Provenance determination of archaeological metal objects

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ABSTRACT

The paper outlines a brief history of the researches in archaeometallurgy, from the origins to today's issues. At European level, the interest for the chemical composition of the metal artefacts and for the determination of the provenance of the raw metals has triggered research in many areas. The paper emphasises the main themes of the present scientific debate about the possibilities and limitations of archaeometallurgic analyses and about different methodologies.

Keywords: History of the research, methodologies of the analysis, chemical analysis, trace elements, lead isotope ratios.

RIASSUNTO

Il contributo traccia una breve storia delle ricerche in campo archeometallurgico, dalle origini alle problematiche attuali. A livello europeo l'interesse per la composizione chimica dei manufatti in metallo e per la determinazione della provenienza dei minerali ha innescato la ricerca in molti settori. Vengono evidenziati i principali temi del dibattito scientifico in corso sulle possibilità e le limitazioni delle analisi archeometallurgiche e sulle diverse metodologie utilizzate.

Parole chiave: Storia delle ricerche, metodologie di analisi, analisi chimiche, elementi in traccia, analisi isotopiche.

A short history of provenance analysis of archaeological metal objects

Archaeometallurgy is an established of the widespread interdisciplinary field of science-based archaeology and is itself multifaceted (for a recent review see Rehren and Pernicka, 2008). This article will mainly deal with the question of the possibility to determine the provenance of ancient metals, a subject that undoubtedly is of major importance in archaeology even though it has often been disputed.

The application of scientific methods to the analysis of metals goes back to the very beginnings of analytical chemistry in the modern sense as the first quantitative analysis of any metal alloy was performed and published by Martin Heinrich Klaproth in the late 18th century. The alloy that he analyzed was a Roman coin. In this study it was mainly the question of material composition that was addressed. But soon the further reaching aim of provenance determination was formulated, e.g. by F. Göbel (1842) who published an article with the programmatic title "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" (my own translation). He suggested from the geographical distribution of about 120 analysed objects that they would represent 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. Not much later it was proposed that minor elements were more useful in determining the nature of the ore from which the metal came and perhaps even its geographical origin (von Fellenberg, 1860-67; von Bibra, 1869). Furthermore it was found that compositional differences between copper metal were to be expected when native copper, oxide or sulphide ores were used for smelting (Wibel, 1863), an idea repeated almost exactly hundred years later by Friedman *et al.* (1966). However, the analytical methods available then did not allow further progress because of large sample requirements and small sample throughput.

Although most scholars agreed that the trace elements were most indicative of the ore sources, the limited analytical means of that time did not allow them to make use of this knowledge. Accordingly, there was little further progress until the late 1920s, when instrumental analytical techniques became available. They were almost immediately applied to the concept of provenance studies of ancient metals. As an example, the Sumerian Metals Committee was appointed by the Royal Anthropological Institute, triggered by the exceptional finds at the Royal Cemetery at Ur in Mesopotamia (Woolley, 1931). It reported on the origin of Sumerian copper, assuming that its nickel content could be indicative of the ore source (Desch, 1928–38). From these interim reports it

is obvious that the original objective was not really achieved, but they resulted in the creation of a further unit, the Ancient Metal Objects Committee, in 1939.

Halle

With atomic emission spectrometry for chemical analysis it became possible to determine many trace elements in reasonably small samples of a few milligrams with sufficient sensitivity (in the range of 0.001 to 0.01%) in a short time. All these features were lacking until then. This opened the door to systematic studies of ancient metals, beginning already 1931 by W. Witter, a prehistoric archaeologist with a background as a mining engineer. He was later joined by H. Otto and the team began to systematically analyze all available metal objects in Germany from the Neolithic to the Early Bronze Age (Otto and Witter, 1952). They were motivated by two questions, namely the possibility of Bronze Age copper mining in Germany and the possibility to relate archaeological objects to specific ore deposits. They developed a method with which they analyzed 10 elements (Fe, Co, Ni, Cu, As, Sn, Ag, Sb, Pb, Bi, and S) some 1300 objects within a few years, much more than had been accomplished over the preceding 100 years. Samples of about 100 mg were taken from the interior of the objects by drilling and then molten and formed into two electrodes. By applying high voltage between the two electrodes an electric spark was triggered that excited light from the elements in the sample in the visible wavelength range which could be quantified. They then classified the objects only according to their compositions into six groups that were based on the general knowledge of copper ore mineralogy (very pure copper (i), unalloyed copper with minor impurities (ii), arsenical copper (iii), fahlore metal with high concentrations of arsenic, antimony, and silver (iv), copper with nickel and arsenic as major impurities (v) and copper-tin alloys (vi)). This is the concept of "Leitlegierungen" (major alloy types) that is generally valid until today with the exception of the last group. While very pure copper is typical of the fifth and early fourth millennia BC in southeastern and central Europe, arsenical copper dominates in the fourth and early third millennium. At the beginning of the Early Bronze Age fahlore metal is most abundant in central Europe which is later replaced by copper with arsenic and nickel as major impurities. As will be shown below some of these copper types can indeed be related to certain mineralized regions although it is usually difficult to pinpoint a certain mine.

