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Previous Approaches to the Chemistry and Provenance of Archaeological Copper Alloys

For more than two million years, hominins have exploited some of the rich mineral resources of the earth's crust. These have provided useful raw materials, such as particular stones for tools and weapons, pigments for painting and body art, brightly coloured minerals and semi-precious stones for body ornamentation, clays for figurines and ceramics, and, more recently, ores from which to extract metals. Although rich, such mineral resources are usually concentrated in particular regions, which tend to be located in mountainous or desert areas, and are hence difficult to reach. In spite of this, humans in the past must have specifically sought out such deposits, and probably transported some of their products over long distances, giving rise to systems of trade and exchange in particular precious commodities. Some such systems can be traced back over millennia, particularly those involving lithics with desirable qualities, such as being decorative or having the capacity to be worked into stone tools. It seems certain that metals, once they began to circulate within society, would have fallen into this class of desirable material. As people began to understand their unique properties, metals transformed human relationships with the material world by providing efficient tools and weapons, but also by acting as symbols of wealth and power.

Unsurprisingly, the origins of metallurgy have been the focus of intense academic speculation for several centuries. Although it was perhaps preceded by the smelting of lead (Krysko 1980; Gale and Stos-Gale 1981), locating the time and place of the first exploitation of copper and its alloys has been a major focus of academic endeavour. It now seems reasonably certain that the first smelted copper in Eurasia is to be found in or near Anatolia, perhaps in the seventh millennium BCE, and spreading to South-East Europe and Western Asia by the fifth millennium BCE (Roberts *et al.* 2009; Kienlin 2013). The knowledge of copper smelting subsequently spread to all of Eurasia by the second millennium BCE, via a process seen by most as a form of direct transmission. An independent origin is presumed for the smelting of copper in the New World, and has also been

suggested for some parts of Eurasia, particularly China, but there is little evidence for this. It is interesting to note that the smelting of copper ore in Anatolia and Western Asia appears to have been preceded by a long period of the use of brightly coloured copper minerals (e.g., malachite, azurite) for personal ornamentation (and occasionally as part of burial rituals), perhaps for several millennia (e.g., Solecki 1969). The desire for such colourful minerals would have led people to search for ore deposits in the mountains, in turn leading to the discovery of occasional rare finds of native copper, and ultimately to the smelting of the ores. Perhaps this was initially a result of some accidental heating of a mineral such as malachite, although the required temperature is higher than might easily be conceived of as 'accidental', and it may therefore have been the consequence of a more systematic experimental inquisitiveness. This sequence of malachite use might suggest an answer to the oft-posed question of why the remarkable Neolithic civilizations of East Asia came so late to the use of copper. The common consensus is that copper and copper smelting did not arrive in central China until the beginning of the second millennium BCE, and was not the result of independent invention. Since the Chinese Neolithic cultures valued jade above all other natural materials for symbols of ritual and power, the same trajectory of malachite - native copper - smelted copper is unlikely to have occurred, and therefore copper smelting was introduced into China from the west. What they did with it subsequently was, of course, remarkable and entirely Chinese. It could even be argued that the whole system of Chinese metallurgy, dominated by casting techniques which depend on metal fluidity, was a consequence of this late arrival, and was based on the notion of metal *as metal* rather than emerging from earlier techniques adapted from the physical working of stone.

As stated, the FLAME project is explicitly *not* concerned with the origins of smelted copper. The primary concern is to better understand the use and circulation of metal, and the development of metallurgical traditions, as these new materials became an intrinsic part of the fabric of prehistoric societies across Eurasia. Broadly speaking, this focusses primarily on the third and second millennia BCE, but since the chronology of the Bronze Age varies markedly across Eurasia, these do not represent strict chronological boundaries for the project. It does mean, however, that we *are* interested in the rise and spread of copper alloying technologies across Eurasia, from arsenical coppers/bronzes, to tin bronze and leaded tin bronze, since their development and transmission falls broadly within this period.

Chemical analysis of archaeological copper alloys

Chemical analysis as we know it today was developed in Europe towards the end of the eighteenth century, but that does not mean that the composition of metal objects was unknown and unknowable before then. The art of assaying the chemical composition of precious metal objects has probably been practised for almost as long as the use of the metals themselves. Greenaway (1962) emphasises that assaying—testing by fire—is the oldest quantitative chemical technique. From written sources it can be traced back to the early 2nd millennium BCE in Mesopotamia, where cuneiform tablets describe in some detail the quantitative assay of gold and silver (Levey 1959), but these techniques were probably old even then. Surviving European medieval texts give us increasingly clear descriptions of the process of assaying, both of metal objects and, in the case of base metals, of the ores from which they come. Book III of Theophilus' *On Divers Arts* (c. 1110–1140 CE; Hawthorne and Smith 1963) describes how to recover gold from scrap gilded metal, and also how to part gold from silver. The *Probierebüchlein* (“*The little book on assaying*”), written by an unknown German goldsmith or assayer around 1520 CE, is the first western book to give a clear description of assaying (Sisco and Smith 1949). Lazarus Ercker's *Beschreibung allerfürnemisten mineralischen Erztz und Berckwercksarten* (“*Description of all forms of minerals and calcareous species*”), originally published in Prague in 1574, rapidly became disseminated throughout Europe, and was reprinted in 1580, 1598 and 1629. It was translated as “*Lazarus Ercker's Treatise on ores and assaying*” by Sisco and Smith (1951).

The art of using the touchstone to assess the fineness of precious metals, especially gold, is probably equally as old as assaying (Oddy 1986). A touchstone is a flat piece of dark fine grained stone upon which the metal is rubbed, with the colour of the streak indicating the purity of the gold. From the calculations made by Oddy based on Theophrastus' book “*On Stones*” (c. 315 BCE; Caley and Richards 1956, 54), the touchstone could detect one part in 144 of impurity in the gold, which is a sensitivity not surpassed until modern times. Oddy (1986, 164) says that the first certain reference to the touchstone is in the 6th century BCE, but the fact that it was so well known to Theophrastus, and that it is also referred to in Sanskrit texts contemporary to Theophrastus, suggests that it is much older than this.

The origins of analytical chemistry as we understand it today are to be found in 18th century Europe, when ‘trial by fire’ gave way to ‘the humid method’, or precipitating known compounds out of solutions, ultimately leading to quantitative gravimetric analysis. Through the technical development of the analytical balance, and increasingly systematic study of aqueous chemical reactions and precipitations by Robert Boyle, Étienne François Geoffroy, and others, Torbern Bergman at the

University of Uppsala, Sweden, published in 1777 a protocol for the aqueous gravimetric analysis of gemstones. This was followed by more detailed protocols from Nicolas Louis Vauquelin in Paris (1799) and Martin Heinrich Klaproth in Berlin (1792/3). The methods of these three pioneer analytical chemists have been described and compared by Oldroyd (1973).

One of the earliest applications of the new method of gravimetric analysis was to archaeological material, probably as part of a broader general interest in the contents of the ‘cabinets of curiosities’ of the time. Thus, Dizé published the analysis of the tin content of some copper alloy coins and other objects in 1790, and Klaproth analysed a wider selection of coins, as well as glass, in 1792/3 (Pollard 2013). In these early stages, the purpose was simply to identify the metals used in these alloys. This was in part prompted by the mid-18th century debate in France over whether bronze was an alloy of copper with iron, or copper with tin (Pollard 2013). These first chemical analyses clearly showed that bronze was an alloy of copper with tin. The discussion then moved on towards understanding changing patterns of alloy use over time and space, most clearly visible in the work of Göbel (1842), and ultimately crystallising as the concept of ‘provenance’.

