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Archaeometallurgy: Examples of the application of scientific methods to the provenance of archaeological metal objects

E. Pernicka

Institut für Archäometrie, TU Bergakademie Freiberg - Germany

Introduction

Archaeometallurgy deals with the production and distribution of metals in antiquity as well as with the technology for working metals. This is a large field of interdisciplinary research, which involves knowledge and experience mainly in economic geology, extractive metallurgy, mineralogy, materials science, and analytical chemistry besides archaeology. Physics enters together with analytical chemistry since most modern methods employ physical principles for analysis. The main emphasis of this lecture will be on the analysis of ancient metal objects in order to determine their authenticity and their provenance.

In antiquity there were seven metals known and described by ancient authors: gold, silver, copper, lead, tin, iron and mercury. Furthermore, the following elements often occur in appreciable concentrations in copper-based metal objects: arsenic, antimony, and nickel. These were most likely impurities of the original ores. There is no indication for their intentional addition to the known metals. Although antimony has occasionally been used as metal, especially in Transcaucasia, it was always mistaken for lead. In the New World platinum was used as white metal in Precolumbian cultures when silver was not available. Although remarkable, these are nevertheless rare exceptions.

The hypothesis that trace element concentrations should be a guide to the provenance of ancient metals has been formulated more than one hundred years ago. One early example is Göbel (1842) with an extended title that reads like an abstract in (my own) translation: "On the impact of chemistry on the tracing of prehistoric peoples or results of

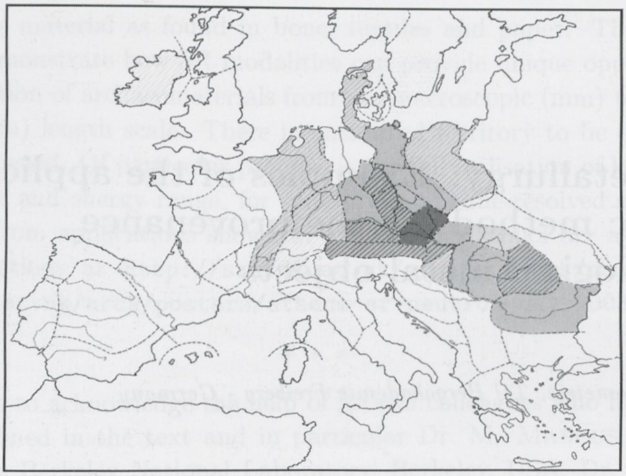


Fig. 1. – Distribution of copper type C2, a natural alloy of copper with arsenic and antimony (fahlore metal) that was most abundant in the Early Bronze Age (after [6]).

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 analyzed objects and ascribed them to seemingly well-defined ethnic groups, as was usual in those days. One has to remember that only shortly before the three-period system was proposed by C. J. Thomsen (1836) and that an additional motivation for the analyses was the hope to be able to date metal objects based on their composition. Soon it was discovered that elements at low concentrations could be used to determine the nature of the ore from which the metal was smelted and possibly the geographical origin of the metal itself [1, 2] and that compositional differences of copper were to be expected when native copper, oxidic or sulfidic ores were used for smelting [3]. This idea was repeated almost exactly one hundred years later by Friedman *et al.* [4].

Although very large analytical programs of ancient metal objects were performed along these lines, their results are still controversial and the conclusions that can be drawn seem to be unclear. Opinions range from complete rejection to close to acceptance. The largest and most heavily criticized project was the one performed at the Württembergisches Landesmuseum in Stuttgart [5-7] with more than 20000 analyses of prehistoric metal objects from all over Europe. They were classified according to their chemical composition and the distributions of these metal groups were studied in time and space (fig. 1). Obviously, the method of grouping (based on the analysis of variance of the elements As, Sb, Ag, Ni, and Bi) was not understood, because the most pronounced critics of this method arrived at almost the same classification when he used a small subset of the data [8]. Another point of concern was the selection of elements. This was actually based on an earlier work [9] in which it was assumed that of all elements

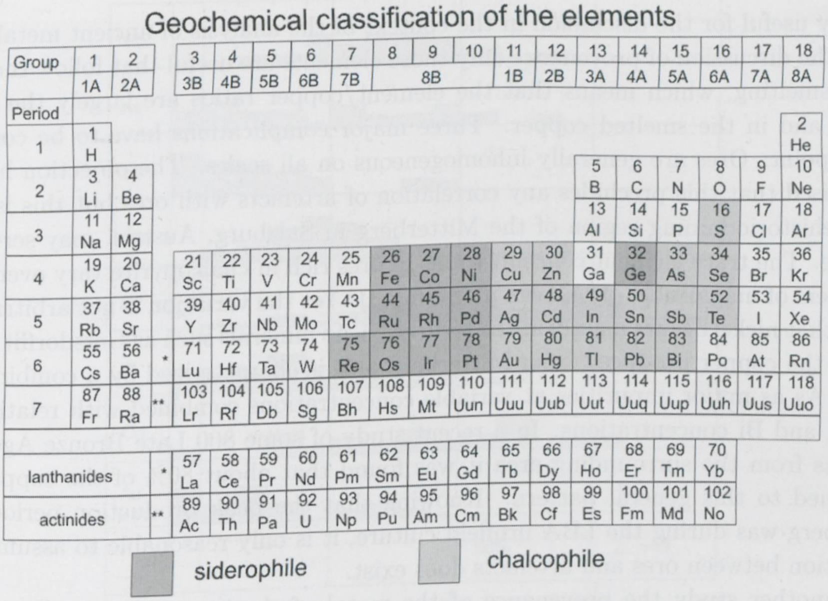


Fig. 2. – Geochemical classification of the elements. Elements not shaded are either lithophile or atmophile and of little use in provenance studies of metals.

analyzed this set should characterize the original ore best.

With the application of lead isotope analysis to copper-based alloys [10] chemical analysis of ancient metal objects seems to have become obsolete. In fact, it is constantly repeated that chemical analyses alone do not allow one to link copper-alloy artefacts with copper ores. Although this is certainly correct, there are exceptions as at Feinan, Jordan, where a chemically rather homogeneous deposit shows large variations of lead isotope ratios [11]. 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 of 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— should provide a better discrimination of sources. This approach has been followed by the Heidelberg/Mainz group from the very beginning [12].