A major deficiency of this study was the lack of an equal number of analyses of copper ores from deposits that were considered as likely sources for the analyzed artefacts, although in their publication (Otto and Witter, 1952) they explicitly emphasized the necessity to analyze also ores and slag form ancient smelting sites. Instead, only a few data from the geological literature were used for comparison. Furthermore, the ore deposits were implicitly considered to be homogenous and to be differentiated in their compositions.

For the comparison of artefact and ore analyses they used all measured elements, including tin that is obviously an alloying element as tin and copper ores rarely occur together. With this approach they concluded that 97% of all prehistoric metal objects found in Germany were produced from copper ores in Saxony. Although this conclusion cannot be held up today and most likely was influenced by nationalistic preoccupations it is nevertheless to be considered a pioneering study, both from the methodological view and the large scope. It was the first large-scale attempt to determine the provenance of prehistoric metals with an appropriate analytical method, based on a large number of analyses and a classification method that was governed by substantial knowledge in economic geology. The importance of field work was also clearly expressed as well as the idea that chemical analyses could provide evidence for ancient exploitation of mines that do not have any visible remains of ancient mining any more due to modern activities.

Vienna

Parallel with the investigations in Halle another group in Vienna, with Richard Pittioni and Ernst Preuschen as key figures, worked along similar lines. They specifically set out to determine "from which production area a specific object would derive" (Preuschen and Pittioni, 1939). Their emphasis was on field work and mining archaeology, both having been educated as mining engineers. Accordingly, they not only had a more realistic view of the problems of characterising ore deposits geochemically but they actually performed a large number of analyses of ore samples, mainly from prehistoric mining districts in Austria. More than 2000 ore analyses formed their data base on which they attempted to establish a clear relationship between "ore deposits and finished object". More than in Halle the Vienna group was aware of the fact that trace element concentrations in ore deposits can be quite variable and that the concentrations are further altered during the production of copper metal. From this knowledge they decided that the sensitivity of the analytical method should be more important than its reproducibility, because only the presence or absence of a certain element would be indicative and the trace element pattern as a whole. While this is generally true it was an unfortunate decision nevertheless, because they did not attempt to actually quantify the spectra but estimated the concentrations by visual inspection of the spectral lines on a film detector. This resulted in semiquantitative analyses without numerical values for the concentrations so that they are hardly usable today. They also used the objects and ores directly as electrodes to avoid any alteration of the chemical composition during sample preparation. This, however, meant that only the surfaces of the objects were analyzed which are often not representative of the whole and original composition.

The Vienna group also classified more than 6000 analyses of artefacts of the central European Bronze Age into five groups that they assigned to different ore deposits in the eastern Alps and in Slovakia. There was much dispute between the

two groups about the correct methodological approach, which continued when the methodology that was developed in Halle was continued in an even larger project in Stuttgart. However, the Vienna group has to be credited to insight that provenance analysis of metal artefacts has be be accompanied by field work in ancient mining districts and, indeed, the results of their mining archaeological research have long remained without parallel.

Stuttgart

Considering the problems of relating metal artefacts to specific ore deposits a new group around Siegfried Junghans and Edward Sangmeister in Stuttgart and Freiburg decided, not to search for the origin of the raw metals but simply to use chemical analyses of metal objects as an independent criterion for classification in addition to the conventional typological classification. It was assumed that prehistoric metal workers would receive their raw metal primarily from the same source(s), similar to potters, and that they also applied similar processes to produce copper. If this assumption holds then one would try to identify workshops rather than to identify the mines where the ore would have come from. By preparing distribution maps of copper types that were identified based on their chemical composition it was hoped that one would obtain insight into the beginnings and the distribution of metallurgy in Europe. For this purpose more than 22000 objects from all over Europe (Junghans et al., 1960, 1968, 1974) were sampled and analyzed practically with the same method as it was developed in Halle and for the same elements, except that less sample mass was used (40 mg) and the sample was molten into a small globule in order to have comparable geometries for all samples. For the excitation they used an electric arc that provides a more stable light output from the sample (Junghans et al., 1954).

Following the original concept to identify workshops the analytical results were grouped according to their chemical similarity first into 12 (Junghans et al., 1960) and later into 29 groups (Fig 1).

The method of grouping used statistical methods of analysis of variance (Junghans et al., 1954) based on histograms of the concentrations of the elements. It was found that five elements contributed most of the variance of the data, namely Ag, Ni, As, Sb, and Bi. In the histograms of these elements several peaks were observed. The minima between such peaks were defined as limits between different groups. This is certainly a reasonable procedure but for many archaeologists it lacked the clearness of the groups defined in Halle and Vienna by their "Leitlegierungen" based on general knowledge of ore deposits. The Stuttgart team then went on to study the distribution of these metal groups in time and space and inferred from these patterns production centers and socio-economic relationships in the early metal-using periods of Europe.