The provenance hypothesis

The observation that raw materials (stone, obsidian, clay, metals) are likely to have been obtained from specific and restricted geographical source areas, and potentially transported over long distances, has given rise to one of the major continuing themes in scientific archaeology, that of *provenance*. Essentially, provenance studies are based on the assumption that some characteristics of the source of the raw material are carried over into the finished object, and that they are sufficiently diagnostic to allow differentiation between geographically distinct sources (Wilson and Pollard 2001). These characteristics can be trace element patterns, rare earth profiles, or isotopic ratios, and are often referred to as a chemical *fingerprint*. The idea that patterns of chemical composition in archaeological artefacts could be used to attribute source had become well established by the mid-19th century in Europe (Pollard *et al.* 2014). Göbel (1842) noted in his monograph (entitled, significantly, “*About the influence of chemistry on the determination of the peoples of the past, or results of the chemical analysis of metallic antiquities...*”) that some Roman copper alloys contained zinc, whereas Greek alloys contained only tin and some lead. Even more significantly, he used the available analyses of Roman coins to divide them up into four groups (Cu + Sn + Pb, Cu + Zn, Cu + Zn + Sn, and Cu + Sn + Zn + Pb), and, with the exception of the first group, noted that

the amount of zinc decreased over time. More than a hundred years later, Caley (1964a) also noticed that the zinc content of Roman brass coins declined from the late 1st century BCE to the early third century CE. He suggested that Roman brass production started in the late 1st century BCE but stopped shortly after, and that brass coins of the late 1st century CE onwards were made from recycled brass. This ‘zinc decline’ was thus thought to be a consequence of the volatility of zinc, which meant that the zinc content of the brass declined after each re-melting (Caley 1964a, 99).

Göbel (1842) thought that the chemical differences he observed could be used to date metal objects from regions outside Greece and Rome. He thus compared the analyses of metals found in graves in the Baltic States with Roman coinage of particular Emperors, in an attempt not only to elucidate the origin of the metal, but also to give a date to the as then undated metal objects from northern Europe. Altogether, Göbel published the analyses of 119 archaeological artefacts, which was the first large-scale attempt to study the chemical composition of ancient metal objects. The first very large compilation of chemical analyses on archaeological metals was published by von Bibra (1869), containing approximately 1250 analyses, of which 600 were his own, and the other 650 were taken from the earlier work of at least 90 other analysts, including Göbel.

The theory of provenancing archaeological materials by chemical means was first fully articulated by Damour (1865, 313):

“When one discovers, in fact, either buried under the ground, either in the caverns, or among the remains of ancient monuments, an object on which the hand of man has marked his work, and whose matter is of distant origin or foreign to the country, it is inferred that there has been transport of the object itself, or at least of the matter of which it is formed. Hence arises inductions on the relations which may have existed between different peoples, on their migrations, their industry, etc.”

Until recently, this statement has essentially remained the main theoretical underpinning for much of the work involving the determination of provenance of archaeological materials using chemical analysis, including metals, ceramics, glass and lithics (Wilson and Pollard 2001). It has been elaborated upon for specific materials (e.g., for metals, Tylecote 1970; Pernicka 1986, 1999; Budd *et al.* 1996), but it is only recently that theoretical considerations such as the influence of the time taken for objects to move between source and deposition site have been explored in more detail (Pollard *et al.* 2014).

Major European programmes of chemical analysis

Although gravimetric analysis continued to be the preferred method of many distinguished metallurgists until at least the 1960s (e.g., Caley 1964b), a major step-change in the analysis of archaeological metals took place in Europe in the early 20th century, and accelerated considerably after the Second World War. This was brought about primarily because of the increased availability of instrumental means of chemical analysis, initially using optical emission spectroscopy (OES: Smith 1933; see Pollard *et al.* 2017, 34–35), which meant that many more samples could be analysed. It also increased the range of trace elements that could be quantified. As a consequence, several large European projects were initiated with an explicit focus on the provenance of the copper used to make Bronze Age archaeological metal artefacts. The earliest in the UK followed the establishment of the Ancient Mining and Metallurgy Committee of the Royal Anthropological Institute in 1945 (Anon. 1946). This Committee was an interdisciplinary panel consisting of some of the leading archaeologists of the day, including V. Gordon Childe (1892–1957), Oliver Davies (1905–1986), Christopher Hawkes (1905–1992) and Stuart Piggott (1910–1996), and scientists E. Voce (1902–1960), Cecil Henry Desch (1874–1958), Harold J. Plenderleith (1898–1997), Cyril E. N. Bromehead (1885–1952) and Herbert Henery Coghlan (1896–1981). The stated aim (Coghlan *et al.* 1949, 6) was summarized as:

“The main question now before this committee is whether there are any means of recognizing the locality from which the metal in a given copper object was obtained. The information already available on the subject has been conveniently assembled, with full references, by J. R. Partington (Origins and Development of Applied Chemistry, 1935).”

The Ancient Mining and Metallurgy Committee published a series of more than 20 papers from 1948 to about 1957, but the deaths of several of the leading members of the Committee in the 1950s seems to have brought about the demise of the initiative (although some, particularly Coghlan, continued to publish through to the 1980s).

Otto and Witter

A little earlier than this, in the 1930s, several groups of German-speaking researchers began large scale programs of chemical analyses on ancient metal artefacts. The first significant compilation of data was that of Helmut Otto (1910–1998) and Wilhelm Witter (1866–1949), from the University of Halle, whose results were summarized in 1952 as *“Handbuch der ältesten vorgeschichtlichen Metallurgie*

in Mitteleuropa". Their aim was to understand prehistoric metallurgy in Europe using chemical analysis, in contrast to the previous typological approach to metal artefacts. They decided to focus on only one period to increase the consistency of their work, namely the very beginning of the Bronze Age. They organized a program of research to initially analyse a substantial number of artefacts (1374 artefacts, of which ca. 1100 were analysed by Otto, and the remainder by J. Winkler, W. Noddack and W. Kroll) from all across Europe, from Ireland and Denmark to Italy and from Spain to Romania (Otto and Witter 1952, 1–21).

They developed their own optical emission spectrometry (OES) methodology that allowed them to obtain quantitative analyses: a sample of approximately 0.2 g of unaltered metal from the artefact was melted to form two electrodes, and then a high voltage was applied between them, causing the emission of light whose wavelength was dependent on the chemical elements in the sample. The intensity of the light emitted gave information about the quantity of each element present in the sample. Moreover, they also emphasized the importance of metallography to study the manufacturing process of the artefacts, giving an input into a programme of creating experimental artefacts.

From their analyses of more than 1300 Early Bronze Age artefacts they created six groups of metal according to the artefacts' compositions: "pure copper (Reinkupfer)", "raw copper (rohkupfer)" (which indicates "copper with small traces of other elements"), "arsenical copper alloy (arsen-kupferlegierung)", "Fahlerzmetalle"¹, divided into "Fahlerz with a high percentage of silver" and "Fahlerz with a low percentage of silver", "other kinds of metal (sonstige metalle mit Ni, As und Ag)", and "copper tin alloy (zinn-kupferlegierung)". These groups were further divided according to the percentage of presence of tin, lead, silver, gold, nickel, cobalt, arsenic, bismuth, zinc (Otto and Witter 1952, tab. I–VI). The creation of these groups was based only on the authors' observations, without any statistical treatment of the data. Although their ability in the visual identification of these groups was subsequently recognized by later authors (e.g., Ottaway 1982, 94–95), such a subjective technique was not thought to be acceptable for scientific research and was soon replaced by statistical analysis (see below). Finally, these authors also investigated chronological and geographical patterns linked to their groups to hypothesize the provenance of the material and to identify trade routes (Otto and Witter 1952, 60–82). As regards chronology, they accepted Childe's theories of a linear technological evolution in metallurgy, from copper, to arsenical copper, Fahlerz, and tin bronze (Childe 1944) and dated the objects according to their chemistry (Otto and Witter 1952, 5). With respect to provenance, they

¹ Fahlerz was defined by them as "copper with a higher percentage of trace elements than raw copper."

claimed that almost all of the German artefacts came from copper ores in Saxony, but this conclusion has subsequently been challenged (Pernicka 2011, 28).