The behaviour of trace elements

In the first half of this century geochemists have divided the elements that occur in the solid Earth into three groups that are concentrated in different parts: siderophile elements in the iron core, chalcophile elements in the outer core and mantle, and lithophile elements in the crust (fig. 2). There is also a group of atmophile elements that are gaseous under normal conditions, but these do not concern us here. This concept was actually derived from the known distribution of the elements during metal smelting and is thus certainly useful for the discussion in the context of the analysis of ancient metals.

For the discussion of provenance only those elements are useful that follow the copper during smelting, which means that the element/copper ratios are largely the same in the ore and in the smelted copper. Three major complications have to be considered at this point: Ores are generally inhomogeneous on all scales. The objection has often been raised that this precludes any correlation of artefacts with ores but this is not so. The prehistoric mining region of the Mitterberg in Salzburg, Austria, may serve as an example. The trace element concentrations in ores rich in chalcopyrite vary over at least two orders of magnitude, often even more (fig. 3). Yet the variation is not arbitrary. It is known that nickel occurs mainly in the form of Ni-As minerals such as Gersdorffit (NiAsS) so that the copper produced from Mitterberg ores is characterized by a combination of Ni and As as major impurities at variable concentrations combined with relatively low Sb, Ag, and Bi concentrations. In a recent study of some 800 Late Bronze Age copper artefacts from the surrounding 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 LBA urnfield culture, it is only reasonable to assume that a correlation between ores and artefacts does exist.

In another study the provenance of the metal of the by now famous Sky Disc of Nebra [13], see fig. 4, was sought. Its chemical composition was compared with a data base of more than 40000 analyses of prehistoric, mostly Bronze Age, metal objects from Europe and the Mediterranean. The result was that copper of this elemental pattern is not equally distributed but concentrated along the eastern Alps between Lake Constance and western Hungary on the one hand, and in Denmark and the German Baltic coast on the other hand. Since there are no known copper deposits in Denmark and northern Germany, it is only reasonable to assume that the copper derived from the eastern Alps where there are several Bronze Age copper mines known, the largest of which is the Mitterberg in Salzburg (fig. 5). It is reassuring that the trace element pattern of the Nebra hoard also conforms to the copper ores of the Mitterberg (fig. 6).

These examples demonstrate that it is essential that an ore deposit that is suspected to have served as a metal source in antiquity needs to be investigated not only chemically but also geologically to obtain all possible information on the structure, mineral content and variability of the ore body. The major disadvantage of this approach is that it needs a sizeable number of samples, preferably enriched in copper minerals and not too small to mimic the ancient smelting charges. This is, of course, not always possible, because modern mining may have removed all ores available to ancient miners as at Majdanpek, Serbia [14]. Under such circumstances only very general conclusions can be drawn from the known type of mineralization.

The second complication arises from the smelting process that differs depending on the type of ore used. The reduction of oxidic ores is quite straightforward and, although one cannot expect those processes to have reached chemical equilibrium, tabulated thermodynamic data can be used to predict the behaviour of certain trace elements [15]. From these data it could also be deduced that the concentration of some elements, *e.g.* nickel and arsenic, strongly depends on the smelting temperature and that copper with

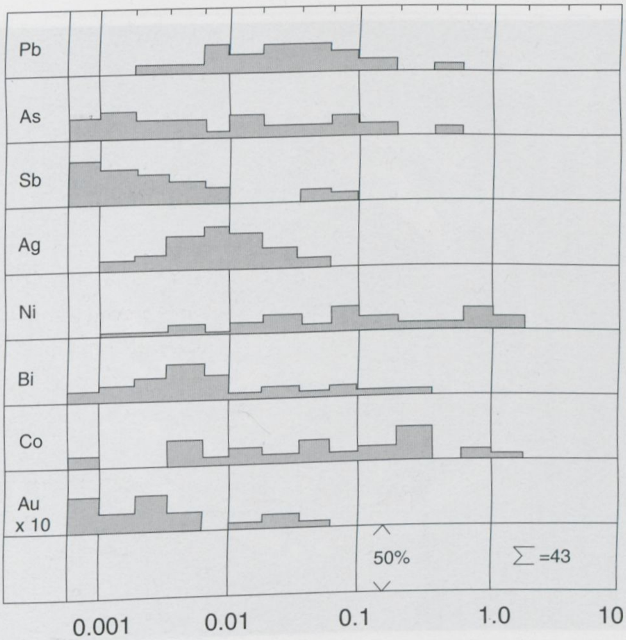


Fig. 3. – Variation of elements with possible relevance to provenance studies in chalcopyrite concentrates from the Mitterberg area (after [15]). The histogram is drawn in the style of Waterbolk and Butler [16] for better comparison with artefact analyses. The raw data have been recalculated so that the concentrations of the elements plotted sum up to 100% together with copper.

and without nickel could be produced from the same ore [17, 18]. Although this is theoretically possible, it is hard to imagine that ancient smelters who knew how to cast copper ever deliberately kept the smelting temperature below the melting point of copper (1087 °C). Under these conditions copper can be reduced without any nickel and little arsenic. The smelting is, however, much more efficient when metal and slag are molten and this was certainly by far the most important process. The maximum temperature to be reached with charcoal is around 1250 °C, so that reasonably only a small temperature range needs to be considered.

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 minerals involved. Nevertheless, it has been suggested that volatile elements like Zn, As, Sb and, presumably, Se and Te are partly lost during roasting [19]. This may need more investigation, as is demonstrated by experimental smelting of fahlore from Cabrières in southern France. At this site several chalcolithic mines have been discovered [20, 21]. Copper mainly occurs in the form of tetrahedrite, a complex Cu-Sb sulfide. It is interesting to note that fahlore type copper prevails in southern France during the late Chalcolithic. Charges of this ore were roasted and

