The Development of Metallurgy in Western Anatolia, the Aegean and Southeastern Europe before Troy

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Abstract: In the Near East copper has been worked and used since ca. 10,000 years ago and it was long assumed that the knowledge and practice slowly diffused to southeastern Europe and beyond, analogous to the Neolithic lifestyle. However, the evidence for this is scarce if not nonexistent. When radiocarbon dates of the southeastern European Chalcolithic demonstrated that abundant metal usage was earlier than in western Anatolia, C. Renfrew proposed a totally independent discovery and development of metallurgy in this region. The discovery of two Chalcolithic copper mines at Aibunar in Bulgaria and Rudna Glava in Serbia seemed to confirm this hypothesis. However, no evidence for smelting was found and chemical and lead isotope analyses have shown that none of the analysed Chalcolithic copper objects can be correlated to the ores of Rudna Glava. Accordingly, a somewhat intermediary model was proposed in which the spread of metal usage and production was explained by the acquisition of metal objects as 'exotica' and often by the movement of people possessing metallurgical expertise. Since the production techniques and object forms used in each early region mostly reflect local standards, this is seen as a process of incorporation and innovation by the communities involved rather than a straightforward or inevitable adoption. Such a model inherently raises the question of contacts between neighbouring regions and, indeed, new finds in the Aegean and in western Anatolia have come to light that may be relevant for this discussion. The paper will summarise the new evidence of metal production and distribution in the 5th and 4th millennia and discuss possible interactions between these regions.

Keywords: Western Anatolia, Aegean, southeast Europe, Copper Age, metallurgy

Beginning of Metal Usage

There is overwhelming evidence that the earliest use of metal, respectively copper, occurred in the Fertile Crescent roughly contemporaneously with the transition to sedentary life. This may be somewhat surprising because gold is generally known to occur as metal in nature and seems to be much more conspicuous than copper. One reason may be that large gold nuggets are much rarer than those of native copper. Furthermore, there is not a single gold deposit known in the Fertile Crescent. On the other hand, since both metals do occur in nature one may well ask why they were used so late in the history of mankind. It seems that they did not offer any practical or aesthetic use for Palaeolithic hunters and gatherers. This is not to say that colours were not appreciated in this period. Indeed, red pigments, especially, were actively sought after since the Middle Pleistocene[2] and even extracted by underground mining in the Upper Palaeolithic on the island of Thasos in the northern Aegean.[3] Its use for covering buried individuals, e.g., the Gravettien burial of two infants,[4] clearly shows that the colour red was associated with blood and, thus, carried an enormous symbolic value. However, the colours green and blue do not appear to play a role in this concept as is demonstrated by Palaeolithic cave paintings where only yellow, red and black pigments were used (red and yellow ochre, hematite, manganese oxide and charcoal).

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2 Marean et al. 2007.