Similar programs were established in other European countries, e.g in Sweden (Oldeberg, 1942), France by J.-R- Maréchal (1963) and Briard and Giot (1956), in Britain by Coghlan and

Case (1957) in London and Blin-Stoyle (1959) and Britton (1961) in Oxford. However, the by far largest programs of systematic analyses were established in the former Soviet Union by Selimchanov (1960) in Baku Černych (1966) in Moscow which resulted in well over 50000 analyses of ancient metal objects mainly from Eurasia.

With so many data at hand one may well ask what this exercise has yielded and what additional information could be gained by those analyses. This is not the place to evaluate the achievements and possible failures of all these studies. It may suffice to remark that we have a profound knowledge of the alloy compositions used in prehistoric times in Europe and in northern Asia. It has been established beyond doubt

Fig. 1: The classification scheme developed and used by the Stuttgart team to find chemically similar prehistoric copper objects
Fig. 1: *Schema classificatorio sviluppato ed usato dal gruppo di Stoccarda per identificare manufatti preistorici chimicamente simili*

that metallurgy began with the use of native copper and that extractive metallurgy does not appear to have been significant before the fifth millennium BCE. Even then copper remained rather pure, probably deriving from very rich ores. In the fourth millennium arsenical copper dominates over a large area and it has been suggested that this may be due to common

metallurgical practices that would imply rapid technological exchange over wide distances (Chernykh, 1992). It has also become clear that all over Europe the compositions of metal objects changed significantly with the beginning of the Bronze Age, not only concerning the major composition but also the minor elements. This means that either very little of the chalcolithic metal survived and was re-used in the Early Bronze Age or that the amount of metal in the system increased substantially so that any re-use would be insignificant. It has also been established that certain metal groups are not equally distributed but are rather concentrated in restricted areas and periods that suggests the occurrence of one or several ore sources within those areas.

Nevertheless, the results of these large analytical programs were received with scepticism among non-specialists and a general opinion gained ground that metal analyses would not be able to make any significant contribution to the question of the provenance of metals (Hall, 1970; Coles, 1982). Major points of criticism of the Stuttgart project were i) the representativity and accuracy of the analyses, ii) the methods of classification, iii) possible changes during metal production and thus the difficulty to actually relate a metal object to a specific ore deposit, and – last not least – the chronological framework used for the evaluation of the analyses.

The first point is certainly justified. There was no interlaboratory comparison and there was no internationally recognized reference material available with which each laboratory could compare its own results. This is standard laboratory practice today but was not applied in the early days of spectral analysis. Indeed, two programs (Chase, 1974; Northover, 1996) to compare the analyses of different laboratories indicated that there were many problems and that some seriously deviating results were produced and published. At least for the two largest series of metal analyses in Stuttgart and Moscow the accuracy of the data could be confirmed although the precision of the spectroscopic method applied was rather low (Pernicka, 1984; Pernicka et al., 1997).

On the other hand, the assertion that small samples of copper alloys would not be representative (e.g. Slater and Charles, 1970) can now be rejected. The sample mass of 40 mg is more than sufficient for a representative analyses (Pernicka, 1984), if it is taken from the interior, usually by drilling with a steel drill. However, this does not prevent that some analyses may still be wrong (e.g. Barker and Slater, 1971) as was demonstrated by Pernicka (1997). Furthermore, with the new mobile X-ray fluorescence spectrometers there is a definite danger that untrained personnel will propagate the possibility that non-destructive analysis is possible and that again series of uncomparable and thus unusable analyses will make it into the literature.

The classification procedure of the Stuttgart team has mainly been criticized by Dutch archaeologists (Butler and van der Waals, 1964; Waterbolk and Butler, 1965) but it soon became clear that they were simply overstrained with the large data set. They suggest a graphical method of grouping of smaller subsets of the data which uses essentially the same reasoning as the Stuttgart team and, not surprisingly, comes to similar results (Härke, 1978). Later cluster analysis was introduced

to deal with the same problem (Hodson, 1969) and, again, the Stuttgart groups were largely confirmed when some 25000 analyses were treated (Pernicka, 1990).

Changes in chemical composition during metal production were actually of no concern as long as work shops were sought and not the geological origin of the copper. Some confusion and reluctance to accept conclusion of the Stuttgart team may well be due to the chronological system used for the archaeological interpretation that adhered to "conventional" dates especially of the southeast European Copper Age. However, it has to be considered that the "Radiocarbon Revolution" (Renfrew, 1973) had not yet occurred in European prehistory. In summary, the very large analytical programs seem to have been ahead of their time in that neither a consistent chronological framework was available for all of Europe nor the computer technology that we have today to deal with such large data sets nor the analytical stringency that nowadays is standard practice in professional laboratories. The high hopes that were originally connected with the analysis of metal objects to determine their provenance were seemingly disappointed.

