalcin & Pernicka 1998).

On the other hand, smelting of copper ores removes mercury very effectively, so that this element might possibly serve as a useful indicator for native copper. A problem of this method is that laboratory tests have shown that, in principle, mercury can also be adsorbed on copper from ground water during burial so that, again, the identification is not unequivocal. This seems to have occurred with three Chalcolithic borers from Kacica, Bulgaria (Pernicka *et al.* 1997) dated to the late fourth millennium BC. Although they are quite different in composition (one contains 2.35% tin) and may even be of different ages they all contain between 6 and 9 ppm mercury. It is very unlikely that this indicates the use of native copper, rather it suggests that the mercury content is due to contamination from the environment either during burial or, more likely, at some later stage.

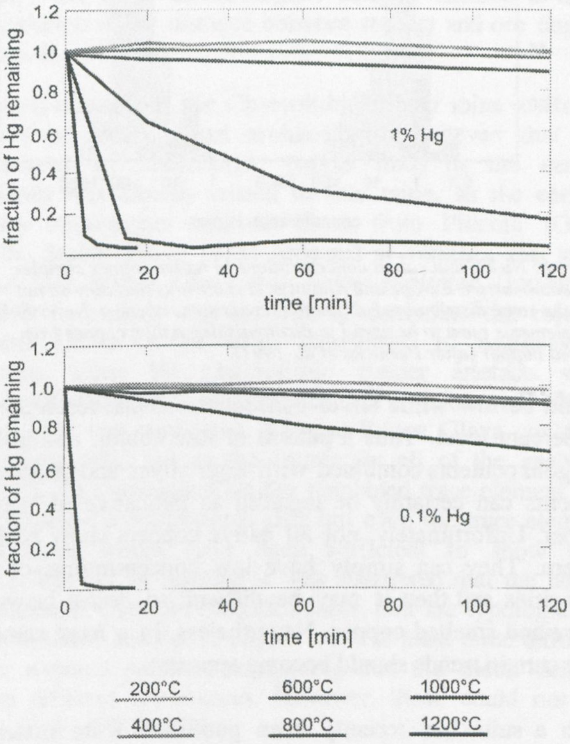

Figure 7: Results of desorption experiments of mercury from copper. Copper with 1% and with 0.1% mercury was prepared and heated in air over the time shown. Especially at lower concentrations (that are still high compared with those found in samples of native copper) mercury is only quantitatively removed above the melting point of copper.

Returning to the trace element pattern, it is true that native copper is usually a high-purity metal, with silver (and locally arsenic) as major impurities. Unfortunately, it is also true that very pure ores do exist that produce similarly pure copper on smelting, as represented by millimeter-sized copper prills found in Chalcolithic and Early Bronze Age slags from Feinan (Hauptmann *et al.* 1992). These demonstrate that silver, gold, and antimony in smelted copper can, for all practical purposes, be as low as those typically found in native copper; that arsenic shows a wide distribution in concentrations overlapping that observed in native copper, but that nickel and cobalt are almost invariably higher than in native copper (FIGURE 8). Most native copper is formed in the lower part of the oxidation zone, lying above primary ore deposits, by dissolution and re-precipitation of the metal. Geochemical considerations indicate that some elements are more mobile than others under these oxidizing conditions. This results in the separation of elemental pairs that behave similarly during smelting, such as arsenic/antimony and cobalt/nickel. It is well known that native copper can contain appreciable concentrations of arsenic but antimony is invariably very low, because antimony is immobile in the oxidation zone due to the formation of antimonates (Pernicka 1990). Similarly, cobalt is always low, because unlike nickel it is often precipitated as a carbonate. For the same reason gold

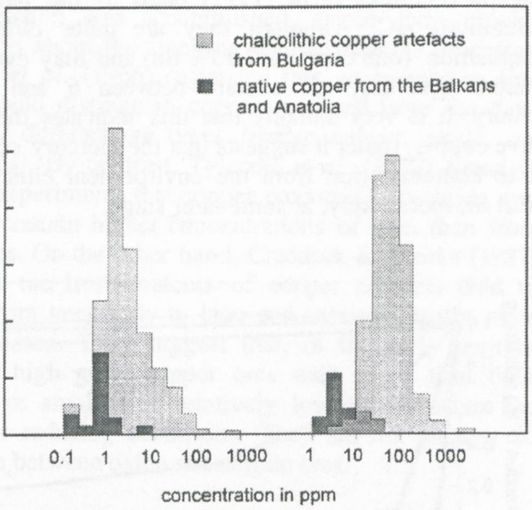

Figure 8: Nickel and cobalt concentrations in native copper samples from southeastern Europe and Anatolia. It is obvious that they do not have the same distributions although there is some overlap. Nevertheless, both elements seem to be useful in distinguishing native copper from smelted copper (after Pernicka et al. 1997).

should be low while silver concentrations can reach up to the percent level. Thus a pattern of low cobalt, antimony, and gold contents combined with high silver and/or arsenic contents can certainly be regarded as indicative of native copper. Unfortunately, not all native coppers show such a pattern. They can simply have low concentrations of all impurities and then it may be difficult to decide between native and smelted copper. Nevertheless, in a large sample suite certain trends should become apparent.