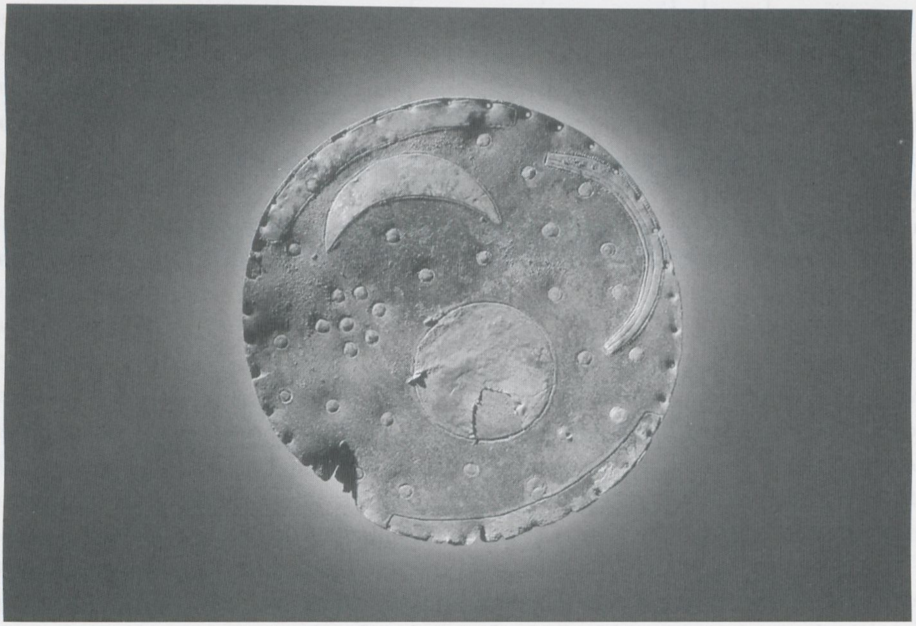


Fig. 4. – Early Bronze Age Sky Disc of Nebra, Germany. The disc was found in a clandestine excavation together with two swords, two axes, a chisel and probably two arm spirals.

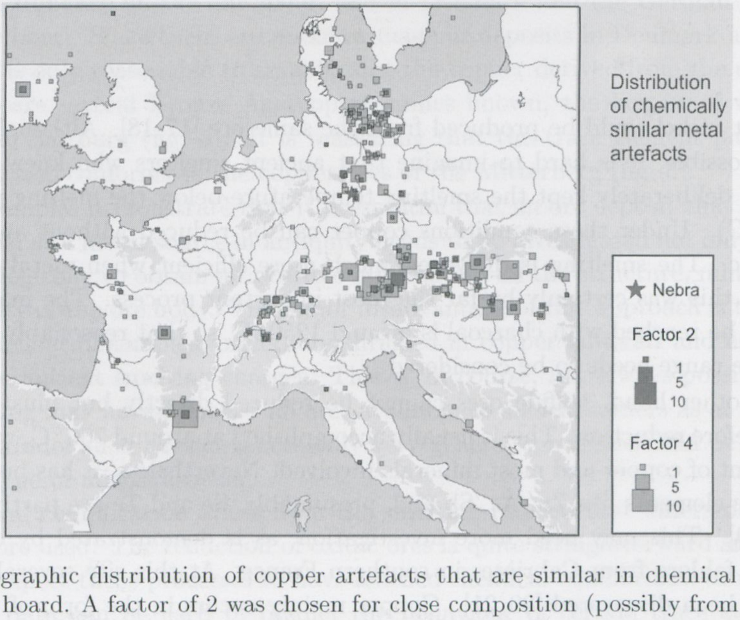


Fig. 5. – Geographic distribution of copper artefacts that are similar in chemical composition to the Nebra hoard. A factor of 2 was chosen for close composition (possibly from one stock of metal) and a factor of 4 for a similar one (possibly from a single mine).

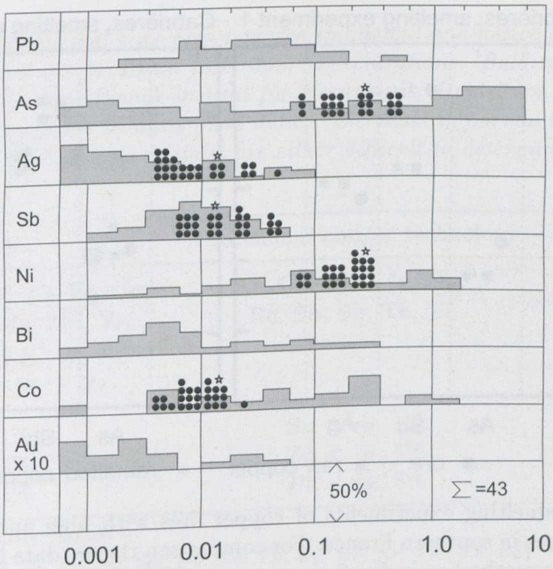


Fig. 6. – The copper of the Nebra hoard has a similar trace element pattern to the copper ores from the Mitterberg area (see also fig. 2).

smelted in April 1996 by P. Ambert and J. Happ on the occasion of the 80th birthday of E. Sangmeister. Figure 7 shows the concentrations of the major impurity elements in the ore, the roasted ore and the raw copper. For comparison all concentrations were recalculated so that the sum of the analyzed elements and copper yields 100%. This is equivalent to the assumption that all three elements (As, Sb, Ag) pass without loss from the ore to the metal. From fig. 7 it is evident that this assumption does not hold for Sb that is consistently reduced by a factor of 10, while Ag stays at the same level, as expected. Interestingly, the As content is much less reduced although As is more volatile. This is almost certainly due to the much lower concentration levels of arsenic in the ore. It seems that under these conditions the volatilization of As is reduced.

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. This may have been practiced also in prehistoric times. This is an easy process because all it needs is remelting of copper. Iron and other easily oxidized impurities are then removed as a dross. It has been maintained that the refining of copper erases most of the characteristics that may have survived from the ore [22, 23]. However, using Merkel's experimental data it can be shown that this is not the case for elements like Ag, Ni, and Sb (fig. 8).

In a similar experiment U. 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 a temperature of 1100 °C was reached and the alloy began to melt. After 4.5 hours a temperature of 1150 °C was reached, the alloy was completely molten but still covered with charcoal.

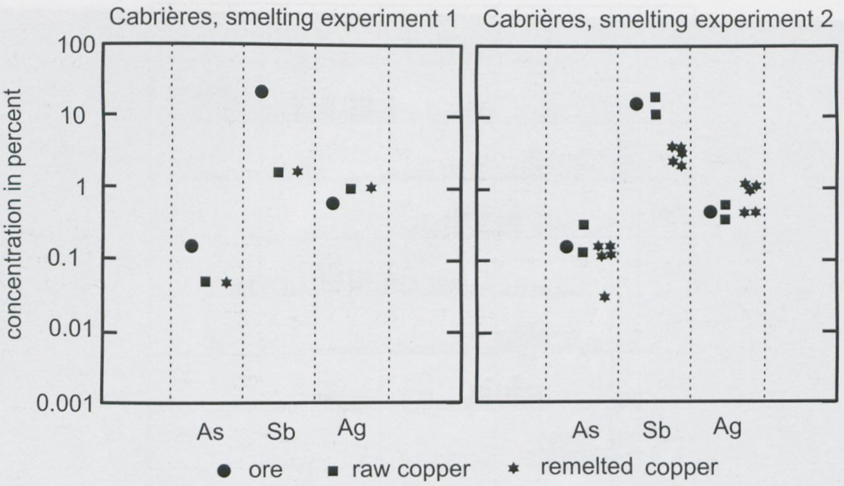


Fig. 7. – Results of smelting experiments of copper ores with high antimony concentrations (fahlore) from Cabrières in southern France. For comparison the ore data have been recalculated according to the same method as in fig. 2.