The revival of metal provenance through isotope analyses

Some fifty years ago new methods seemed to open a way out of this somewhat depressing situation. The first was the introduction of lead isotope analysis, application beginning with lead (Brill and Wampler, 1965; Grögler et al., 1966) and silver (Gale et al., 1978) and later extended to copper and copper-based alloys (Gale and Stos-Gale, 1982; Pernicka et al., 1984). The second was the application of new analytical techniques that were more sensitive and more precise than the previously prevailing optical emission spectrometry. Most elements consist of different isotopes, i.e. atoms with very similar chemical characteristics but varying in weight. Compounds of elements of low atomic number can thus differ significantly in their molecular weight.

For example, H_2O exists in the form of nine different isotopic varieties ranging from 16 to 22 amu (atomic mass units). The differences in the molecular weights affect the way these molecules respond to certain kinds of physical processes that are mass dependent. This leads to slightly varying isotopic compositions of different reservoirs. For example, seawater and rainwater differ in their isotopic composition as well as rainwater collected at different geographical latitudes. The study of these subtle effects that are referred to as isotope fractionation has become very important not only for the Earth Sciences but also for provenance studies of materials that contain elements of low atomic number such as marble or for the study of prehistoric diet. The application of this method requires that the raw material of the artefact has not undergone any change of chemical or physical state, because such processes could induce additional isotope fractionations that could delete the original differences of the geological sources. Thus they are generally of little value for the study of metal artefacts.

Elements of high atomic number, on the other hand, generally

show no measurable isotope fractionation in the natural environment. However, some elements such as lead consist partly of isotopes that are products of radioactive decay. For example, uranium and thorium decay with half-lives of several billion years eventually into the lead isotopes ^{206}Pb, ^{207}Pb, and ^{208}Pb. Lead consists of these three isotopes and a fourth, ^{204}Pb, that is not produced by radioactive decay. It is evident that the lead isotope composition of the Earth will change through geologic time scales and it is also evident that lead deposits in the Earth's crust can also vary in their isotope composition, depending on their geological age and the U/Pb and Th/Pb ratios of the geological reservoir that supplied the lead. By the formation of a lead deposit these elemental ratios are changed by many orders of magnitude so that any further contribution by the decay of uranium and thorium becomes insignificant and the lead isotope composition becomes fixed. It is then extremely unlikely that the lead isotope ratios are altered by any of the physical and chemical processes that occur on the way from the ore to the finished artefact save for mixing of lead of different origin. By and large the same arguments apply to lead in copper deposits and thus lead isotope analysis can also be applied to copper-based metal objects (Fig. 2).

The advantage of looking at the isotopic composition of an element rather than at abundances, or the abundance pattern, of minor and trace elements is that the isotopic composition of an element does not change on the way from ore to artefact. Regardless of the processes involved in the treatment of ores or metal, whether it is roasting or smelting, cupellation or melting, alloying, dissolution or corrosion - the isotopic composition remains constant. This has two important consequences. Firstly, neither the exact pathway from ore to artefact nor the metallurgical processes employed need to be known. Both affect the behavior of trace elements and they govern how the elemental abundance pattern in ores is related to that in the metal derived therefrom, but they have no bearing on the isotopic composition.

Secondly, the isotopic composition is not dependent on how lead is distributed between different phases. Different segregated phases in artefacts may have grossly different lead contents but the lead will have the same isotopic composition, just as there are no differences in the isotope abundances between the lead in slags and that in the complementary metal. Thus, sample heterogeneity which is notorious for making many chemical analyses difficult to interpret at best, is of no relevance for the isotopic composition. Of course, a prerequisite for even an attempt to utilize the potential of such isotope abundance measurements for provenance studies is that the isotopic composition of lead from different parts of the world must vary. This is indeed the case and the variations found in nature are many times larger than the analytical precision with which the composition can be determined.

Once there are a sufficient number of isotope measurements of an ore deposit available, it can be considered to be isotopically characterized. The question, how many measurements are required, cannot be answered in a general way. Some deposits show a small variation in their lead isotope ratios and those are the ones that can best be used for provenance discussions. It is often found that lead deposits show this behaviour. In such cases 5 to 10 analyses may be sufficient for their characterization. On the other hand, there are even lead deposits with large variations (e.g. the so-called Mississippi Valley Type deposits or MVT deposits) and then even 50 analyses may not be sufficient. It is now increasingly recognized that also many copper deposits with low lead concentrations exhibit large variations in their lead isotope ratios. In such deposits the assumption described above that the lead isotope ratios do not change after their formation does not apply, because the U/Pb and Th/Pb ratios may not be reduced to insignificant values. Accordingly, radiogenic lead will alter the lead isotope ratios even after the formation of the deposit. Since uranium and thorium are bound to be inhomogeneously distributed in minerals on a small (mm to cm) scale, a large range of lead isotope ratios can develop in the time since the formation of the deposit. This was first recognized in the chalcolithic copper mine at Rudna Glava in Serbia (Pernicka et al., 1993) and later in many other copper deposits like Feinan in Jordan, the Erzgebirge in Saxony and in the graywacke zone of the eastern Alps.