3 Koukouli-Chrysanthaki – Weisgerber 1999.

4 Einwögerer et al. 2008.

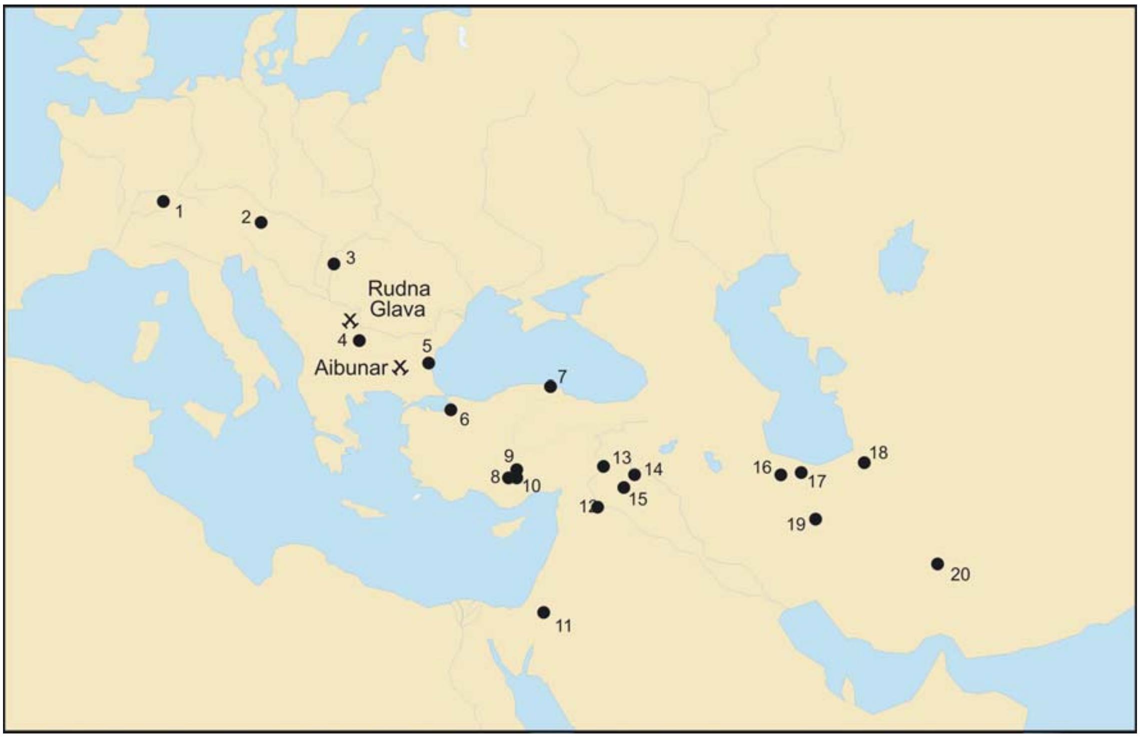

Fig. 1 Sites mentioned in the text: 1. Cortaillod; 2. Mondsee; 3. Herpaly, Hodmezövasarhely-Gorzsa; 4. Belovode, Majdanpek; 5. Varna; 6. Ilıpınar; 7. İkiztepe; 8. Can Hasan; 9. Aşıklı Höyük; 10. Çatal Höyük; 11. Nahal Mishmar; 12. Habuba Kabira; 13. Norsuntepe; 14. Çayönü, Hallan Çemi; 15. Yarim Tepe; 16. Chesmeh Ali; 17. Tepe Zageh; 18. Tepe Hissar; 19. Arisman; 20. Tal-i-Iblis.

This changed decisively around 10,000 BC when varieties of green stones were used for pendants and other jewellery, mainly beads so that their appearance is even considered a hallmark of the pre-pottery Neolithic of the Near East.[5] Since many oxidised copper ores are green, this provided the possibility that occasionally native copper was also collected by chance. At one of the earliest sites where native copper was worked, namely Çayönü in eastern Anatolia (Fig. 1), many more malachite beads than beads of native copper were found. The identification of native copper was accomplished by metallography[6] and the detection of trace element patterns in the copper finds.[7] Moreover, it was found that the native copper lumps were hammered into foils to produce rolled beads by applying intermittent heating,[8] which technically makes sense because on deformation copper becomes hard and brittle and tends to crack. Annealing makes it soft and ductile again. The application of heat to stone material should be no surprise. Heated stones were used for cooking and heat was applied to alter the mechanical properties of stones, e.g., for cleaving. However, the application of elevated temperatures (a few 100°C are easily achieved in an open fire) to copper minerals changes their colours, first from green to black and occasionally even to red under reducing conditions. This was certainly observed and may have provided the stimulus for more experimentation until eventually copper ores could be reduced to copper metal. The decisive role of colours for the beginning of metal usage was

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5 Bar-Yosef Mayer – Porat 2008.
6 Muhly 1989.
7 Pernicka, unpublished analyses.
8 Annealing in metallurgical terms, also identified at slightly later Aşıklı Hüyük, Yalçın – Pernicka 1999.

already formulated in the 1980s by Gerd Weisgerber and the author[9] and has recently been re-examined without referring to earlier literature.[10]

It is much less clear, where and when this decisive step towards pyrometallurgy proper was made and if it was a unique invention or if it occurred at several locations at different times independently. One thing is clear though: It cannot have been a chance discovery in an open campfire, because the reduction of copper oxides requires high temperatures of more than 1100°C, beyond the melting temperature of 1083°C, and reducing conditions with oxygen largely removed. Such conditions are best achieved in a closed reaction vessel but experiments have shown that, in principle, it is also possible to reduce copper with low yields in an open crucible under a charcoal cover. In the early Neolithic settlement of Çatal Höyük in central Anatolia, copper ore displaying signs of strong heating was recovered from layers dating to the 7th millennium BC. However, it is unclear if the heating was due to destruction by fire or intentional. In any case, all copper finds investigated so far consist of native copper.[11]

Beginning of Pyrometallurgy

Unequivocal evidence for the transformation of ores to metal is the occurrence of metallurgical slag and/or slagged crucibles. Such finds are presently only known from the 5th millennium BC creating a gap of more than three millennia between the earliest working and the smelting of copper. It is suggested that the subsequent step for melting copper was caused by excessive annealing.[12] The foremost evidence for this hypothesis comes from a mace head from Can Hasan in southeastern Turkey that was dated to around 6000 BC. The thick hole of the mace head could not have been produced by drilling; therefore, it was concluded that it must have been created by casting, which of course requires the melting of copper. However, it was later shown that the mace head was made from a large chunk of native copper similar to a large copper bead.[13] Another hypothesis suggests that lead may have guided the way to smelting.[14] Other than copper and gold, lead practically does not occur as metal in nature. If lead metal is found in early archaeological contexts, it is by itself evidence for the smelting of ores. Furthermore, lead is much easier to reduce from its major mineral, galena (PbS), and melts at a much lower temperature, namely 327°C. Accordingly, it is conceivable that liquid lead metal may have been produced accidentally in an open fire. Such an incidence would certainly not have passed unnoticed and may have shown the principle of smelting. In this context, the lead bangle from Yarimtepe I in northern Iraq, dated to the 6th millennium BC is of great significance. Galena was also found among the minerals at Çayönü and Çatal Höyük,[15] where it was made into elongated, drilled beads. Galena is a heavy, black, soft mineral with an intensive gloss and can easily be shaped with stone working techniques. Apparently it was occasionally used for ornaments; consequently, it is not so surprising that lead is the second metal to be worked by man.

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9 Pernicka 1995.