Pittioni and the Vienna group

Another important contemporary group of researchers was established in Vienna in the 1930s, led by Richard Pittioni (1906–1985). This group was also interested in the provenance of ancient metal artefacts through compositional analysis, and focused their research on the Alpine and Balkans regions (Preuschen and Pittioni 1937). They brought a strong metallurgical background to the study, since they were both mining engineers (Pernicka 2011, 28). They argued against the methodology of Otto and Witter, pointing out that only with a significant amount of data of the same period and of specific forms can a consistent hypothesis be formulated about the provenance of the ore used for a group of artefacts (Pittioni 1957, 3). Furthermore, they declared explicitly that it is quite impossible to understand the provenance of a single object because metal ores are too heterogeneous, and the composition of the copper is not the same at all depths within the ore deposit. Consequently, two objects with different compositions could derive from two different points in a single ore source. The heterogeneous nature of metal ores also implies that the presence of a single specific chemical element in an artefact is never crucial in characterizing metal groups (Pittioni 1957, 4). Useful information can only be derived by the combination of the presence of some specific elements: antimony, arsenic, lead, nickel, silver, bismuth and tin (Pittioni 1957, 7). Iron was considered not to be diagnostic, as it is universally present in copper ores; aluminium, calcium, magnesium and silicon were also ruled out as non-specific (Pittioni 1957, 7). A crucial consequence of the Viennese group's idea of the combination of presence/absence of elements as being the main priority in data collection was their decision to undertake only semi-quantitative analysis, without giving numerical values for their concentrations (**Table 1**).

This approach was heavily questioned at the time (see discussion following Pittioni 1960), and, unfortunately, it also means that their data are not useful for modern research using a statistical perspective. This was pointed out by Ottaway (1982, 175–176), who tried to convert their data expressed as symbols into numerical data. As discussed in Chapter 3, although her efforts were successful with the more limited set of symbols used by Otto and Witter and the Stuttgart group (see below), the data from Pittioni's work were impossible to convert and, hence, could not be included in her database. For this reason, in the end, more than 6000 valuable analyses are now completely unusable. Despite this considerable drawback, the group from Vienna deserve credit for pointing out the need for a large number of contemporary objects in order to theorize provenance,

and also for recognizing the importance of a multidisciplinary approach in archaeometallurgical research, including the contribution of geology. Indeed, the Vienna group analysed not only finished artefacts, but also slags and metal ores. Consequently, they initiated geological research in the alpine region to identify the possible ore sources and to look for sites that could provide evidence for ancient smelting processes (Pittioni 1957, 7–16).

Nr	Objects	Cu	Sn	Ag	Al	As	Ca	Fe	Mg	Mn	Ni	Pb	Sb	Zn	Bi	Au	V
Barreringen A																	
1	Metallkern 1	HM	Sp	++	-	++	-	++		Sp	-	Sp	+	-	+	-	-
2	Metallkern 2	HM	Sp	++	-	++	-	++		Sp	-	Sp	+	-	+	-	-
3	Oberfläche 1	HM	Sp	++	-	++	-	++		Sp	-	Sp	+	-	+	-	-
4	Oberfläche 2	HM	Sp	++	-	++	-	+		Sp	-	Sp	+	-	+	-	-
Barreringen B																	
5	Metallkern 1	HM	Sp	++	-	++	-	++	-	-	Sp	Sp	+	-	+	-	-
6	Metallkern 2	HM	Sp	++	-	++	-	++	-	-	Sp	Sp	+	-	+	-	-
7	Oberfläche 1	HM	Sp	++	-	++	-	+	-	-	Sp	Sp	+	-	+	-	-
8	Oberfläche 2	HM	Sp	++	-	++	-	+	-	-	Sp	Sp	+	-	+	-	Sp
Barreringen B																	
9	Metallkern 1	HM	+	++	-	++	-	++	-	-	Sp	Sp	+	-	+	-	-
10	Metallkern 2	HM	+	++	-	++	-	+	-	-	Sp	Sp	+	-	+	-	Sp
11	Oberfläche 1	HM	+	++	-	++	-	+	-	-	Sp	Sp	+	-	+	-	Sp
12	Oberfläche 2	HM	+	++	-	++	-	+	-	-	Sp	Sp	+	-	+	-	Sp

Table 1: Example of the data published by Pittioni (1957, Tab. 1).

Stuttgart and the SAM project

Around the middle of the 20th century a project was started in Stuttgart by a group of researchers, the most eminent of whom were Siegfried Junghans (1915-1999), Edward Sangmeister (1916-2016) and Manfred Schröder (1926-2009). Their work is usually referred to by later authors, and also here, as “the SAM project”, in abbreviation of the full title, “*Studien zu den Anfängen der Metallurgie*”. The explicit aim of their research was to study the origin and spread of copper and bronze in Europe by scientifically examining the material itself, by means of optical emission spectroscopy and statistical analysis (Junghans *et al.* 1968, 6). Their field of research was broader than that of their predecessors: for the first time the entire European continent was taken into consideration. They created European distribution maps of objects with common chemical compositions. The extent of

the territory of interest and the necessity to have a statistically valid sample caused the authors to make as many analyses as possible, ultimately producing more than 22,000. They published the first 1000 results in 1960, added 9,000 more in 1968 and finally reached 22,000 in 1974. In this last publication, they also reconsidered their previous analyses, republishing some of them because in some cases arsenic and antimony had been underestimated by their instrument (Junghans *et al.* 1974). Fortunately, following in the footsteps of Otto and Witter, they produced fully quantitative analyses.

They focused on eleven elements: tin, lead, arsenic, antimony, silver, nickel, bismuth, gold, zinc, cobalt, and iron. The quantity of copper was not determined directly. The authors recognised the most distinct boundaries between different types of copper in the percentages of bismuth, antimony, silver, nickel and arsenic (Junghans *et al.* 1960, 57). From this, Hans Klein, the statistician of the group, used these elements to develop his statistical frequency analysis. He tried to create groups in which the frequency distribution of each element could be represented as a Gaussian (normal) curve. As a result, Klein defined 12 groups of metal, as shown in **Figure 1** (A, B1, B2, C1, C2, C3, E00, E01, E10, E11, F1, F2). A group was considered to be “secure” only when it reached a threshold that did not change even with an increasing number of samples (Junghans *et al.* 1960, 58). However, they noted that, due to the statistical method applied, a few samples very close to the boundaries of the groups could be assigned to either group (Junghans *et al.* 1960, 58).

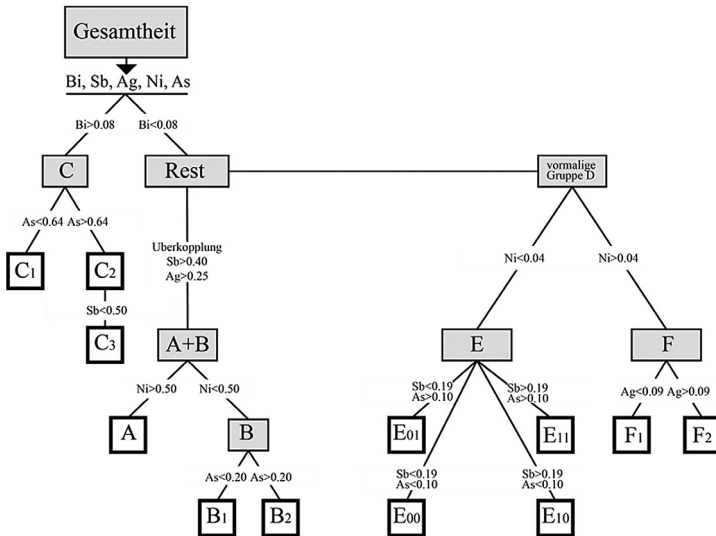


Figure 1: Groups of metal artefacts according to their composition, re-drawn after Junghans *et al.* (1960, Tabelle 1, p. 210)

When the Stuttgart group published their second set of analyses in 1968, they decided to perform their statistical analysis by plotting each element against the other elements, which they called “two dimensional analysis” (Junghans *et al.* 1968, 13). With this technique, they created a first subdivision of artefacts into groups, which was then refined by considering the percentages of individual elements, in particular Ag, As, Bi, Ni and Sb. As a result, instead of the original 12 groups, 29 groups were created, as shown in **Figure 2**. However, most of the groups already identified in the 1960s publication were confirmed, and it was felt that the new results only helped to further refine these groups (Junghans *et al.* 1968, 15).