Nevertheless, lead isotope ratios of artefacts can be compared with those of an ore deposit. If they are different then it can safely be concluded that the artefacts do not derive from that
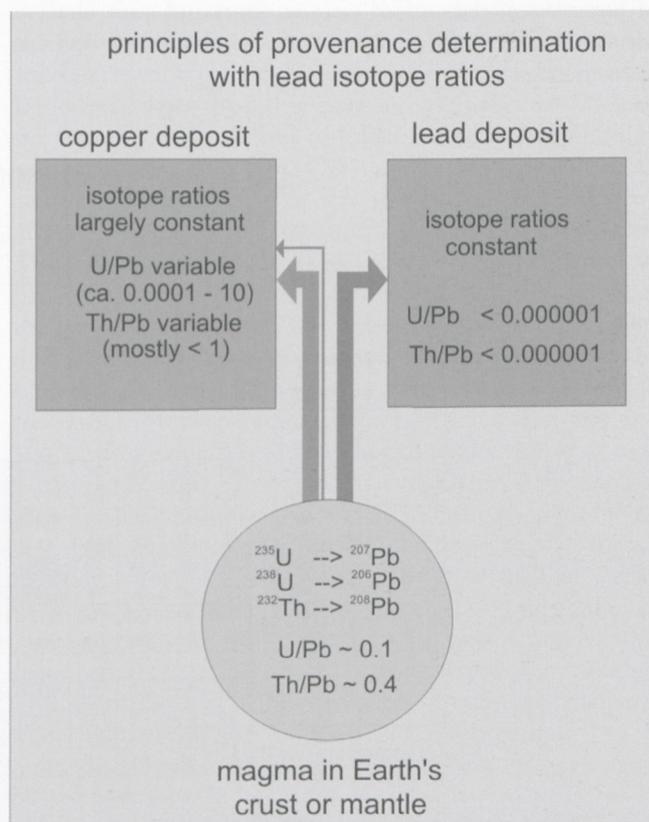

principles of provenance determination with lead isotope ratios

copper deposit

isotope ratios largely constant

U/Pb variable (ca. 0.0001 - 10) Th/Pb variable (mostly < 1)

lead deposit

isotope ratios constant

U/Pb < 0.000001

Th/Pb < 0.000001

^{235}U --> ^{207}Pb
^{238}U --> ^{206}Pb
^{232}Th --> ^{208}Pb

U/Pb ~ 0.1
Th/Pb ~ 0.4

magma in Earth's crust or mantle

Fig. 2: Basic principles of provenance determination of ancient metal objects with lead isotope ratios

Fig. 2: *Principi di base per la determinazione della provenienza degli antichi manufatti in metallo attraverso i rapporti isotopici del piombo.*

specific ore source. Conversely, it is not possible to regard a relationship as proven, if they do agree. The reason is that although the variation of lead isotope ratios in ore deposits is much smaller than that of trace element concentrations there exists nevertheless the possibility that another deposit has the same lead isotope ratios and this is indeed increasingly being recognized as more deposits become characterized.

In the early days of lead isotope analysis in archaeology the neglection of this simple logic has sometimes led to affirmative statements concerning the provenance of copper artefacts that did not stand up to later results. Thus, the general pattern of overoptimistic expectations followed by disappointment as with trace element studies seems to have been repeated with isotope analysis. It has even been maintained that only lead isotope ratios will be useful for provenance studies while chemical analyses 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.

The information from trace elements

In the first half of this century geochemists divided the elements into three groups. Siderophile elements that are concentrated in the Earth's iron core, chalcophile elements in the outer core and mantle, and lithophile elements are concentrated in the crust (Fig. 3). 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.

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 product. Three major complications have to be considered at this point: Ores are generally inhomogeneous on all scales. The opinion has often prevailed 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, 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 characterised by a combination of about equal concentrations of nickel and arsenic as major impurities at variable concentrations combined with relatively low contents of antimony, silver and bismuth (Fig. 4). In a study of some 1200 Bronze Age copper artefacts from the adjacent area it was found that about 80% of the copper

Geochemical classification of the elements

Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	1A	2A		3B	4B	5B	6B	7B		8B		1B	2B	3A	4A	5A	6A	7A	8A
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

lanthanides	*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
actinides	**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