10 Roberts et al. 2009. Incidentally, there seems to be an error in the distribution maps of this article. In the legends areas denoted with different colours are described as >10,000 BC and so forth. This sign means ‘larger than’ and cannot be right. There is no real copper working before 10,000 BC. It probably should be written as <10,000 BC, which would mean ‘10,000 BC or younger’.

11 Birch et al. 2013.

12 Wertime 1964; Wertime 1973.

13 Yalçın 1998.

14 Krysko 1979.

15 Sperl 1990.

Origin and Spread of Pyrometallurgy

Besides the lack of information on the technological development of pyrometallurgy, it is also unknown, where it took place and if it happened more than once. It was long assumed that the knowledge and practice slowly diffused to southeastern Europe and beyond, similar to the Neolithic lifestyle. However, the evidence for this is scarce if not non-existent. When radiocarbon dates of the southeastern European Chalcolithic showed that abundant metal usage occurred earlier than in western Anatolia Colin Renfrew (1969) proposed a totally independent discovery and development of metallurgy in this region. The discovery of two chalcolithic copper mines at Aibunar in Bulgaria and Rudna Glava in Serbia seemed to confirm this hypothesis. However, no evidence for smelting was found; moreover, chemical and lead isotope analyses have shown that none of the analysed chalcolithic copper objects can be related to the ores of Rudna Glava. Accordingly, a somewhat intermediary model was proposed in which the spread of metal usage and production was explained by the acquisition of metal objects as 'exotica' and often by the movement of people possessing metallurgical expertise. Since the production techniques and object forms used in each early region mostly reflect local standards, this is seen as a process of incorporation and innovation by the communities involved rather than a straightforward or inevitable adoption.

In the 5th millennium BC, there are at least four regions in the Near and Middle East that have yielded evidence for early pyrometallurgy: i) In the Iranian highland west and south of Teheran (Tepe Zageh, Cheshme Ali), ii) another one in the southern foothills of the Zagros mountain chain (Tal-i-Iblis), iii) in southeastern Anatolia along the middle Euphrates in the Taurus mountains (Norşuntepe) and iv) in the Levant in the Jordan valley and the Arabah between the Dead Sea and the Red Sea (Nahal Mishmar, Feinan). Nahal Mishmar also provided some of the earliest evidence for lost-wax casting.

On the other hand, the earliest indication for copper smelting was recently reported from Serbia.[16] A small amount of copper slag was found near Belovode in contexts of the early 5th millennium BC, demonstrating that within one millennium we have a few indications extending over a very large area ranging from southeastern Europe until southern Iran (Fig. 2). It is hard to imagine that independent developments took place in this area within a relatively short time span, especially since it is known that the Neolithic package of cultural techniques spread out from the Fertile Crescent exactly over this area in the millennia before. In principle, the new discoveries in Serbia together with the still earliest copper mines of Rudna Glava in Serbia and Aibunar in Bulgaria could alter the direction of the presumed spreading of pyrometallurgy. Nevertheless, even the collective evidence is rather slim and may only be a snapshot of present knowledge.

A strong argument in favour of a monocentric origin of pyrometallurgy is supported by the fact that it is a rather complex technology that was not generally known but rather kept secret by a few specialists even in later periods. In addition, the shapes of the metal objects produced are quite similar as well as the installations for smelting, e.g., in Feinan in Jordan and Arisman in central Iran. Furthermore, the spread of pyrometallurgy in Europe shows a similar chronological drift from southeast to northwest similar to the spread of Neolithic subsistence two millennia earlier (Fig. 3). Consequently, metal production on the British Isles begins in the 3rd millennium BC while it is already flourishing in the 4th millennium BC in central Europe.

Early Gold Metallurgy

Although according to present knowledge lead appears earlier than gold in the archaeological record, it did not have an impact on the use of other metals. It became more abundant only when it was discovered that it often contains silver, but mainly as waste or cheap and little useful material