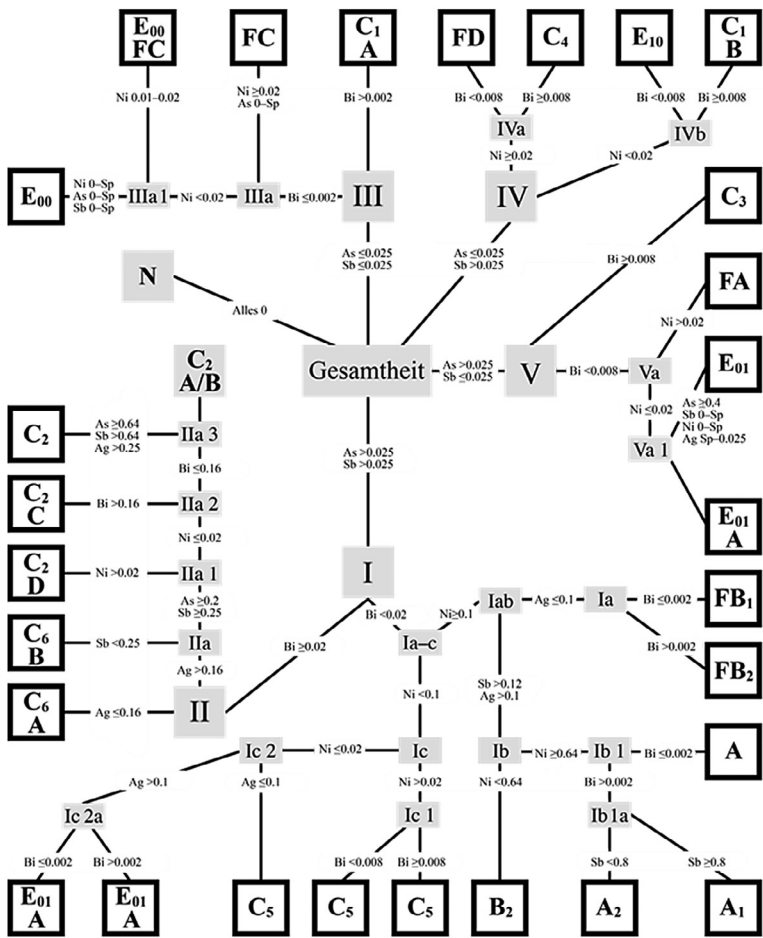


Figure 2: SAM ‘decision tree’ redrawn after Junghans *et al.* (1968) (SAM 2.2, Tabellen und Diagramme, Diagramm 1).

Nevertheless, as stated by Muhly (1993),

“the reaction to the SAM Project was uniformly negative, ... archaeologists were sceptical of the SAM metal groupings chiefly because the different classes of metal were presented within the context of an outmoded diffusionist archaeology that was (unfairly) used to discredit the entire project.”

In particular, the statistical methodology of the Stuttgart group was heavily criticised, most specifically by Waterbolk and Butler (1965), who argued against both the methodology and the presentation of their results. They strongly criticized the lack of consideration of the archaeological background in their methodology. Waterbolk and Butler (1965, 230) stated that the Stuttgart team had “*thrown the analyses all into one pot, with the hope that mathematical means will bring them out of the pot again in a logical order.*” Some artefacts were assigned to groups with characteristics of a different period (Waterbolk and Butler 1965, 232). Other groups of objects were considered as belonging to several different groups, even though they were from a single homogenous archaeological context and had a mostly homogenous composition (Waterbolk and Butler 1965, 237). Another criticism of the methodology was that it had not been consistently applied to all the defined groups: in fact only group A had all elements distributed in a Gaussian curve (Waterbolk and Butler 1965, 231). Moreover, they pointed out that in certain cases the significant information was not the percentage of an element, but its ratio to other elements (Waterbolk and Butler 1965, 238). The Stuttgart group was also criticized for the adoption of bismuth as a discriminating element. Slater and Charles (1970) pointed out that the behaviour of bismuth, with its low solubility in copper and lower melting point than copper, leads to a high degree of segregation during solidification, which causes unreliable analyses. Consequently, these authors felt that this element should not be chosen to discriminate between groups of artefacts based on their composition.

In terms of data presentation, Waterbolk and Butler (1965, 233) also pointed out that if new analysis were undertaken it would be difficult to compare these results with the proposed groups, so that judging the probability of the artefact belonging to one group or another would be impossible. The alternative methodology proposed by these two authors was to start with artefacts from a homogenous archaeological context, such as a hoard, and represent graphically the distributions of the elements considered to be important (e.g., **Figure 3**). These criticisms of the Stuttgart group’s statistical methodology have been generally accepted, but, as pointed out by Ottaway (1982, 97), the methodology proposed

by Waterbolk and Butler is hardly usable with large complex datasets. However, the acceptance of such critiques does not undermine the fundamental importance of the Stuttgart group’s work. A critical point was the decision to adopt the analytical methodology proposed by Otto and Witter, rejecting Pittioni’s use of qualitative data. For the European Bronze Age, these data remain the largest and most comprehensive dataset available, which subsequent workers have attempted to re-interpret and evaluate (e.g., Krause and Pernicka 1996: see below). The full database was published electronically by Krause (2003), and this forms the core of the FLAME data for Europe.

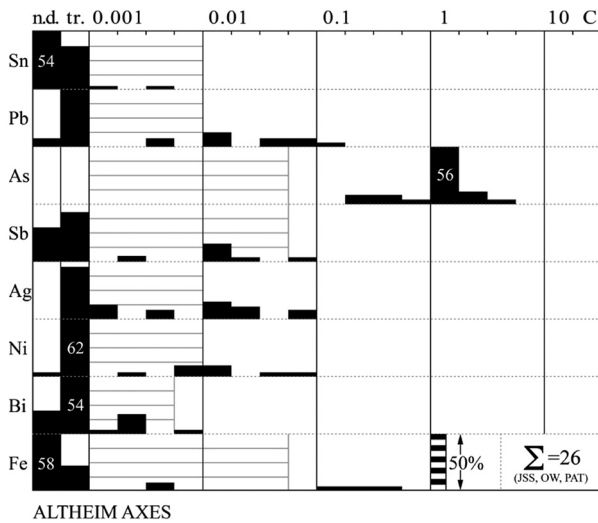


Figure 3: The composition of 26 Bronze Age axes from Altheim as presented by Waterbolk and Butler (1965, Graph 3).

Evgenij Chernykh in Moscow

Until the 1960s, the history of archaeometallurgical research in Russia and the Soviet Union followed much the same pattern as was seen across the rest of Europe. Indeed, many of the early analyses of archaeological artefacts from Eurasia were carried out by the very same researchers who were active in Europe (e.g., Struve 1866). As elsewhere, the growth of quantitative spectrometric methods during the early part of the 20th century—which provided complete, rapid analysis at low cost, on small samples with little or no pre-treatment—led to an increase in the pace of archaeological research. By the end of the 1950s dedicated laboratories had

been founded in Baku (Azerbaijan), Tbilisi (Georgia), St Petersburg and Moscow. Each of these produced substantial quantities of data and led to important regional and macro-regional studies. The most significant change, however, came with the foundation of a second analytical laboratory in Moscow within the Institute of Archaeology of the Soviet Academy of Sciences under the direction of Boris Kolchin, and associated from its inception with the work of Evgenij Chernykh. The subsequent work of this laboratory, which for prehistoric archaeology was driven forward by Chernykh, is known to most Western researchers through a single book—*Ancient Metallurgy in the USSR*—published in English in 1992, only a few months after the structure of the Soviet Union itself had collapsed. Intended as an accessible English summary of three decades of intensive analytical and archaeological work, this unintentional epitaph to a fallen empire (described as such by Chernykh 2017) was simultaneously praised for its clarity and scope as the first extended presentation of Soviet scholarship on this subject and harshly (though quite unfairly) criticized for its non-publication of data, its lack of analytical detail, and its perceived origins in the work of the Stuttgart group (see, for example, the review by Muhly (1993)). Nevertheless, it has remained the primary citation for most English-speaking students of archaeometallurgy in northern Eurasia. Certainly, in formulating our own ideas, this text remained almost our only window onto Russian archaeometallurgical research until the inception of the FLAME project.