◼ siderophile   ◼ chalcophile

Fig. 3: Geochemical classification of the elements.
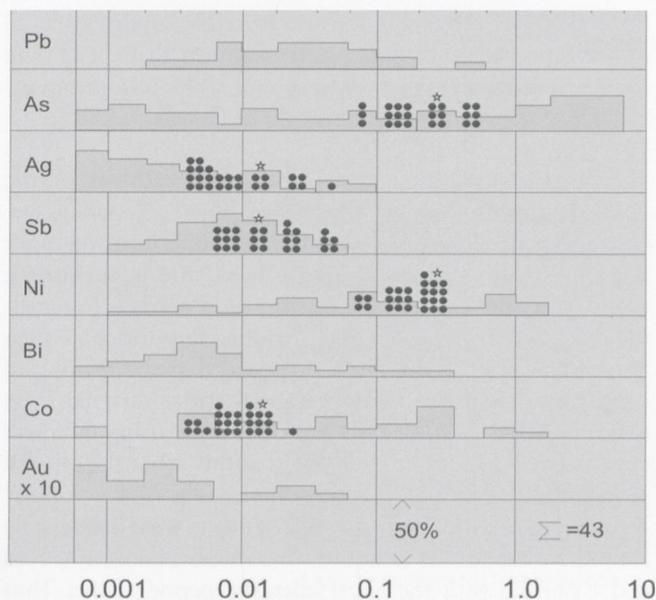*Fig. 3: Classificazione geochimica degli elementi.*

Fig. 4: Variation of trace element concentrations in the Bronze Age copper mine of Mitterberg (Austria). Although arsenic and nickel concentrations vary over several orders of magnitude they are tightly related so that in copper metal there are always roughly equal concentrations of arsenic and nickel. The star indicates the concentrations in the Sky Disc of Nebra and the dots the metal objects that were found with it.

Fig. 4: Variazione della concentrazione degli elementi in traccia nella miniera di rame di Mitterberg - età del Bronzo (Austria). Benché le concentrazioni di arsenico e nikel presentino variazioni su diversi ordini di grandezza, esse sono strettamente correlate così che nel metallo di rame (derivato) ci sono sempre grossomodo le stesse concentrazioni. La stella indica le concentrazioni nel Disco di Nebra e i punti gli oggetti in metallo rinvenuti in associazione al disco.

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.

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 sulphide 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 was 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). This is, however, a very theoretical possibility and requires 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.

It has even been suggested that early smelting can be separated into two discrete steps; the reduction of copper ore to copper metal which requires reducing conditions and temperatures from 700 °C upwards (Budd, 1991), and the melting of the copper metal, which requires temperatures in excess of 1080°C. In this model, the reducing stage is characterised by the necessarily incomplete burning of charcoal which results in limited heat generation and may lead to the reduction of some copper oxide to copper metal. This metal would form in a finely dispersed form within any gangue components such as iron oxides or silicates that come together with the copper mineral. Any copper formed in this hypothetical process would then have to be melted in order to collect it, and for casting into artefact shape. To do this one would have to raise the temperature above 1084°C, the melting point of copper. This hypothetical scenario is rather unrealistic. There are several physical-chemical and practical arguments against it: i) Reduction of copper to metal is much more efficient in the liquid phase due to much higher diffusion rates. ii) The reducing agent is gaseous carbon monoxide in all cases, which is produced when there is an excess of charcoal in contact with the burning charcoal. This so-called Boudouard equilibrium of the reaction $CO_2 + C = 2\ CO$ is on the right side only above ca. 800°C (Fig. 5). Below this temperature the reduction efficiency would be very low so that the postulated solid-state reduction at such a moderate temperature would be very slow. iii) Finally, it would be very difficult for the smelter to keep the temperature relatively low throughout the reaction vessel, due to inevitable temperature gradients from the tip of the blow pipe to areas further away. In effect, it would be difficult to control the temperature in the region between 800 and 900°C, if one would be determined to reduce copper at such a low temperature. Therefore, it is highly unlikely that the early smelters consciously aimed at such a two-step process. It is much more likely that the two discrete aspects of copper smelting – chemical reduction and physical melting – may well have been combined in one process. The suggestion of a purely solid-state and "slagless" copper production remains hypothetical at best, even for the earliest periods of metallurgy. This is corroborated by finds of slag wherever copper appears in the archaeological record, even in the early periods. Sulphide ores are more difficult to smelt, because they cannot be reduced directly but must be oxidised (roasted) before reduction. This is usually accomplished at around 700°C, well below the melting point of copper and most ore minerals. However, it is possible that volatile elements like zinc, arsenic antimony and, presumably, selenium and tellurium, are lost during roasting (Tylecote et al., 1977). In this case
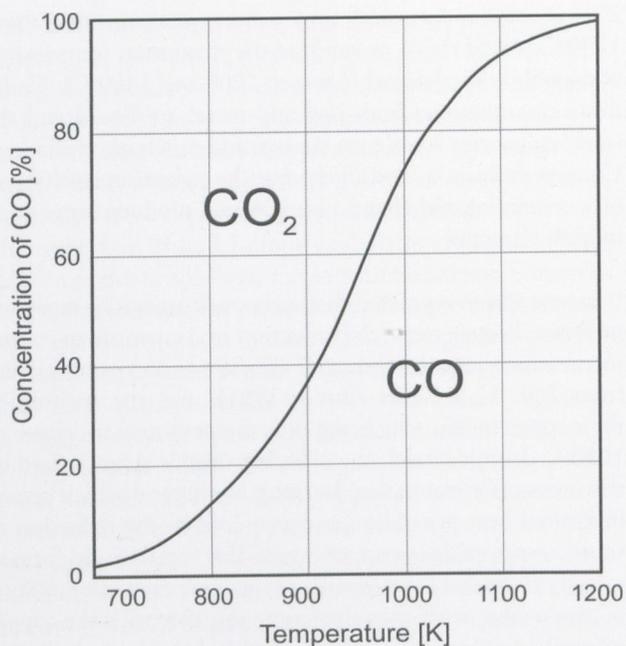
Fig. 5: Curve 1 in the figure shows the equilibrium relationship for the reaction CO2 + C = 2 CO, which is called Boudouard's equilibrium. In the neighborhood of 1,200K, carbon dioxide that has been formed by burning of charcoal is changed into carbon monoxide by this reaction, making it possible to maintain the reducing capability of the gas. It is evident that below 1000K the reducing capability of the gas decreases rapidly.