16 Radivojević et al. 2010.

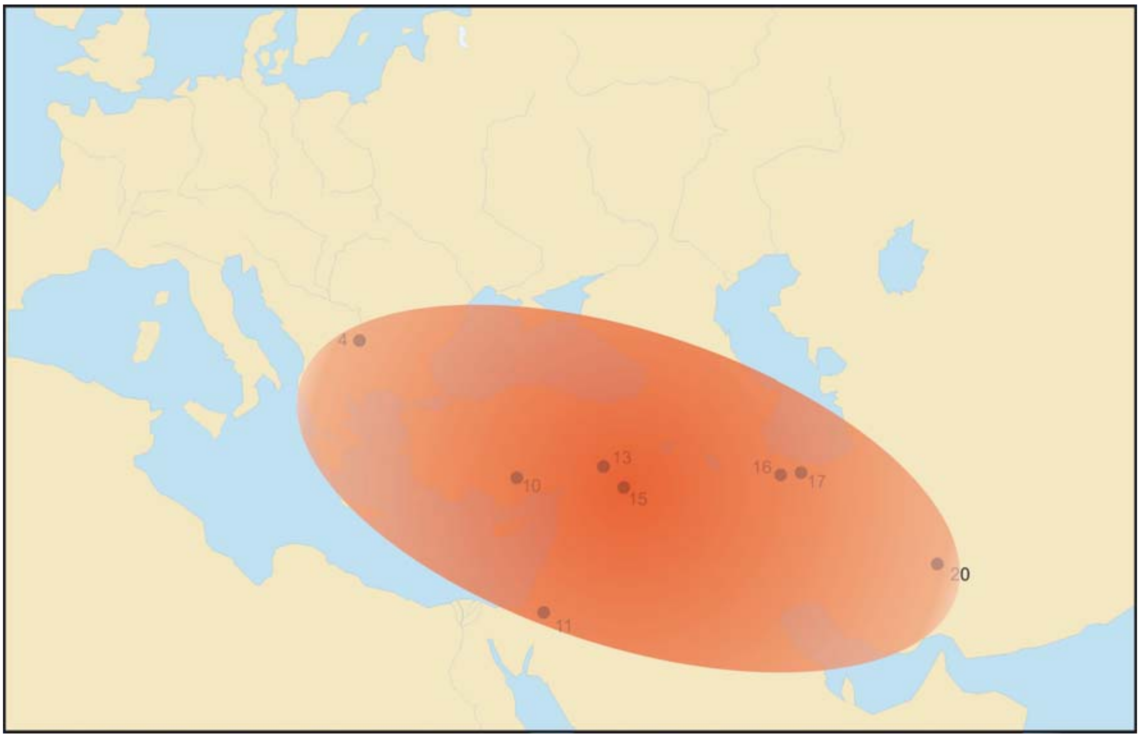


Fig. 2 Sites with proven or possible evidence for smelting in the 5th millennium BC.

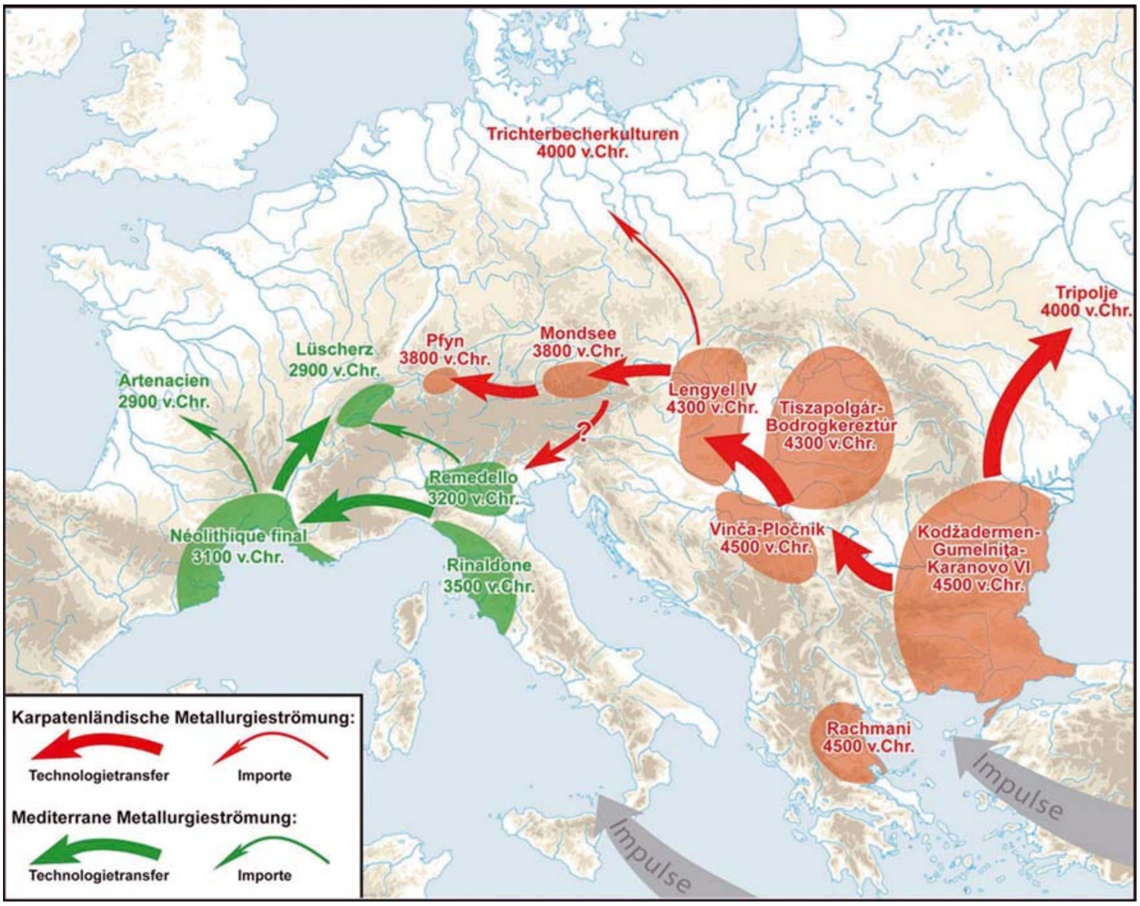


Fig. 3 Spread of metallurgy in Europe (after Strahm 2012, 28, fig. 1).