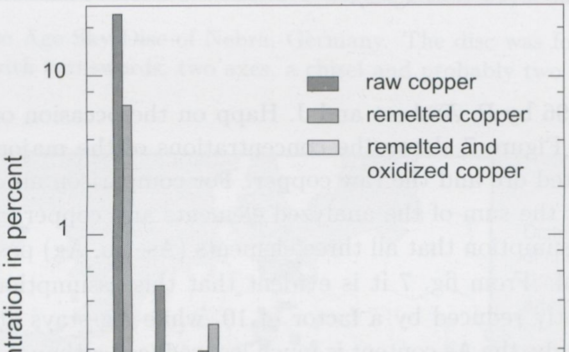


Fig. 8. – Summary of refining experiments performed by Merkel [22, 23]. It is evident that the concentrations of most elements relative to copper do not significantly change on simple remelting, except for Fe, S, and Mo, all of which are irrelevant for provenance studies. It is unlikely that molten copper 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 [15]).

TABLE I. – *List of elements that have been reported in ancient and native copper according to the type of information that can be drawn from their concentrations. Bold typed elements are routinely determined at the Max-Planck-Institut für Kernphysik, Heidelberg, by neutron activation (NAA) and atomic absorption analysis (bold italic). Elements in normal type can be determined by NAA, if desired* [24]. *Elements in italic are either difficult to determine in copper with NAA or not at all.*

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	**As**, **Cd**[a], **Co**, In, **Hg**[a], Re, **Sb**, **Se**, **Te**, *Tl*[a]	**Au**, **Ag**, ***Bi***, **Ir**, **Ni**, Os, Pd, Pt, *Rh*, Ru
Sn > *ca.* 1% **Zn** > *ca.* 5% ***Pb*** > *ca.* 5%	**Sn** < *ca.* 1% **Zn** < *ca.* 5% ***Pb*** < *ca.* 5%	

[a] Only applicable with native copper.

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

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. A part 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 yielded 1.57% Ni for sample 1, 1.23% and 0.97% for samples 2 and 3, respectively. This demonstrates that some nickel is lost during simple remelting but not so much to make any inferences impossible. It has to be remembered that all processes involved, from ore formation to smelting and refining, depend on the distribution of the elements between various phases. Since the distribution laws are multiplicative, it is vital to compare ores and artefacts on a logarithmic scale, as in fig. 4. In such a diagram a loss of 25% nickel as in sample 1 does not appear dramatic, especially if the variation in ores is considered.

Finally, one has to consider the fact that some elements were alloyed to copper. In antiquity these were mainly Sn, Pb, and —starting with the late Hellenistic period— Zn. Thus we arrive at a summary of the information provided by various elements that can in principle be found in ancient copper (table I). There are only few elements that are pure indicators of provenance but especially in the early periods a whole suite of elements are available (columns 2 and 3).

Trace elements and technology

Most copper ores contain iron and sulfur as major elements. In fact, the principal task of smelting is the separation of copper from these two elements. Accordingly, their concentrations in copper alloys reflect how efficiently this was accomplished, *i.e.* they provide only information on the smelting and purification processes. Friedman *et al.* [4] have suggested that copper produced from the three basically different ore types (native copper, oxidic, and sulfidic) could be distinguished, mainly based on their increasing iron content. Quite in contrast, Tylecote *et al.* [19] found in smelting experiments that copper produced from oxidic ores tends to contain higher concentrations of iron than the one from sulfidic ores. On the other hand, Craddock and Meeks [25] found that the iron contents of copper artefacts tend to increase from very early to later and technologically more advanced periods. They suggested that in the early periods only very high grade copper ores with more than 60% copper were smelted at relatively low temperatures and poor reducing conditions. They did not attempt to distinguish between oxidic and sulfidic ores. The smelting of sulfide ores always includes the formation of matte (a mixture of copper and iron sulfides of variable composition that takes up most of the iron together with the slag). The matte can then be dead roasted and afterwards reduced like an oxidic ore (an unfavourable process regarding fuel consumption) or it can be partly oxidized, *e.g.* in an open crucible, whereupon it gives off rather pure copper. When oxidic ores are reduced, then the iron content of the raw copper is bound to increase with increasing efficiency of the smelting conditions, *i.e.* with more reducing conditions. This is nicely demonstrated at Feinan [11] where the copper ore is largely oxidic and where there is a clear increase of the iron contents between the Early Bronze Age and the Iron Age (fig. 9) by about an order of magnitude. This increase is accompanied by an increase of other elements that are sensitive to the redox conditions in the furnace, like lead, zinc, and cobalt (not shown in fig. 9). Although part of this change may be due to the exploitation of different ore loads, field evidence shows that considerable changes in basic features of furnace construction have occurred during this period. Presumably, these changes resulted in more reducing and generally better controlled furnace conditions, as indicated by the less variable 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 oxidic form, *e.g.* magnetite or iron-rich slag, while in the Iron Age iron in copper occurs mainly as metallic iron or as carbon-containing iron phosphides [11].

It is well known from the Stuttgart analyses [5-7] that there occurred a major change in the metal composition between the European late Chalcolithic and the Early Bronze Age. The most abundant metal groups resemble the composition of fahlore so that it has been suggested that this may reflect the change from oxidic to sulfidic ores. In this case one would expect rather low concentrations of iron, which is indeed observed in some 2500 Early Bronze Age copper-based artefacts from eastern Germany (fig. 10). The analyses were performed with an energy-dispersive X-ray spectrometer on drill samples [26]. In roughly half of the objects the iron content was below the detection limit of about 0.03%. A similar number of Early Bronze Age artefacts from Mesopotamia analyzed with the same method exhibit a clearly different distribution of iron that was above the detection limit in almost all samples and ranges up to several percent (fig. 10). 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 were eroded by the last glaciation, so the oxide zones are much shallower.