Such a suite has recently been published from material found in southeastern Europe (Pernicka *et al.* 1997). This is where most early, very pure, copper metal artefacts have been found (Junghans *et al.* 1968). They are generally interpreted as being made from native copper although many objects were undoubtedly cast. This interpretation has had a profound impact on our perception of the beginnings of metallurgy in southeastern Europe. It has been suggested that abundant sources of native copper may have given rise to an independent invention of metallurgy in this region (Renfrew 1969). However, new analyses with improved precision and detection limits provide evidence that, contrary to common belief, most Chalcolithic copper objects in Bulgaria were made out of smelted copper and it seems that metallurgy began in this area with smelting without a recognisable native copper phase (FIGURE 9). The iron contents have a bimodal distribution (FIGURE 10) that indicate that oxide ores were smelted along with either sulfide ones or, more likely, very pure ores with high copper concentrations. Since smelting of copper ores is a complex technique that requires considerable experience, it seems more likely that this knowledge was already available when metallurgy began in Bulgaria. Thus transfer of technology, most likely from Anatolia, seems to be a better model for the development of metallurgy in southeastern Europe than an indigenous re-invention. A similar model has recently been proposed for central Europe (Strahm 1994).

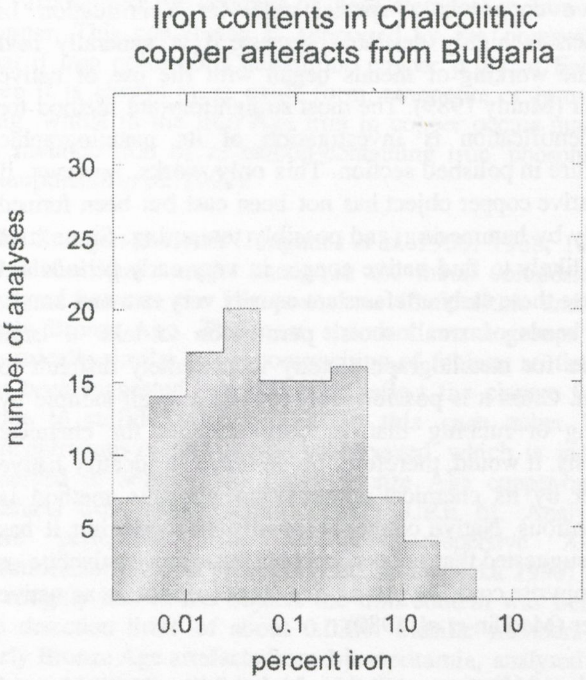

Figure 9: There is a clear difference in the distribution of S, Au and Se in native copper and Chalcolithic copper objects from Bulgaria suggesting that native copper did not play a major role in the early metallurgy of southeastern Europe.