(see below). However, when gold was added to the range of metals available, it was apparently considered as valuable from the beginning and a material used to display rank and status. It also appears in rather large quantities in the burial site of Varna I on the Black Sea coast dated to the second half of the 5th millennium.[17] More than 300 burials were excavated, which contained altogether more than 3000 gold objects comprising some 6kg gold. This spectacular entry of gold into the cultural history is the more extraordinary considering that the number and masses of the gold objects are unequally distributed to a few burials containing more than 90% of the objects and more than 99% of the gold. It has frequently been suggested that this may indicate a hierarchically organised early society whose members wanted to display their wealth and rank. From the metallurgical point of view, it appears that, within the short period of use of the burial site a development from small and simple forms to elaborate and technologically challenging ones becomes visible. The latter were certainly cast by various techniques including lost-wax casting and even intentional alloying of gold with copper and represent the earliest evidence for the intentional mixing of metals to alter their properties.[18]

Copper was also cast although this is substantially more difficult with pure copper, since molten copper absorbs oxygen, which it releases on cooling. This produces gas bubbles that can cause major defects in the finished product. However, it was nevertheless mastered as indicated by biconvex shapes such as the axe adzes produced in southeastern Europe in great numbers beginning in the 5th millennium BC. Such shapes require at least bivalve moulds and some complex shapes can only be made by lost-wax casting. In this period metal objects are rare in the Aegean and in western Anatolia and the few that are known are typologically related to the Balkan region. This seeming geographical gap in the distribution of metal finds between southeastern Anatolia and beyond and southeastern Europe led to the suggestion of an independent development of metallurgy there.[19] During the last two decades, new research with new finds may eventually close this gap as it has already happened for the 4th millennium BC.

Copper Alloys

According to the present evidence it seems that copper was first alloyed with gold. By the end of the 5th millennium BC, pure unalloyed copper mainly used for the production of ornaments and implements was replaced by copper rich in arsenic. This type of copper is usually termed 'arsenical copper', because it is unclear and disputed if it represents an actual alloy, i.e. the intentional mixture of metals. The advantages of this new material were at least twofold: It is substantially harder and it has much better casting properties than pure copper. In addition, high arsenic concentrations changes the colour to a silvery appearance.

After the climax of metal production during the late 5th millennium BC comes a period that is remarkably poor in metal finds in southeastern Europe as well as in the Aegean. However, shortly thereafter arsenical copper appears as a new material almost simultaneously from the Near and Middle East to central Europe (Mondsee, Cortaillod).[20] According to Chernykh, Aviloval, Borceva and Orlovskaja[21] this marks the restructuring of cultural relations between Anatolia and Europe that led to the formation of the so-called Circumpontic Metallurgical Province, extending into Iran and central Asia as we now know (Fig. 4). Until recently, the only evidence from western

17 Ivanov 1991.
18 Leusch et al. forthcoming
19 Renfrew 1969.
20 Sangmeister 1971; Schubert 1981.
21 Chernykh et al. 1991 describe the distribution of arsenical copper in what they term Early Bronze Age and include the Kura-Araxes and the Maikop cultures. However, this terminology is only consistent with the EB1 period in eastern Anatolia, which already begins in the second half of the 4th millennium BC.