A special case is the identification of native copper. Its identification in artefacts is highly desirable, because it is generally held that the working of metals began with

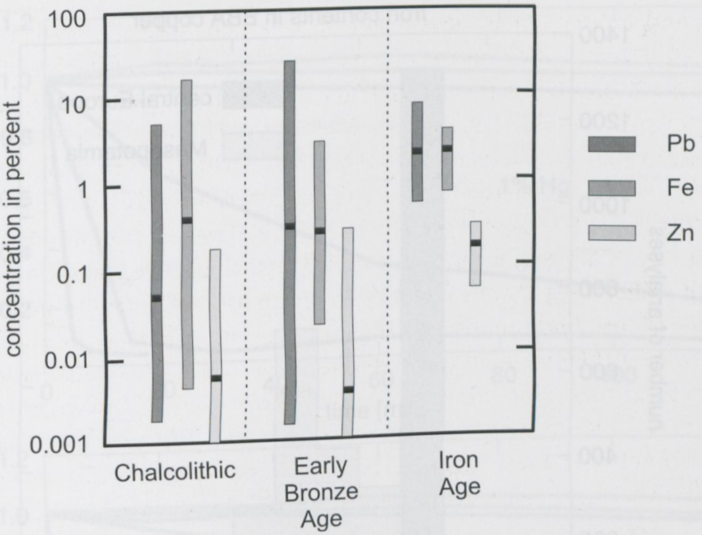


Fig. 9. – Variation of three elements that may be sensitive to redox conditions during smelting. The diagram shows that there was a major change of the technology of copper production between the early periods and the Iron Age. In the later period the furnace conditions were presumably more reducing and better controlled, as is indicated by the much smaller variation of Fe, Pb, and Zn in copper prills extracted from slags (after Hauptmann *et al.* [11]).

the use of native copper (*e.g.* [27]). The most straightforward method of identification is the investigation of the metallographic structure in a polished section. However this works only if the object has not been cast but formed simply by hammering, and possibly tempering, of native copper. But by such a technique only small objects can be manufactured and this, in turn, makes it usually difficult to get a sample for such a metallographic study because it is, by necessity, destructive to some extent. Since it is more likely to find native copper in very early periods, the situation is aggravated, because these early artefacts are usually very rare and small, *e.g.* beads or small tools, and permission to take a large sample is extremely difficult to obtain. More often it is possible to take a small sample, by drilling or rubbing, that can only be analyzed chemically. It would, therefore, be desirable to identify native copper also by its chemical composition but this has often been disputed. Native copper is usually very pure but it has been maintained that copper smelted from a pure malachite or even chalcopyrite ore could be as free from impurities as native copper [28].

The suggestion that native and smelted copper may be distinguished by the purity of native copper goes back to the last century already when it was proposed that the high purity of Neolithic and Chalcolithic copper artifacts from southeastern Europe should be evidence, if not proof, that they were manufactured from native copper [3]. Coghlan [29] cast some doubts on the use of the chemical composition for the identification of native copper but conceded that it might provide at least an indication. This possibility was also

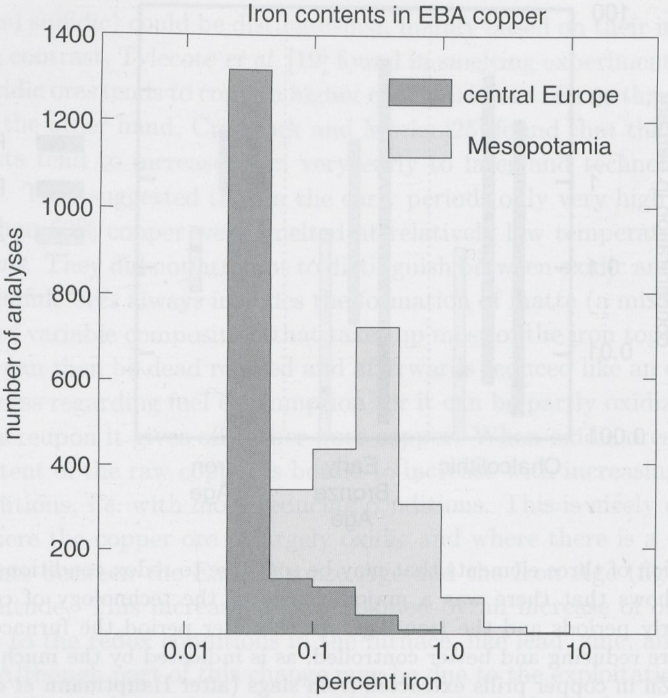


Fig. 10. – Iron contents in Early Bronze Age copper-based artefacts from eastern Germany and from Mesoptamia. Analyses were performed with energy-dispersive X-ray fluorescence on drill shavings.

investigated by Otto and Witter [9] who substantiated the purity of the metal through analyses by optical emission spectroscopy. Junghans *et al.* [6], 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 and Witter that this was most probably native copper, and so did Charles [30], also on the basis of the chemical purity of two Chalcolithic axe-adzes from Hungary and former Yugoslavia.

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.* [14] after it had been found that many samples of native copper contain a few ppm mercury. Contrary to common expectations, mercury is not easily volatilized from copper, even at temperatures of several hundred °C (fig. 11). Thus it could easily survive tempering of native copper that seems to have been applied from the very earliest periods on [31, 32]. 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