Fig. 5: La curva 1 nella figura mostra la relazione di equilibrio per la reazione CO2 + C = 2 CO, detta equilibrio di Boudouard. Intorno a circa 1,200K, il diossido di carbone che si è formato per la combustione del carbone si trasforma in monossido di carbone attraverso questa reazione, rendendo possibile il mantenimento della capacità riducente del gas. E' evidente che al di sotto dei 1000K la capacità riducente diminuisce rapidamente.
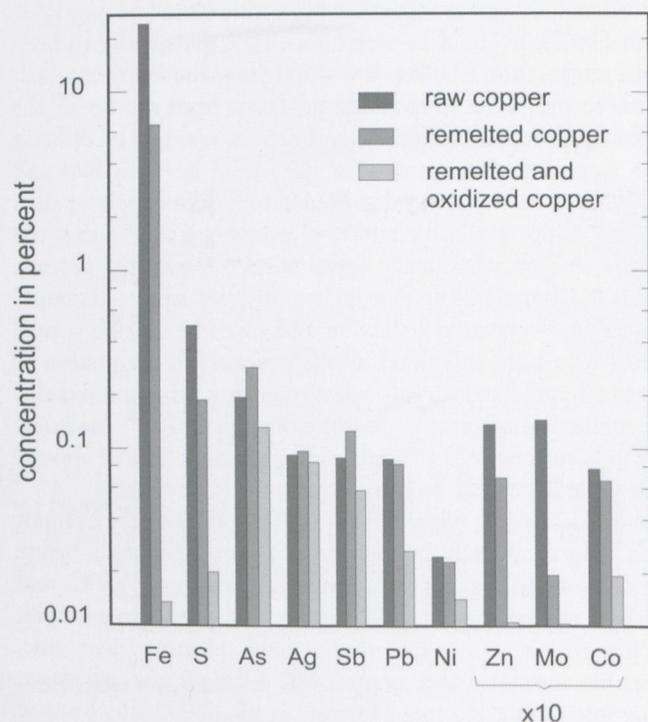
these elements are of limited use to relate copper artefacts to ore deposits, although it has been shown that the fahlore signature, high arsenic, antimony, and silver concentrations are at least partly preserved in the metal (Pernicka, 1999).

The third complication arises from the treatment of the smelted copper to produce the finished object. Nowadays raw copper is generally refined to remove sulphur, 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 oxidised 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 (Fig. 6).

A final consideration is that some elements were deliberately alloyed to copper. In antiquity these were mainly tin, lead and - starting with the late Hellenistic period - zinc. Thus Table 1 contains 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. The provenance of chalcolithic copper in the Balkans (Pernicka et al., 1993, 1997) may serve as an example. Two of the earliest copper mines presently known, Ai Bunar in Bulgaria and Majdanpek in Serbia (only indirectly shown to have been exploited in the fifth millennium BC) have partly overlapping lead isotope signatures (Fig. 7) but can be differentiated by their trace element pattern (Fig. 8).

Fig. 6: 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 oxidised 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).

Fig. 6: Sintesi degli esperimenti di raffinazione effettuati da Merkel (1983; 1990). E' evidente che la concentrazione della maggior parte degli elementi relativi al rame non cambia significativamente con la semplice rifusione, ad eccezione di Fe, S e Mo, tutti irrilevanti per gli studi sulla provenienza. E' improbabile che il metallo fuso fosse regolarmente esposto ad un getto d'aria per un tempo prolungato come indicato nella terza colonna (rame rifuso e ossidato). Ma anche in questo caso solamente Co, Ni e Pb verrebbero ridotti di un fattore 2 [= della metà, no?], che è poco significativo quando i minerali vengono comparati ai manufatti in metallo (da Pernicka 1987).