Most English language descriptions of his work, including those of Chernykh himself, have focussed only on his archaeological results—the networks of central production and peripheral exchange, or *Metallurgical Provinces*, which shape the structure of his interpretations (see Chernykh 1992, 7–10; Kohl 2007; Chernykh 2008). It is worth, however, highlighting some of the fundamental justifications of his approach, which, far from being a mere Russian reflection of the SAM project, is one which emerged from a comprehensive critique of the existing methodologies in European archaeometallurgy. The complexity and subtlety of his approach are only apparent from a detailed study of his original Russian language publications.

Although Chernykh placed the question of provenance at the centre of his archaeological interest, he did not assume that it was straightforward, either from a geological or a metallurgical perspective. In the initial presentation of his methodology, Chernykh (1966, 13–17) reviews the problems of differentiating ore sources, using Russian data as an example. He concludes that while a general insufficiency of data on ore sources, from both archaeological and geochemical perspectives, usually reduces the theoretical scope of provenance studies to the regional level, we should not assume that the reliable differentiation of specific ore sources is impossible—a position he later developed in his research on mining

in the Urals and Bulgaria (Chernykh 1970; 1978; 2004; 2002-2007). However, he was equally interested in understanding chemical change between ores and objects as a result of human action. Rejecting Thompson's (1958) negative assessment of the possibility of relating objects and ores, he was instead inclined to follow Biek (1957) in recognizing that arguments about relationships between archaeological ores and artefacts are typically sustainable only at the general level and not in individual cases. He nevertheless made a thorough review of the metallurgical literature, including experimental studies of the preferential movement of elements between metal, slag and vapour (Okunev 1960), to establish a reasoned baseline for the choice of key elements in his analysis (Chernykh 1966, 18–21): Sn, Pb, As, Sb, Bi, Ag, Au, Co, Ni and Zn. Using both geochemical arguments and explorations of elemental distributions from a large number of analyses he established a coherent approach to the definition of the boundary between artificial and natural alloys (e.g., at around 1% for tin). Throughout this discussion, he also provided basic notes on several key problems relating to the recycling of metal, including the differentiation of primary alloys and alloyed metal resulting from the re-melting of scrap bronze with clean metal, and the impact of oxidative loss of particular elements on the overall composition of the metallurgical group. He concludes:

“One of the most complex and difficult tasks is the identification of secondary, mixed metal [within the system]. Such [metal] derives from the re-melting of broken artefacts, made from metal smelted from different ores... and containing a complex array of elements... derived from its [original components]. Evidently, in some archaeological cultures it is possible to identify such mixed groups... [but] the methodology by which to differentiate this metal is not entirely clear” (Chernykh 1966, 20–21).

What is equally important, but often missed in English-language discussions of his methodology, is his integration of archaeological and chemical information within a standardized statistical approach, described more fully in his second thesis (Chernykh 1970). The first step is to define and codify various groups:

- Chemical—based on a characteristic suite of natural components—defined through a combination of visual and chemical analyses— and deemed distinctive of a particular region, mineralogical formation, or mine,
- Metallurgical—based on characteristic alloying components (e.g., Sn>1%) and independent of chemical groups,
- Typological—based on various characteristics and proportions within broad functional-stylistic groupings.

Up until 1989, the chemical analyses were made by OES using 5-10 mg of sample, and recording originally on a photographic plate, but employing two or three exposures at different excitation currents to ensure adequate recording of the different elements. He states in Chernykh and Lun'kov (2009) that their laboratory produced around 40,000 analyses by this method, of which so far only about half have been fully published. With the collapse of government funding at the end of the 1980s, the primary focus of the laboratory shifted towards the publication of these data and their synthesis with the growing body of radiocarbon results, a task which is still ongoing. After 2007, analytical work at his laboratory resumed using a desk mounted pXRF instrument, primarily on sampled material.

His approach to these chemical data was to assign the compositions to a limited number of metallurgical (alloy recipes) and chemical groups (trace elements) on the basis of visual examination of the data, which are specific to each area of study. An example of his classification of Eneolithic Bulgarian copper objects with Sn<1% is shown in **Table 2**, where the data are divided into six groups, labelled 1-6 (Chernykh 1978). In other areas he named the groups on the basis of their presumed association with sources or source regions (e.g., Chernykh 1970). His analysis of the data, however, then explicitly combines typological and chemical analysis. He carries out two sets of correlations between assemblages, one for typology (R) and one for chemistry (S). For typology, he defines a set of typological categories, and allocates every object in the assemblage to one of these categories, producing a numerical summary of how many objects belong to each category for each assemblage. He then compares assemblages on a pair-wise basis using the formula:

$$R_{AB} = \sum_{j=1}^n \sqrt{\frac{k_j m_j}{KM}}$$

where R is the correlation between assemblages A and B, k_j and m_j are the numbers of objects in groups A and B respectively classified into group j, and K and M are the total number of objects in assemblages A and B. He performs exactly the same correlation (S) for the objects classified into chemical groups. He then compares both correlations between all of his cultural assemblages in a correlation table, which is presented graphically as a series of columns, showing the relationship between one cultural assemblage and all the other assemblages in his analysis (**Figure 4**). This allows an evaluation of the relationship between cultural assemblages for both typological and chemical data. This approach forms the basis of his derivation of metallurgical provinces.

	I	II	III	IV	V	VI
Sn	0–0.005	0–0.005	0–0.01	0–0.01	0–0.01	0–0.01
Pb	0–0.01	0–0.01	0.001–0.3	0.001–0.1	0.01–1	0.001–0.01
Zn	0–(0.008)	0–(0.008)	0–(0.008)	0–(0.008)	0–(0.008)	0–(0.008)
Bi	0–0.0015	0–0.0015	0.002–0.03	0–0.02	0.002–0.03	0–0.002
Ag	0.0001–0.001	0.002–0.2	0.003–0.03	0.01–0.1	0.01–0.2	0–0.02
Sb	0–(0.003)	0–(0.003)	0–(0.003)	0.005–0.1	0.003–0.02	0–0.02
As	0–(0.02)	0–(0.02)	0–(0.02)	0–(0.02)	0.03–0.8	0.1–2.3
Ni	0.001–0.02	0.001–0.02	0–0.02	0–0.02	0–0.01	0.003–0.02
Co	0–(0.003)	0–(0.003)	0–(0.003)	0–(0.003)	0–(0.003)	0–(0.003)
Au	0	0–(0.005)	0–0.01	0–0.005	0–0.01	0–0.01

Table 2:

Chernykh's definition of six chemical groups in the objects from Eneolithic Bulgaria (Chernykh 1978, 79).

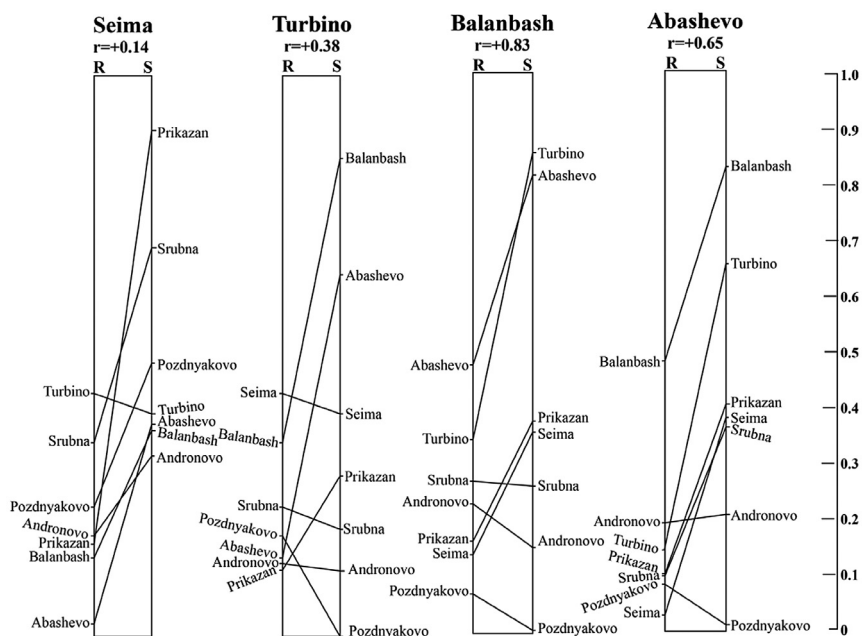


Figure 4:

Part of the comparison of correlations between typological (R) and chemical groups (S) for eight cultural assemblages from the Eurasian steppe and forest zone (Chernykh 1970, 81). Each column represents one cultural assemblage, and the R and S correlations with the other assemblages are marked on the left and right side of each column respectively.