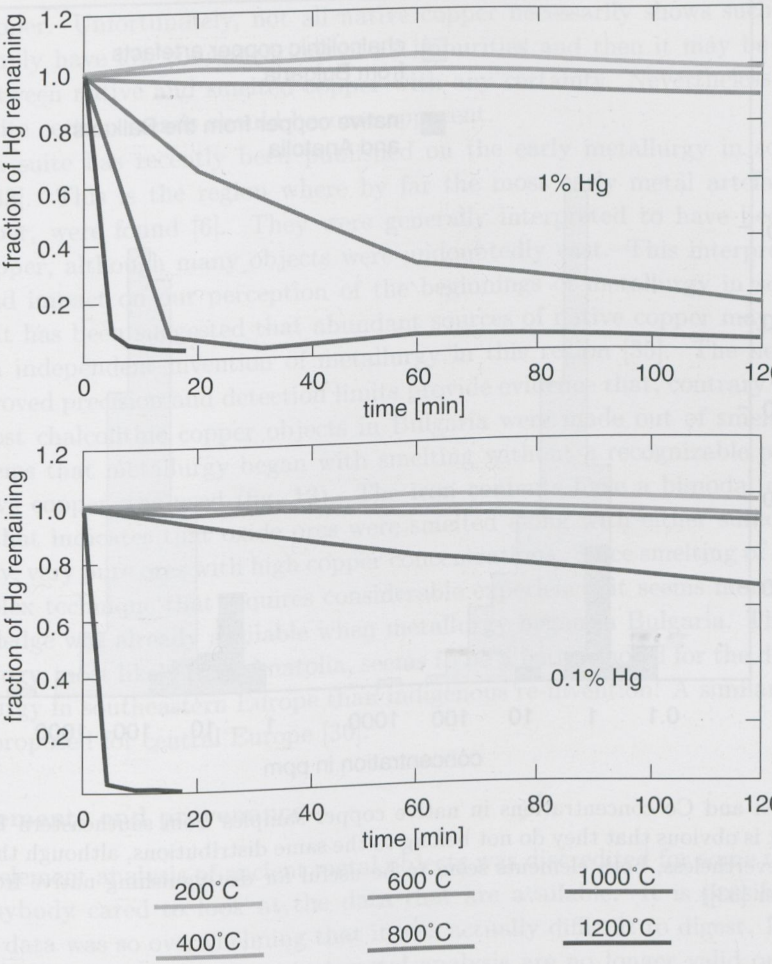


Fig. 11. – Results of desorption experiments of mercury from copper. Copper with 1% and with 0.1% mercury was prepared and heated in air over the time shown. Especially at lower concentrations, that are still high compared with those found in samples of native copper, mercury is only quantitatively removed above the melting point of copper.

from ground water during burial so that, again, the identification is not unequivocal. This seems to have occurred with three Chalcolithic samples from Bulgaria [33].

Returning to the trace element pattern, it is still true that native copper is usually a high-purity metal, with Ag (and occasionally As) as major impurities. Unfortunately, it is also still true that very pure ores can and 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 [11]. These authors demonstrate that silver, gold, and antimony in smelted copper can for all practical purposes be as low as they are typ-

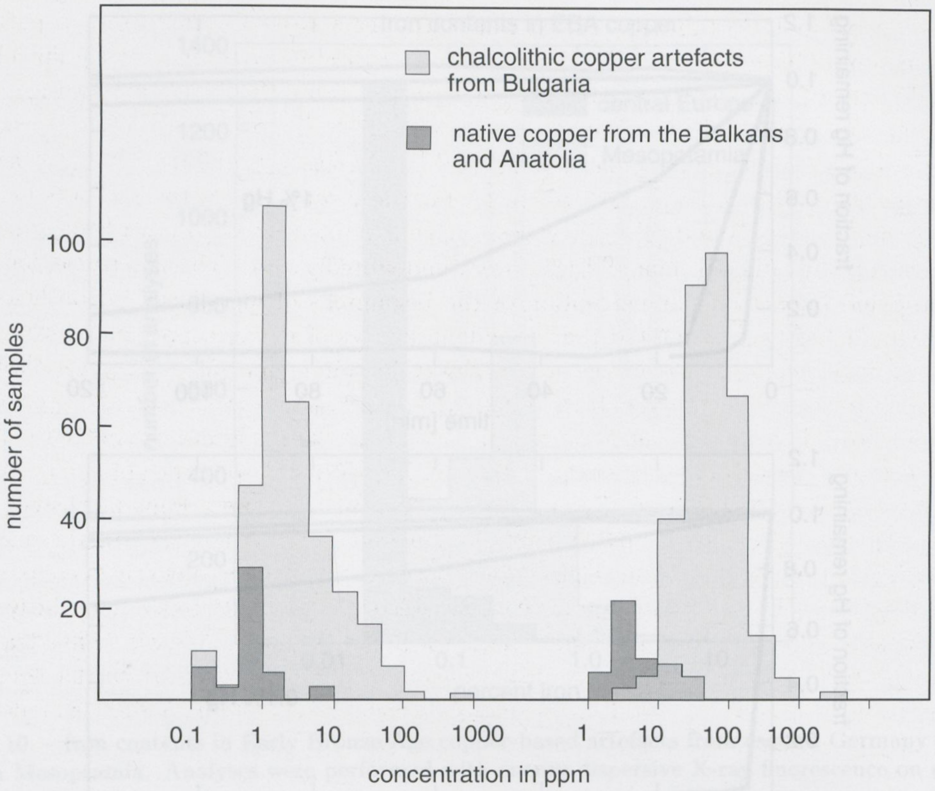


Fig. 12. – Ni and Co concentrations in native copper samples from southeastern Europe and Anatolia. It is obvious that they do not belong to the same distributions, although there is some overlap. Nevertheless, both elements seem to be useful for distinguishing native from smelted copper (after [33]).

ically 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 (fig. 12). By far most native copper is formed on the lower part of the oxidation zone of a primary ore deposit by dissolution and redeposition. Geochemical considerations indicate that some elements are more mobile than others under these circumstances, which 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 it is immobile in the oxidation zone due to the formation of antimonates [34]. Similarly, cobalt is always low because, contrary to nickel, it can be precipitated as carbonate. For the same reason gold should be low, while silver concentrations can reach the percent level. Thus a pattern of low Co, Sb, and Au contents combined with high Ag and/or As contents can certainly be regarded as indicative of native copper. Unfortunately, not all native copper necessarily shows such a pattern. It can simply have low concentrations of all impurities and then it may be difficult to decide between native and smelted copper with any certainty. Nevertheless, in a large sample suite certain trends should become apparent.

Such a suite has recently been published on the early metallurgy in southeastern Europe [33]. This is the region where by far the most early metal artefacts of very pure copper, were found [6]. They were generally interpreted to have been made of native copper, although many objects were undoubtedly cast. This interpretation 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 [35]. The 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 with smelting without a recognizable phase where only native copper was used (fig. 13). The iron contents have a bimodal distribution (fig. 14) that indicates that oxide ores were smelted along with either sulfidic 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 the 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 indigenous re-invention. A similar model has recently proposed for central Europe [36].

Trace elements and provenance

Trace element analysis of ancient metal objects was discredited for some time so that hardly anybody cared to look at the data that are available. 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 have been wrong from the beginning. It has been shown that the largest data base published by the Stuttgart group [5-7] is quite accurate but the precision is only moderate compared with modern analytical techniques [37]. The selection of the elements used for grouping appears to be sensible from what has been said above. 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 were left that could be determined in most samples, namely As, Sb, Ag, Ni, and Bi. It happens that all of them are indicative of the ore source, at least to a certain extent. Analysis of variance shows that groups of artefacts can be found with narrow quasi-normal distributions of all elements, which suggest that all of them were produced in the same ore by applying similar processes. This is now increasingly being acknowledged by archaeologists (*e.g.*, [38,39]) and the metal composition is regarded as a valuable tool for the grouping of artefacts.