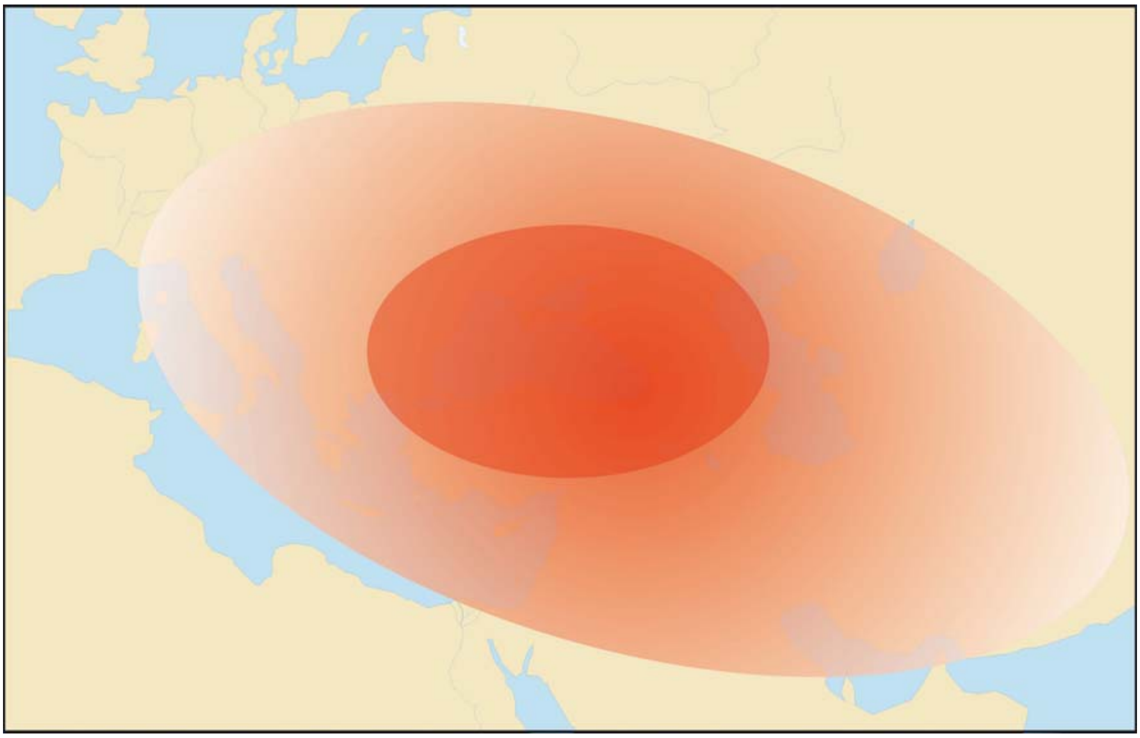


Fig. 4 Distribution of arsenical copper in the 4th millennium BC (outer ellipse). The inner ellipse roughly describes the extent of the Circumpontic Metallurgical Province according to Chernykh et al. (1991).

Anatolia for such a cultural and technological affinity is the metal finds from İkiztepe[22] and Ilıpınar[23] that consist almost exclusively of arsenical copper and the earliest of which also date to the middle of the 4th millennium BC.

There has been a long debate whether arsenical copper was produced by deliberately adding arsenic to copper or, for that matter, as-rich ores to copper ores, or whether a mixture of the two just happened to be available. The main arguments for an accidental production was the observation that there was little control of the arsenic concentrations, which range roughly between 0.5 and 5% (Fig. 5) and the fact that minerals containing arsenic are often present as minor components in copper deposits. This is not to say that the superior qualities of arsenical copper went unnoticed. It is certainly possible that copper ores containing arsenic were actively sought or that accidentally produced arsenical copper was selected by some kind of material testing and used for specific purposes.

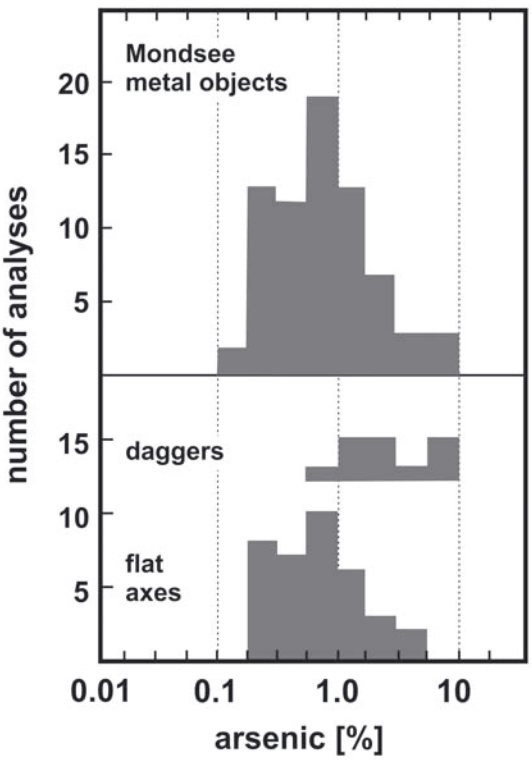


Fig. 5 Concentrations of arsenic in metal objects of the Mondsee group dated to the middle of the fourth millennium BC. Practically all objects consist of arsenical copper with arsenic ranging between 0.5 and 5%. Daggers generally contain more arsenic than the average.

22 Bilgi 1984; Bilgi 1990.
23 Begemann et al. 1994.

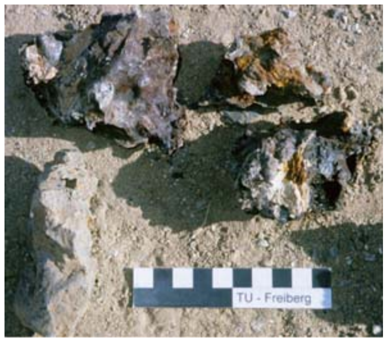
A  B  C 

Fig. 6 A. Slag heap in area A at Arisman in central Iran dated to the beginning of the third millennium BC. B. Typical 'green' slag of Arisman A with green stains of oxidised copper. C. 'Brown' slag of Arisman A with stains of iron oxides.

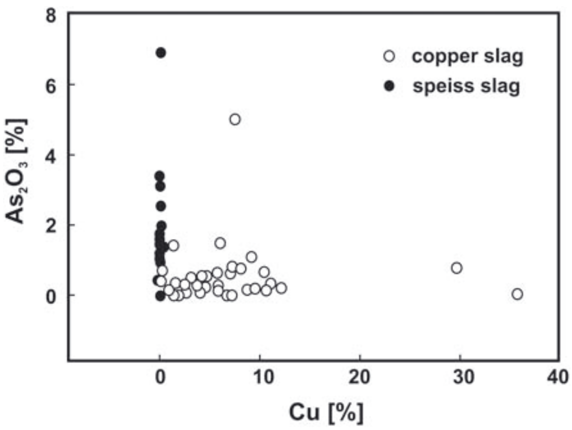


Fig. 7 Copper and arsenic concentrations 'green' and 'brown' slag from Arisman A. The 'green' slag is from copper production and generally has low con entrations of arsenic while the 'brown' slag virtually contains no copper but considerable concentrations of arsenic which is due to inclusions of small droplets of *speiss.*

Less controversial is the notion that the ancient metalsmiths were aware of the superior mechanical qualities and, of course, the different colour of arsenical copper. This is borne out by the observation that frequently daggers and axe blades were considerably re-worked after casting which increases their hardness decisively. In fact, as a weapon the geometrical form of a dagger makes sense only when using a hard material like arsenical copper and it is certainly no coincidence that such daggers appeared for the first time together with the first appearance of the new metal.