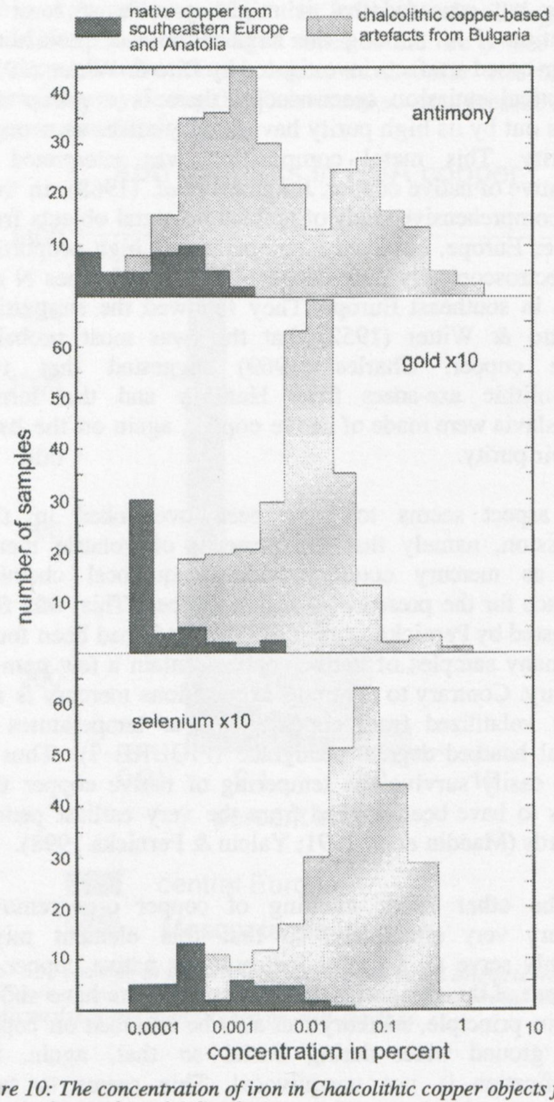

Figure 10: The concentration of iron in Chalcolithic copper objects from Bulgaria shows a bimodal distribution.

Trace elements and provenance

Trace element analysis of ancient metal objects was so discredited that for some time hardly anybody looked at the data that were available. Indeed, it is possible that the wealth of data was so overwhelming that it was actually difficult to digest. In any case, many of the arguments raised against metal analysis are no longer valid or were wrong from the start. It has been shown that the largest database namely that published by the Stuttgart group (Junghans *et al.* 1960; 1968; 1974) is quite accurate but that its precision is only moderate compared with modern analytical techniques (Pernicka 1984). The selection of elements used for grouping appears to be sensible. Tin was not used, because it was a deliberate addition in most cases and is, therefore, irrelevant to the source of copper. The same could apply to lead but in European Early Bronze Age artefacts lead concentrations are usually low and vary rather irregularly. Thus only five elements are left that can be determined in most samples, namely As, Sb, Ag, Ni, and Bi. It happens that all of them are indicative of ore sources, at least to a certain extent. Frequency analysis shows that groups of artefacts can be found with narrow quasi-normal distributions of all elements, which suggests that all of them were produced from the same ore applying similar processes. This is now increasingly being acknowledged by archaeologists (Krause 1988; Liversage 1993; Krause & Pernicka 1996) and metal composition is regarded a valuable tool for the grouping of artefacts.

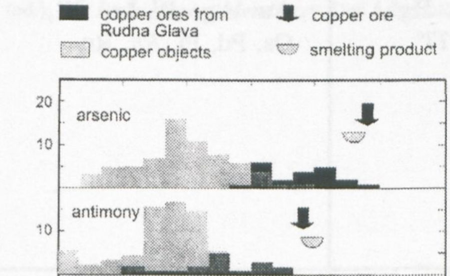

Figure 11: Concentration ranges of elements in Chalcolithic copper artefacts from Serbia and in copper ores from Rudna Glava. Ore analyses have been recalculated in the same manner as in Fig.2. Arrows indicate the concentrations in a prehistoric ore concentrate from Rudna Glava (Tylecote 1982) and bowls indicate copper smelted from the same ore (after Pernicka et al. 1993).

However, few cases have been reported where there is a convincing association between a group of artefacts and a specific ore deposit. This is mainly due to the lack of a comparable number of ore analyses and the similarity of many copper deposits, which makes it difficult to distinguish them unequivocally. Incidentally, this problem is shared with lead isotope analysis, for its real value lies in the exclusion of suspected ore sources. These are often situated in the geographical vicinity of the artefacts under study, and most archaeologists tend to assume a direct association if the distance between artefact and ore deposit is small.

A good example is the Chalcolithic copper mine at Rudna Glava in Serbia. Most archaeologists believed that the abundance of Chalcolithic copper finds in the central Balkans was directly related to this mine, as the earliest heavy implements such as those from Plocnik (Grbic 1929, Stalio 1964; 1973) appeared at roughly the same time that Rudna Glava was being exploited (Jovanovic 1982). In a study that set out to determine the role of Rudna Glava in the early metallurgy of southeastern Europe, some 90 Chalcolithic copper artefacts were analysed chemically and isotopically (Pernicka *et al.* 1993). The result was surprising, because Rudna Glava could be definitely ruled out as the source for all of the analysed objects. This was based on the combined trace element and lead isotope compositional data but even the trace element data alone would have been sufficient to show this (FIGURE 11). In addition it was discovered that the heavy implements from the Plocnik hoards, that are typologically very similar, consist of copper with at least three different trace element patterns, suggesting that the metal derives from different ore sources. However, these could not be identified (FIGURE 12).