At smaller scales, working within individual cultures or regional traditions of production, he also compared the levels of particular elements in different groups of artefacts to explore functional differentiation in alloy use (e.g., Chernykh 1966, 42). Like Waterbolk and Butler (1962), he focussed heavily on hoards, where these occurred within his study area, and often undertook focussed examinations of their character in order to establish key groupings and better interpret wider regional patterns. In all of his writing, he regularly breaks free from the constraints of his methodology to draw upon his original (and very significant) experience as an archaeologist. Since establishing his laboratory, he has been followed in this tradition by a number of equally dedicated archaeological metallurgists, of whom Sergey Kuzminykh and S.A. Agapov are probably the most widely known outside Russia. Unfortunately, much of their work still remains inaccessible to the majority of European researchers and, in consequence, has rarely been given the credit it deserves. The same is true for the many other Russian and Soviet archaometallurgists who have not been explicitly mentioned here (Bogdanov–Berezovskaya, Degtyareva, Grigoriyev, Grishin, Khavrin, Ryndina, Ruzanov, Semilkhanov, Sergeeva and others) and whose work is rarely read outside the CIS or understood in its proper context.

We have chosen to focus at length on the contribution of Evgenij Chernykh, because without his work it would have been impossible to imagine that a complete Eurasian synthesis could be attempted. As we began to understand the details of his approach, it became increasingly clear that, of all of the major analytical programmes described in this chapter, his remains the closest and most comparable, in both methodology and philosophy, to the one we have developed. To quote Kohl (2007, xx):

“Although many problems remain unresolved and many paradoxes raised by his work are difficult to ponder, it is impossible to overestimate Evgenij’s incredible contribution to our overall understanding of Bronze Age Eurasia. In a sense, we all follow in his footsteps.”

Barbara Ottaway and the introduction of numerical taxonomy

In the 1970s, Barbara Ottaway was one of the first researchers to work not only with her own analyses, but also to use other published data extensively in order to have a more comprehensive picture of the situation in her study region. Her PhD thesis “*Aspects of the Earliest Copper Metallurgy in the Northern Sub-Alpine Area and its Cultural setting*”, published in 1978, was followed by two books, one dedicated to archaeology and society, and the other, “*Earliest Copper Artefacts of the North alpine Region: Their Analysis and Evaluation*”, published in 1982, to

the analysis of metal artefacts. Her aim was “*to study the earliest metal artefacts in the north alpine region in their cultural context*” (Ottaway 1982, 11). In her own analyses she measured Zn, As, Ag, Sn, Sb and Au with neutron activation analysis (NAA), and Pb, Bi, Ni and Fe with atomic absorption spectroscopy (AAS). Her approach to using the results from different analysts and analytical methodologies, however, raised for the first time the question of data compatibility (see Chapter 3).

Ottaway (1982) was the first to apply cluster analysis and discriminant analysis in a systematic way to the composition of ancient metal artefacts. Cluster analysis is a methodology which uses all the analytical data simultaneously to group artefacts. Typically, each measured element is considered to define a dimension in multivariate space, so that the coordinates of each analysed object in this space are defined by their composition. Thus, if nine elements are measured, an object is defined to be a point in nine dimensional space. Distances between objects in this space can then be calculated using an extension of Euclidean algebra, and thus the proximity of objects to each other in these nine dimensions can be calculated. This is usually followed by a grouping algorithm, which clusters objects together according to the measured proximity in multidimensional space. A feature of this methodology is that it can also be used to combine several different sorts of measurements, such as chemical composition, weight and size dimensions, and even non-numerical data such as shape, providing it is converted into a numerical code. This overall approach to numerical data began in the 1960s under the title of *numerical taxonomy* (e.g., Sneath and Sokal 1973), but the first application in archaeology was by Hodson (1969) when he undertook the analysis of 50 Upper Palaeolithic assemblages of stone tools, and also of a group of 100 chemical analyses of copper and bronze objects, 90 taken from SAM 1 (Junghans *et al.* 1960), and 10 from Schubert and Schubert (1967).

Cluster analysis is a more flexible approach than that used previously by the SAM group, although if new objects are added, then the computer needs to recalculate the similarities between all objects and create new groups. It has also been claimed that the use of a computer to perform the calculations reduces the subjectivity of the analysis, although this is not necessarily the case, since a number of choices have to be made about how the clustering algorithm should work, amongst several other things (see Chapter 2). Since the early work of Ottaway, the methodology of cluster analysis (and related techniques, such as principal components analysis, PCA) has become routine in most archaeometallurgical chemical studies (e.g., Krause 2003; Merkl 2011). Even the critics of such methodologies (e.g., Pollard 1983: see also Chapter 2) do not deny the importance of Barbara Ottaway’s work as a milestone in the history of numerical methods applied to archaeometallurgical data.

According to her results on Early Alpine bronzes (Ottaway 1982), the artefacts were initially divided into two groups: bronzes (objects containing more than 2% of tin, an amount that she thought could be related to deliberate alloying) and “copper” artefacts, which have mostly copper with traces of other minor elements (Zn, As, Ag, Sn, Sb, Pb, Bi, Ni, Co, Au, Fe). Cluster analysis identified ten groups (or clusters) of copper, the first of which, representing copper with only small traces of impurities, was further divided into five sub-clusters (see **Figure 5**). The bronzes were divided into six clusters.

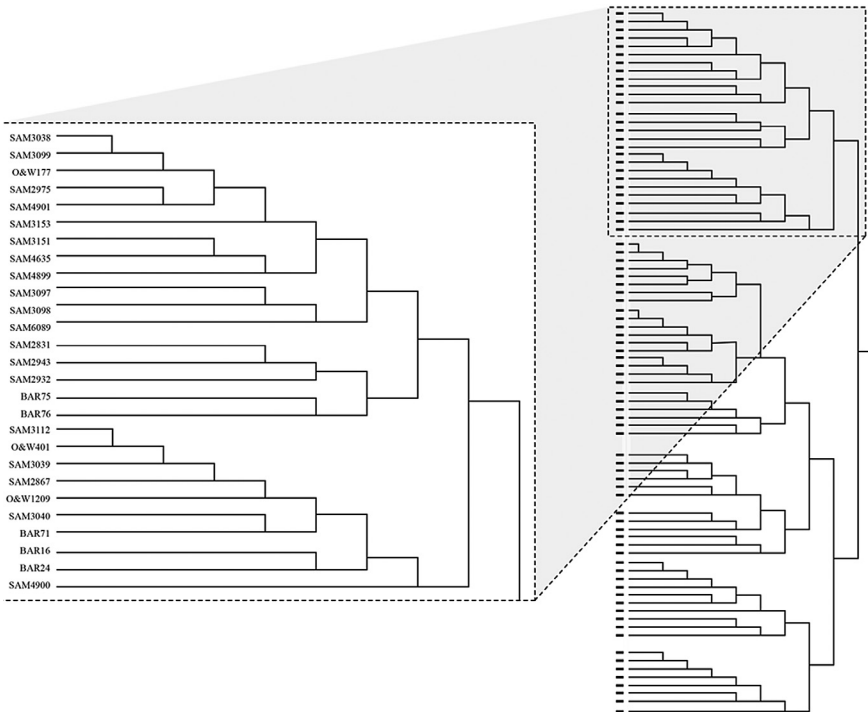


Figure 5:

Section of the output from the cluster analysis of 81 copper objects using 11 elements as input (redrawn and modified after Ottaway 1978).

A further step was to use a numerical approach to verify the correlation between clusters and cultures, clusters and typology, and cultures and typology. She highlighted the relationship between arsenical copper and the earliest cultures (Ottaway 1982, 121–131) and explained this as representing intentional alloying. She also noticed a difference between the compositions of daggers and axes, namely that daggers contained a higher percentage of impurities (Ottaway 1982, 156),

opening up a discussion which continues to this day (see Chapter 4). Significantly, she recognized a difference between the copper used for copper objects and that used for bronze production (Ottaway 1982, 156), which the methodology described here allows us to do relatively simply (Chapter 5). She tried to relate different clusters to different copper ores, but in the end she admitted that this was unsuccessful (Ottaway 1982, 171–180). Finally, she posed the question of whether the aim of elemental analysis should be to identify ancient metal ore sources, especially on a large scale, such as the entire European continent. Considering that all the attempts made in the past to do this, including her own, had been largely unsatisfactory, she began a debate about the use of trace elements to determine provenance.