The metallurgical problem lies in the high volatility of arsenic (sublimation point 615°C) so that – other than tin metal – it cannot be added directly to molten copper although the element also occurs in nature. Previous research has shown that a number of different routes could lead to arsenical copper, including the smelting of fahlore,[24] the co-smelting of native copper and copper-arsenide minerals,[25] and the conscious addition of an arsenic-rich mineral, such as realgar/orpiment, arsenopyrite or löllingite, to copper metal or copper ore.[26] More recently, Thornton and others[27] proposed that an artificial iron-arsenic alloy, called *speiss*, was produced in Early Bronze Age Tepe Hissar, north Iran, presumably to be added to copper metal for the production of arsenical copper. Rehren, Boscher and Pernicka[28] found that this material was produced in large quantities at Arisman side-by-side with copper in a different process (Figs. 6–7), accordingly, it appears that the majority of arsenical copper was produced intentionally. Arsenopyrite (FeAsS) is the most frequently occurring arsenic mineral that is occasionally found as an accessory mineral in copper deposits but more often in hydrothermal veins together with gold and tin. At Arisman, it was apparently not co-smelted with copper ores but smelted separately to form *speiss*. The reason for this seemingly more elaborate procedure may have been a better efficiency and at least some con-

24 Lechtman – Klein 1999.
25 Budd et al. 1992.
26 Heskel 1983; Thornton et al. 2002.
27 Thornton et al. 2009.
28 Rehren et al. 2012.

trol in adding arsenic to copper. This suggests a fundamental progress in the understanding and control of metallurgical processes already in the 4th millennium BC. The motivation for this development could have been the introduction of the dagger.

Again the question arises if the development from the use of pure copper to arsenical copper was more or less unavoidable and could have taken place independently in different regions or if this new knowledge was acquired in a single region and spread out from there. The coincidence in time and space of this new technology clearly favours the latter model. Subsequent to any technical breakthrough leading to the discovery or invention of a previously unknown material, or one with superior qualities, a lively trade in the new commodity can be expected to develop between its place of invention and production and more or less distant customers. However, considering that ideas travel more lightly than material goods and assuming that reasons not to keep a technical secret in its place of origin will always exist, the monopoly in the production of such materials or goods could presumably never be maintained for long. Competing production centres will come into being wherever required raw materials are available and where there was a need, or where such a need could be created, for the new material. Indeed, *speiss* could have been traded in its own right for alloying purposes like tin metal. Incidentally, since arsenic commonly occurs together with gold and tin it is conceivable that this combination may have eventually paved the way to tin smelting and consequently to the production of tin bronzes.

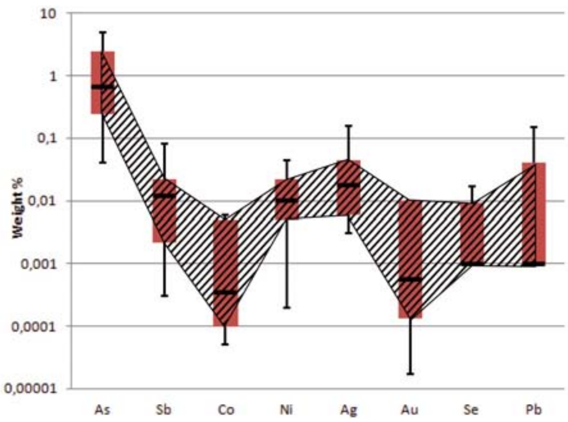


Fig. 8 Chemical ‘fingerprint’ of the metal objects of the Mondsee group. The shaded area encompasses the area of the boxplots showing 80% of the measured values for each element. The protruding antennae indicate the whole range of the measurements; the black horizontal bar indicates the median value for each element.

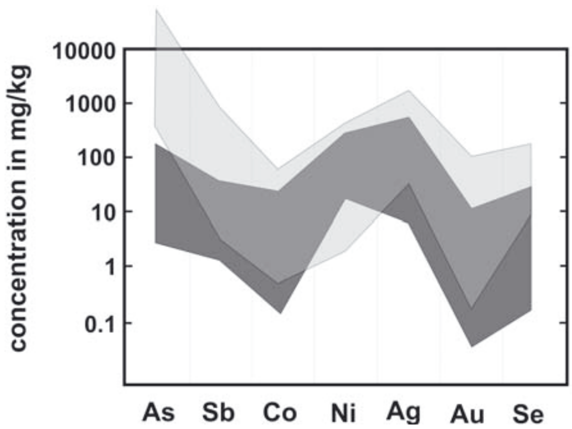


Fig. 9 Comparison of the trace element pattern in chalcolithic copper objects from Serbia and Bulgaria which can be related to the copper deposit of Majdanpek (dark area) with copper objects of the Mondsee group (light grey area with the total spread of concentrations from Fig. 8).