Copper and copper alloys

Production technology	Provenance and/or production technology	Provenance
Al[a], B, Be, Ba, Ca, Cr, Cs, Fe, Ga, Ge, Hf, K, Li, Mg[a], Mn[a], Mo, Na, Nb, P[a], Pb, Rb, S, Sc, REE[c], Si[a], Sn, Sr, Ta, Ti[a], Th, U, V, W, Y, Zn, Zr	As, Co, In, Pb, Re, Sb, Sn, Se, Te, Zn	Ag, Au, Bi, Ir, Ni Os, Pd, Pt, Rh, Ru Cd[b], Hg[b], Tl[b]
Sn > ca. 1% Pb > ca. 5% Zn > ca. 2%	Sn < ca. 1% Pb < ca. 5% Zn < ca. 2%	routinely analyzed routinely analyzed

[a] only for authenticity investigations
[b] only for native copper
[c] Rare Earth Elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu)

Table 1: Classification of elements reported in analyses of ancient copper-based objects concerning their bearing on provenance and/or smelting technology.

Table 1: Classificazione degli elementi rilevati nelle analisi di antichi oggetti in rame in relazione alla loro rilevanza rispetto alla provenienza e/o alla tecnologia di fusione
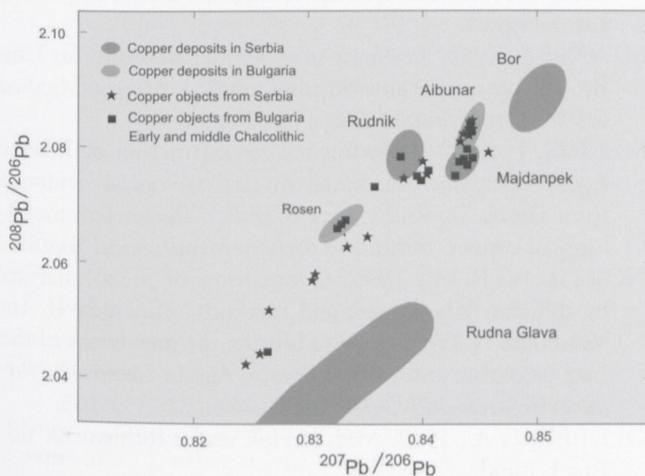
Fig. 7: Lead isotope ratios in various copper deposits in southeast Europe and in chalcolithic copper artefacts (Pernicka et alii, 1993, 1997). This is to show that the major copper sources in this period, namely Ai Bunar in Bulgaria and Majdanpek in Serbia, partly overlap in their lead isotope ratios.

Fig. 7: Rapporti isotopici del Piombo in vari depositi di rame dell'Europa sud-orientale e in manufatti dell'età del Rame (Pernicka et alii, 1993, 1997). Si evidenzia come le maggiori risorse di rame di questo periodo, cioè Ai Bunar in Bulgaria e Majdanpek in Serbia, in parte si sovrappongono nei loro rapporti isotopici del piombo.
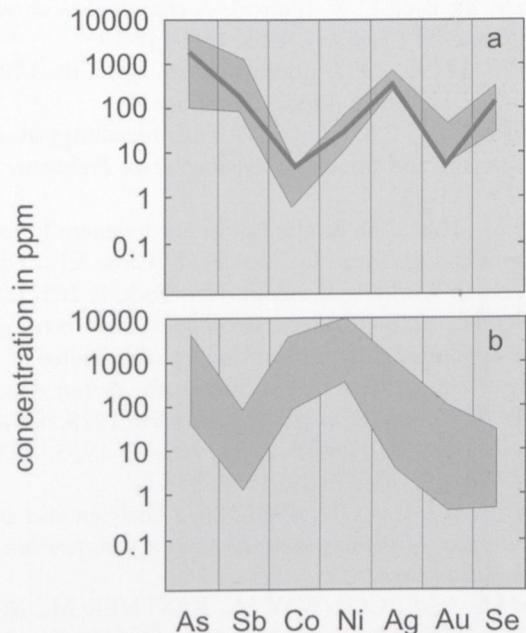

Fig. 8: Trace element patterns of chalcolithic copper objects that are attributed to a) Ai Bunar (Bulgaria) and b) Majdanpek (Serbia) based on lead isotope ratios and their chemical compositions. The richest ore sample from Ai Bunar (solid line) is entirely consistent with this pattern.

Fig. 8: Modelli degli elementi in traccia di manufatti in rame del Calcolitico attribuiti a a) Ai Bunar (Bulgaria) e b) Majdanpek (Serbia) basati sia sui rapporti isotopici del piombo sia sulla loro composizione chimica. Il campione di minerali più ricco da Ai Bunar (linea continua) è del tutto coerente con questo modello.

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