SMAP and Heidelberg

The legacy of the Stuttgart (SAM) group (samples and data) was inherited by Ernst Pernicka's group at the Max Planck Institute in Heidelberg in 1987 (Krause and Pernicka 1996). Attention was focused on Neolithic/Early Bronze Age artefacts, since they were mainly interested in the origin of the Metal Age, particularly on the origin of copper and of tin-bronze production. In particular, Krause dedicated a study to the origin of metallurgy in the zone between the Carpathian basin and Baltic Sea (Krause 2003).

They contributed to expanding the database by adding many new analyses within the *Frühe Metallurgie in Zentralen Mitteleuropa* project (FMZM). They also reconsidered all the work produced by the Stuttgart group within the framework of new ideas and new technologies in the *Stuttgarter Metallanalysen-Projekt* (SMAP). FMZM focused on eastern Germany, the region formerly known as the German Democratic Republic, which had fallen behind Western Europe in terms of archaeological research. Within this project about 2,400 new analyses were undertaken in Heidelberg using neutron activation analysis (NAA) and X-ray fluorescence (XRF). The analyses undertaken using both methods demonstrated that XRF analyses were not always reliable and, consequently, some of the results obtained with XRF were not included in the SMAP database (Krause 2003, 26). The new analyses obtained within the FMZM project contributed to the creation of the SMAP project, which also included many analyses by other workers. With these new data, the SAM database of 22,000 analyses was expanded to more than 40,000. One aim of this project was the creation of a digital map of all these data. This was very ambitious considering the computers available at the time: neither the computing power nor the GIS packages were then capable of easily managing such a large amount of data.

A fundamental issue raised by SMAP was understanding if and how data obtained from different laboratories using different techniques could be compared, a recurrent topic in the history of archaeometric research since Ottaway's work. As discussed in Chapter 3, the Heidelberg group undertook a study of the reliability of SAM OES data. According to Krause (2003, 18–22), from a comparison of the results obtained by re-analysing the same objects, the analyses undertaken using optical emission spectroscopy (OES) were 'broadly comparable' with modern data in terms of precision and detection limits.

The method of statistical analysis employed in SMAP was cluster analyses, following in the footsteps of Ottaway. The data was based on the elemental concentrations of arsenic (As), antimony (Sb), silver (Ag), nickel (Ni) and bismuth (Bi). These elements were the same as those used by the Stuttgart group, therefore they took the opportunity to re-evaluate the results obtained by the Stuttgart group's statistical analysis, finding that their conclusions were broadly correct (Pernicka 1995, 97). They also considered gold, silver, nickel and—with limitations—cobalt as markers for provenance, and the other elements as characteristic of both provenance and processing. The element pairs silver/nickel, arsenic/antimony and arsenic/tin were chosen to clarify questions of the source of the initial ore and the processing conditions (Krause 2003, 19). Gold was excluded, since in most cases it was below the detection limit with OES (the technique used by SAM). According to the SMAP researchers, recycling of material was probably happening, but this did not change significantly the chemistry of the artefacts and its effect on the cluster analysis was considered as irrelevant (Krause 2003, 145). After statistical analyses, they felt that there were two categories of cluster. One group—"major clusters"—referred to metal that was widespread in Europe, strongly linked to specific cultures (e.g., Corded Ware, Bell Beakers and Únětice) and that signify specific changes at the beginning of the Early Bronze Age. Minor clusters, with a smaller number of artefacts, were seen as expressions of local metallurgical activities.

The work of the Heidelberg group is remarkable for their attempt to reorganize and manage the large amount of data from decades of research on ancient metal compositions. Their idea of integrating data within a GIS package was also valuable and is now achievable with the new technologies available. Their choice of using cluster analysis as the main tool to interpret the data might, however, be suspect in some case where mixing and recycling were prevalent, although the main outcomes outlined above are almost certainly correct (see Chapter 3).

Early Bronze Age	
"A"	<i>Principal impurities: As, Sb, Ag.</i>
	<i>Three Subgroups: "A1" (As>Sb>Ag); "A2" (As<Sb>Ag); "A3" (As~Sb~Ag)</i>
"B"	<i>Principal impurities: As, Ni.</i>
	<i>Three Subgroups: "B1" (As>0.75%, Ni>0.06%); "B3" (As<0.75%, Ni>0.06%); "B4" (As<0.25%, Ni<0.06%)</i>
"C"	<i>No principal impurities. Trace impurities only.</i>
"D"	<i>Principal impurities: As, Sb, Ag, Ni.</i>
	<i>Three Subgroups (based on A1–3): "D1" (As>Sb>Ag); "D2" (As<Sb>Ag); "D3" (As~Sb~Ag)</i>
"E"	<i>Principal impurities: As, Sb, Ni. Subgroups:</i>
	<i>None defined.</i>
"F"	<i>Principal impurities: As, Ag.</i>
	<i>Three Subgroups: "F1" (As>Ag); "F2" (As~Ag); "F3" (As<Ag)</i>
"G"	<i>Principal impurities: Ni.</i>
	<i>Subgroups: None defined.</i>
Middle Bronze Age	
"M1"	<i>As between 0.65% and 1.05%; Ni between 0.2% and 0.45%; 0.05% Co; trace Sb</i>
"M2"	<i>Similar to "M1" but with As above 1.05%</i>
"N1"	<i>As between 0.35% and 0.70%; Ni between 0.25% and 0.5%; 0.05% Co; 0.05% to 0.15% Sb</i>
"N2"	<i>Similar to "N1" but with Ni above 0.5%</i>
"O"	<i>As between 0.50% and 1.25%; Ni below 0.2%; Sb; Ag around 0.10% and 0.20%</i>
"P"	<i>As between 0.1% and 0.4%; Ni between 0.10% and 0.30%, 0.05% to 0.10% Co; Trace Sb</i>
"R"	<i>Ni only principal impurity</i>
Late Bronze Age	
"S"	<i>Principal impurities are: As, Sb, Ni, Ag. Both As and Sb are generally over 0.40 to 0.50% with 0.25% Ni and 0.25% Ag. Sub-groups are defined by the ratios of Sb to As. "S1" with Sb:As = 1:1; "S2" with Sb:As = 2:1</i>
"T"	<i>Similar in character to "S" but with lower levels of impurities, all below 0.40%</i>

Table 3:

Northover's chemical classifications of Early, Middle and Late Bronze Age European metals (Northover 1980, 230–231).

One factor contributing to the lack of consistency between the results of all of these projects is that each group of researchers derived their own methodology for separating out ‘chemical groups’—initially variations on the themes of ‘decision trees’, with break-points for particular elements calculated from the distributions of each element, and latterly based on cluster analysis. A system that combines the most consistent features of all of these previous ‘decision tree’ type studies is that developed by Northover (1980: see **Table 3**), which has become the most widely used classificatory system in recent western European metallurgy. Noting the issues over interpretational differences between major analytical programmes, Ernst Pernicka, one of the leading archaeometallurgists of the last few decades, has concluded that this lack of consistency is due to insufficient attention being given to the geochemistry and metallurgical behaviour of the trace elements. He asserted that by applying careful consideration to these factors, reliable provenance determinations can be made (Pernicka 1999). He noted the lack of consensus about what conclusions archaeologists can draw from these major European programs of chemical analysis of Bronze Age metalwork, and stated that “[*T*]race element analysis of ancient metal objects was so discredited that for some time hardly anybody looked at the data available” (Pernicka 1990, 169). He emphasised that, for sound geochemical reasons, not all trace elements can be taken as reliable indicators of provenance, and concluded (as Chernykh had done in the 1960s) that only those which follow copper in the smelting process (as opposed to concentrating in the slag phase) are likely to be reliable in provenance studies. The most widely reported of these elements are As, Sb, Ni, Ag and Bi, although even some of these can also be partially affected by subsequent technological processing. He also considered the volatility of some of these elements, and noted that when smelting sulfosalts from Cabrières in southern France, primarily tetrahedrite ((Cu,Fe)₁₂Sb₄S₁₃) but with some tennantite (Cu₁₂As₄S₁₃), the Sb was significantly lost during smelting, whereas As, which is more volatile under oxidation than Sb, was lost proportionately less because it is present at lower levels.