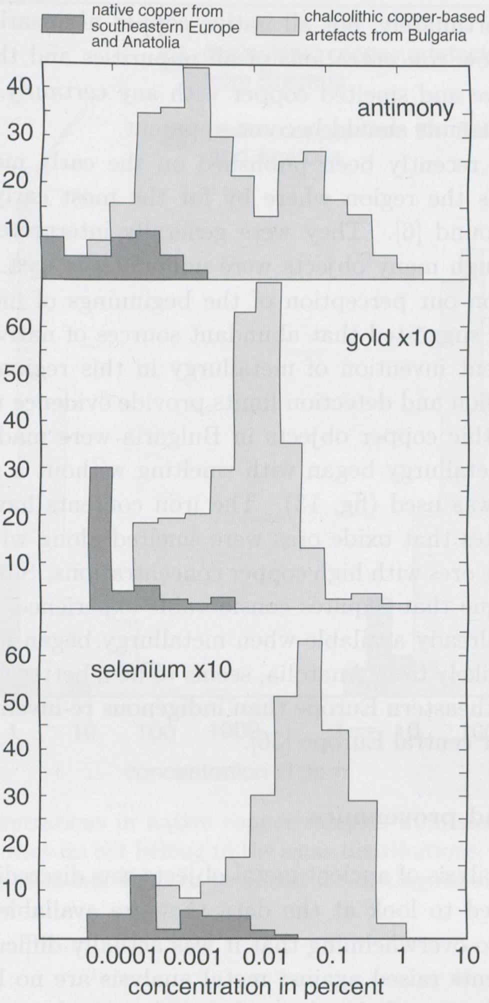


Fig. 13. – There is a clear difference in the distribution of S, Au, and Se in native copper and chalcolithic copper objects from Bulgaria, suggesting that native copper did not play a major role in the early metallurgy of southeastern Europe.

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

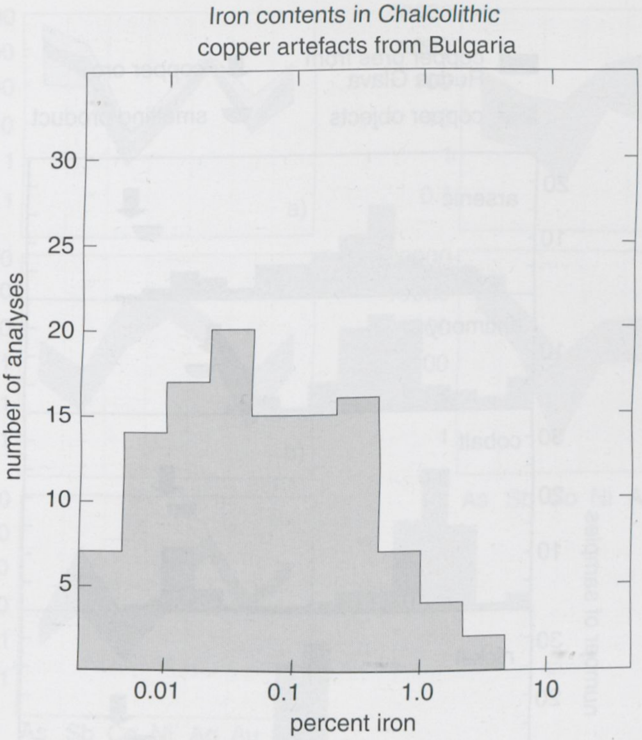
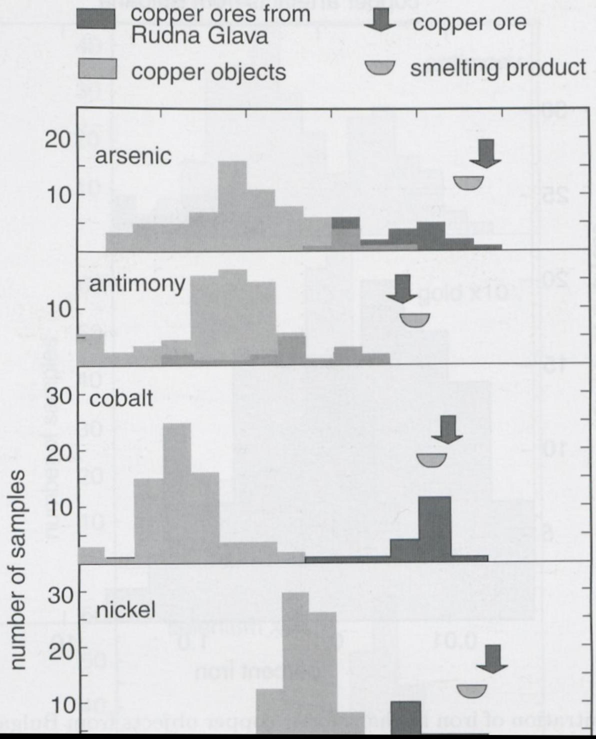


Fig. 14. – The concentration of iron in chalcolithic copper objects from Bulgaria shows a bimodal distribution.

A model case 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 Pločnik [40-42] appeared at roughly the same time in which Rudna Glava was exploited [43]. In a study that aimed to determine the role of Rudna Glava for the early metallurgy in southeastern Europe some 90 chalcolithic copper artefacts were analyzed chemically and isotopically [14]. The result was surprising, because for all of the analyzed objects Rudna Glava could be definitely ruled out as the source. This firm statement was based on the combined information from trace element and lead isotope composition but even the trace element data set alone would have allowed this conclusion (fig. 15). As another result, it was discovered that the heavy implements from the Pločnik 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 that could not be identified at that stage (fig. 16).