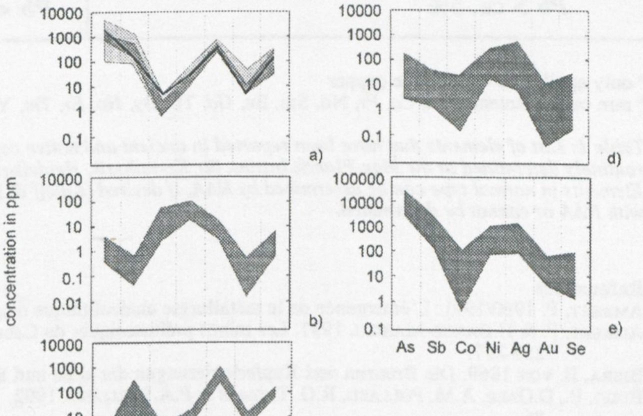

Figure 12: Trace element patterns of three different chemical groups found among heavy implements from the Plocnik hoard (a – c), in other Chalcolithic copper artefacts, and in final Chalcolithic copper-based objects from Serbia. Also included in panel a is a group of Chalcolithic copper artefacts from Bulgaria that are chemically indistinguishable from those from Plocnik lighter shaded area and one ore sample from the Chalcolithic mine at Ai Bunar near Stara Zagora, Bulgaria (solid line). The very similar trace element patterns, in shape as well as in concentrations, suggest a common origin of the objects and, in addition, Ai Bunar as the source of this copper. This conclusion is decisively strengthened by matching lead isotope ratios in the artefacts and in ores from Ai Bunar (Pernicka et al. 1997).

An extension of this study into present-day Bulgaria (Pernicka *et al.* 1997) revealed that more Chalcolithic copper objects with similar compositions occurred there and, moreover and most important, that one group chemically and isotopically resembled ores from another Chalcolithic copper mine, namely Ai Bunar near Stara Zagora. Leaving aside the isotopic evidence, the similarity of one ore sample from Ai Bunar with this group of objects is rather striking (FIGURE 12a). However, only one out of nine ore samples provided such a close match but it is by far the most relevant one with 53% copper whilst the other samples contained between 3 and 22% copper. These lower grade samples possibly represent rejected ore rather than that smelted. Again this confirms the major difficulty connected with the chemical characterization of ore deposits, for it is desirable to analyse many more samples than is considered necessary for lead isotope analysis. Yet it is often difficult to find enough ore that is representative of the material available in prehistoric times and left over by the miners. Fortunately, at Rudna Glava and Ai Bunar this was possible. However, at Majdanpek in Serbia modern opencast mining has completely removed the ore body and, in addition, covered a large area with waste rock so that finding any remains of ancient mining and the ore exploited in antiquity is very unlikely. Under such circumstances lead isotope ratios are virtually the only available tool that will allow inferences to be made about ancient exploitation (Pernicka *et al.* 1993).

In both studies it became clear that the two sets of data provide independent information on the provenance of ancient copper. These may or may not agree with each other. In the case of agreement between the data sets (still rare) this comes very close to a positive identification of an ore source, since it is extremely unlikely that several deposits have exactly the same chemical and isotopic patterns. On the other hand, some deposits turned out to be chemically homogeneous but not isotopically, such as Rudna Glava and others are isotopically homogeneous but show distinct chemical variation as is suggested by some groups of Bulgarian artefacts (Pernicka *et al.* 1997).

technology	provenance and/or technology	provenance
Al, *B*, Ba, *Be*, *Ca*, **Cr**, *Cs*, **Fe**, *Ga*, *Ge*, Hf, *K*, *Li*, *Mg*, *Mn*, Mo, *Na*, *Nb*, *P*, Rb, *S*, Sc, REE[b], *Si*, *Sr*, Ta, *Ti*, Th, U, *V*, *W*, *Y*, Zr **Sn** > ca. 1% **Zn** > ca. 5% ***Pb*** > ca. 5%	**As**, **Cd**[a], **Co**, In, **Hg**[a], Re, **Sb**, **Se**, **Te**, *Tl*[a] **Sn** < ca. 1% **Zn** < ca. 5% ***Pb*** < ca. 5%	**Au** **Ag**, ***Bi***, **Ir**, **Ni**, Os, Pd, Pt, *Rh*, Ru

[a] only applicable with native copper

[b] rare earth elements (La, Ce, *Pr*, Nd, Sm, Eu, *Gd*, Tb, *Dy*, *Ho*, *Er*, *Tm*, Yb, Lu)

Table 1: List of elements that have been reported in ancient and native copper and their potential uses in archaeometallurgy. Elements in bold type are routinely determined at the Max-Planck-Institut für Kernphysik, Heidelberg, by neutron activation (NAA) and atomic absorption analysis (bold italics). Elements in normal type can be determined by NAA, if desired (Kuleff & Pernicka 1995). Elements in italics are either difficult to determine in copper with NAA or cannot be determined.

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