Lead isotopes

Largely because of the growing scepticism concerning the use of trace elements for determining the provenance of copper alloy objects, during the 1980s archaeologists enthusiastically adopted the newly developing technique of lead isotope analysis. Brill and Wampler (1967) had shown that it was possible to differentiate the lead from Laurion in Greece from that obtained in England and Spain by using measurements of the lead isotope ratios. They did note, however, that an ore sample from north-eastern Turkey fell into the same ‘isotope space’ as that occupied by three ores from England, thus suggesting that not all ore deposits

had unique isotopic signatures. The scope for using lead isotopes was widened once it was realised that not only could it be applied to metallic lead artefacts (which are, archaeologically speaking, rare), but also to the traces of lead left in silver objects extracted from argentiferous lead ores by cupellation (Barnes *et al.* 1974). However, its full potential was subsequently developed following the discovery that it could also be applied to the traces of lead remaining in copper objects smelted from impure copper ores (Gale and Stos-Gale 1982). This latter discovery potentially provided archaeometallurgists with a powerful new tool to provenance copper alloys, but unfortunately it became somewhat bogged down in controversies over the interpretation of the data during the 1990s (see, for example, Pollard 2009). A re-thinking of the use of lead isotopes in archaeological copper alloys is presented in Chapter 6.

Beyond Provenance?

The title of this volume is intended to be provocative, and is aimed at encouraging archaeometallurgists to think beyond the simple question of ‘provenance’—taken here to mean ‘where does this metal originally come from?’—and to focus more on the causes of change within the archaeometallurgical record, which includes provenance but goes much wider. As shown above, the chemical analysis of archaeological copper alloy objects began in Europe more than two hundred years ago, and there have been several major analytical programmes of European Bronze Age metalwork during the 20th century. There can be no doubt about the immense contribution made by all of these projects and others, not least of which is the publication of the chemical analyses of at least 50,000 Bronze Age metal objects, mostly from Europe, but with a significant number from the Caucasus, the Urals and Central Asia. Nevertheless, this rich data legacy also presents us with several challenges. Can we afford to ignore such a large corpus of data, simply because it does not conform to modern standards of analytical quality? We could choose to restrict ourselves only to data produced after, let us say, the year 2000, using methods such as the electron microprobe or inductively coupled plasma–mass spectrometry (ICP–MS), but to do so would be to severely reduce the volume and geographical spread of the available data. An alternative, and the approach taken here, would be to develop an interpretative protocol which can accommodate the obvious shortcomings in some of the data. This vast legacy of data, without which we could not have begun to undertake the project which underpins this volume, provides the foundation for the methodological developments presented here. The original interpretations of these data, although perhaps now in need of review,

have set the benchmark for the development of modern archaeometallurgy, and have provided insights about the exploitation patterns of copper in the Bronze Age which continue to be used today (e.g., Thornton and Roberts 2014).

In a recent valuable summary of the current state of affairs in European archaeometallurgy, Radivojević *et al.* (2018) demonstrate the deep hold that the concept of provenance still has on the minds of many European archaeometallurgists. This is most clearly seen in the conclusion, which states that the purpose of archaeometallurgical research has been to “address archaeological questions of alloy selection, development, distribution, and provenance, the latter long considered the ‘Holy Grail’ of the discipline.” Despite the generally negative view, as expressed by Ottaway and others, of the usefulness of chemically provenancing metals to specific ore sources when it is applied as a “black box” technique, there can be no doubt that when focussed on a specific region and carried out in combination with a detailed holistic view of the ore mineralogy and metal smelting debris, provenance studies can produce significant results (e.g., Stöllner and Samašev 2013). To be done well, however, such work is extremely time-consuming, since it requires considerable archaeological and geological fieldwork, combined with a very large number of chemical, metallographic and petrological analyses. We outline a different option, as explained in Chapter 2, which is to suggest that in some circumstances provenance may not be the only, nor perhaps the most meaningful, archaeological question to be asking.

Radivojević *et al.* (2018) also point to the increasing practice of hoarding metal in Europe from the mid-second millennium BCE onwards, and associate this with increased metal recycling. They note that: “*how to recognize recycling and determine when and the degree to which it occurred is a promising research area*”. Many of the previous studies (with the notable exception of Chernykh) have either ignored completely the potential complexities arising from the mixing or recycling of metal from different sources, or have acknowledged that such practices would invalidate the simple hypothesis of provenance, but have then largely dismissed the problem. Crucially, what is not yet clear is the balance between situations where traditional provenance is meaningful and achievable, and situations where, because of intense recycling, it is not. We argue in Chapter 2 that this balance is likely to be different over time and place, and even between classes of object. In other words, there will be circumstances in which a ‘traditional’ approach to provenance is worthwhile, and those where it is not. We have focussed our attention on developing methodologies to address this latter situation, but we should note that the methods developed here to consider such complex circumstances work equally well in situations where provenance is meaningful, and therefore nothing is lost by taking such an approach. Furthermore, given the plethora of mutually

exclusive interpretational methods applied to chemical data in the past, another of our objectives has been to provide a ‘universal’ system for approaching the initial classification of chemical data. This is not to imply that the *archaeological* contexts and interpretations are universally similar, but merely to say that the initial methodological approach to the data is the same wherever the data originate, and that new data can be added without requiring complete recalculation of the results.

Archaeology has progressed much since the launch of the major analytical programmes on copper alloy artefacts in the 1930s and 1940s, and certainly since the idea of determining the provenance of archaeological artefacts by chemical means was first articulated in the 1860s. Our questions have evolved from the apparently simple, but in fact quite complex, one of “*whether there are any means of recognizing the locality from which the metal in a given copper object was obtained*” (Coghlan *et al.* 1949), to a set of more complicated and socially-embedded questions about how humans actually *used* and *circulated* metal objects (see, for example, Kienlen 2013). As summarized by Radivojević *et al.* (2018), modern views on the history of metal use have evolved considerably from the early assumptions driven by either technological or geological determinism. The older vision of bronze reflecting a static sequence of ‘metal industries’, as articulated by Childe and others, has been replaced by ideas of a “*dynamic ‘metallurgical landscape’ during the European Bronze Age, with numerous local and regional metal producers feeding the demand for metal*” (Radivojević *et al.* 2018).

Our approach, as explained in Chapter 2, is an attempt to visualize this much more fluid world. It entails understanding not only the life history (*object biography*) of individual objects, but also emphasizing the characteristics of *assemblages* of objects, and consequently the life history of the flows of metal from which these objects were made. To use a simple analogy, if we think of the extraction of metal and the manufacture of an artefact, then this is merely the ‘birth’ of the artefact, which might subsequently go on to have a long and varied life history. A focus on provenance then becomes analogous to thinking that the only factor of importance in a person’s life is where he or she was born. We aim to show that the chemical and isotopic composition of assemblages of objects contain patterning which can potentially reveal not only the ‘birthplace’ of such objects (i.e., the provenance), but also other significant events in their life history. Sometimes these events might render the determination of provenance difficult if not impossible, if they involve the mixing of metal from more than one source, or the recycling of objects. Nevertheless, we would argue that valuable information (and indeed, archaeologically speaking, information potentially even more valuable than provenance) can be derived from a chemical study of the life history of these objects, which is, of course, a history of the interaction between objects

and humans. Put simply, we believe that the focus of the interpretation of chemical and isotopic data from archaeological copper alloys should start with detecting *change* in the material record, rather than concentrating solely on determining the *source* of the metal. After all, the basic methodology of archaeology is to detect and interpret change in the archaeological record. Our aim here is to show how we might build upon and add to the achievements made during the earlier phases of archaeometallurgical study, by developing a new set of methodologies based on these ideas, which ultimately aim to put the use of metal more firmly into its social context.