An extension of the study into present-day Bulgaria [30] revealed that more chalcolithic copper objects with similar compositions occurred there and, moreover and most importantly, that one group chemically and isotopically resembled ores from another


copper ores from Rudna Glava
copper objects
copper ore
smelting product
arsenic
20
10
antimony
10
cobalt
30
20
10
nickel
30
20
10
number of samples

[redacted]

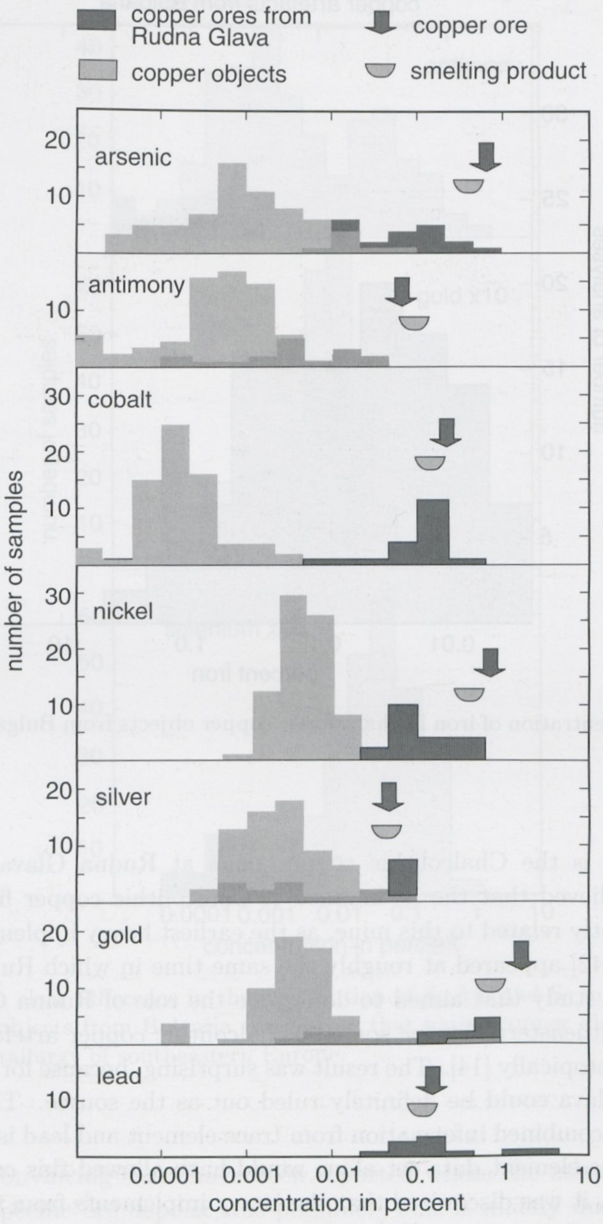


Fig. 15. – Concentration ranges of elements in chalcolithic copper artefacts from Serbia and in copper ores from Rudna Glava. Ore analyses have been recalculated in the same manner as in fig. 2. Arrows indicate the concentrations in a prehistoric ore concentrate from Rudna Glava [44] and bowls indicate copper smelted from the same ore (after [13]).

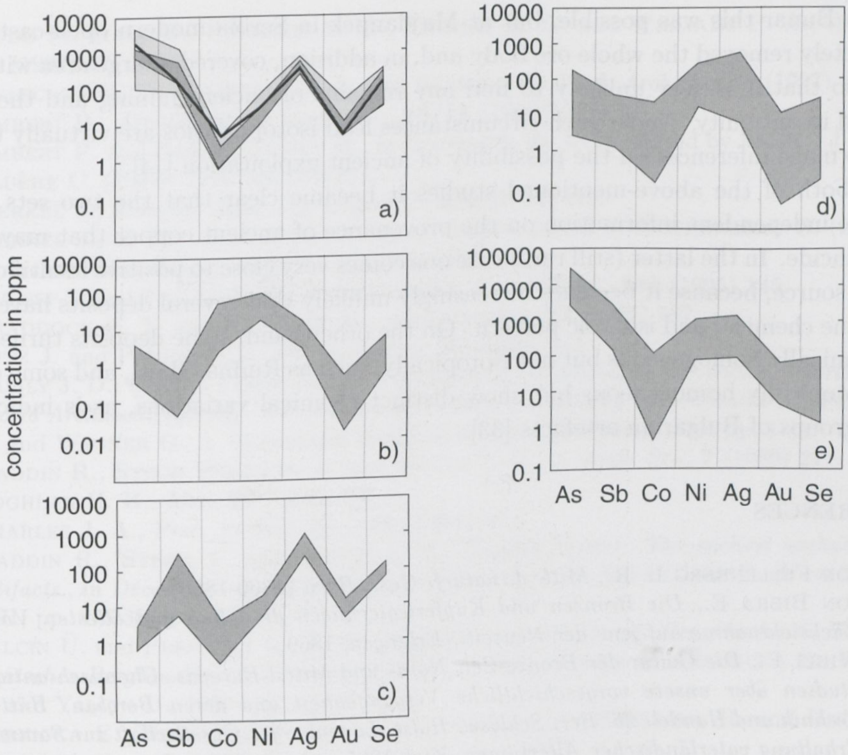


Fig. 16. – Trace element patterns of three different chemical groups found among heavy implements from the Pločnik hoard (a)-c)), in other chalcolithic copper artefacts, and in final chalcolithic copper-based objcts from Serbia. Also included in panel a) is a group of chalcolithic copper artefacts from Bulgaria that are chemically indistinguishable from those from Pločnik (light-shaded area) and one ore sample from the chalcolithic mine at Ai Bunar near Stara Zagora, Bulgaria (thick 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 [30].

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 (fig. 16a). It has to be admitted, however, that only one out of nine ore samples provided such a close match, but it is by far the most relevant one with 53% copper, while the other samples contained only between 3 and 22% copper, possibly representing rejected ore rather than the one smelted. This is also the major difficulty connected with the chemical characterization of ore deposits. It would be desirable to analyze more samples than is considered necessary for lead isotope analysis. Yet it is often difficult to find enough ore that is left over by the miners and that is also representative of the material available in prehistoric times. Fortunately, at Rudna Glava and Ai Bunar this was possible, but at Majdanpek in Serbia modern open-cast mining completely removed the whole ore body and, in addition, covered a large area with waste rock, so that it is very unlikely to find any remains of ancient mining and the ore recovered in antiquity. Under such circumstances lead isotope ratios are virtually the only tool to make inferences on the possibility of ancient exploitation [14].

In both of the above-mentioned studies it became clear that the two sets of data provide independent information on the provenance of ancient copper that may or may not coincide. In the latter (still rare) case one comes very close to positive identification of an ore source, because it becomes increasingly unlikely that several deposits have exactly the same chemical and isotopic pattern. On the other hand, some deposits turned out to be chemically homogeneous but not isotopically, such as Rudna Glava, and some deposits are isotopically homogeneous but show distinct chemical variations, as is indicated by some groups of Bulgarian artefacts [33].

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