This raises a problem for the discussion of metal provenance studies, because the trace element patterns and the lead isotope ratios are a mixture of two different materials which need not come from the same deposit. This example resembles the discussion on provenance determination of tin bronze and similar arguments apply to arsenical copper. There are no systematic trace element analyses of arsenopyrite but as common impurities Ag, Au, Co, Sn, Ni, Sb, Bi, Cu, and Pb are mentioned. Unfortunately, these are the same elements that are used for the classification of archaeological copper artefacts. On the other hand, most prehistoric metal objects consisting of arsenical copper have low concentrations of impurities (Fig. 8), like the 4th millennium BC artefacts of the Mondsee cultural group[29] and of Ilıpınar in northwest Anatolia.[30] If those objects were made from copper that was alloyed with arsenic by the

[29] Frank – Pernicka 2012.

[30] Begemann et al. 1994.

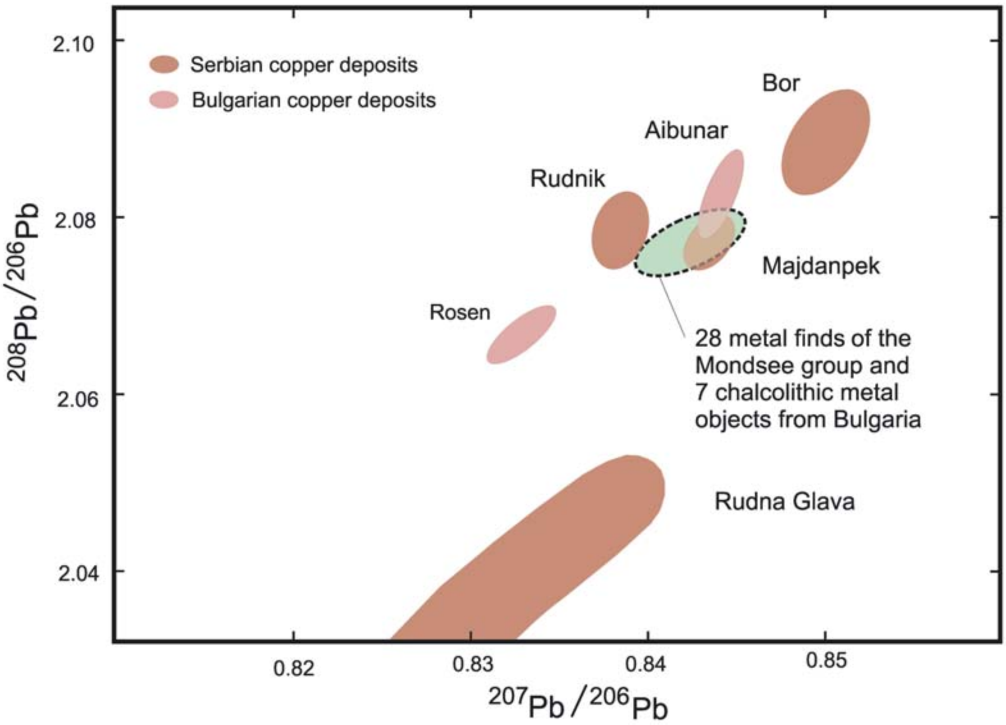


Fig. 10 Lead isotope ratios of copper deposits in Serbia and Bulgaria and of metal artefacts of the Mondsee group. Almost all analysed metal objects are more or less consistent with Majdanpek. The slightly extended range of Mondsee artefacts may be due to alteration of the lead isotope ratios by the addition of arsenic.

addition of *speiss* then we may assume that arsenopyrites generally have low levels of impurities or that they are not completely absorbed by the molten copper. This may also apply for lead and tin bronze; one may conclude that the lead isotope ratios in arsenical copper are dominated by the lead from copper and not from the *speiss*. For the metal artefacts of the Mondsee group no good match with copper ores of the east Alpine region has been observed, neither in trace element composition nor in lead isotope ratios. Typological aspects and the distribution of arsenical copper in the 4th millennium BC suggest an origin from southeastern Europe. The best isotopically matching copper ores from this region are from Majdanpek in Serbia, a very large deposit that was exploited as early as the 5th millennium BC.[31] The copper produced from those ores was rather pure and assuming that only arsenic was added then the trace element pattern of the Mondsee metal would also fit (Fig. 9). In this case, the lead isotope ratios may also have been slightly modified, which may explain the not so perfect fit of Majdanpek ores with Mondsee copper (Fig. 10).

At the beginning of the 3rd millennium BC, arsenical copper began to be replaced by a copper tin alloy, usually called bronze or, better, tin bronze.[32] It is still not clear where and why this happened because the material properties of arsenical copper and tin bronze are rather similar. One reason may be related to the aesthetic appearance of the alloy, particularly because its gold colour. Another incentive may be the better control of the composition of the alloy as indicated by recipes on cuneiform tablets from Mesopotamia, which archive the exact weight proportions for the production of tin bronze. Recently it has been suggested that tin bronze may have already

[31] Pernicka et al. 1993.

[32] In modern metallurgical terms, any alloy with copper as the major component is called 'bronze' except the alloy of copper and zinc which is brass. Accordingly arsenical copper could be called bronze or arsenic bronze. To avoid ambiguity it has become common practice in archaeology to call the alloy of copper with tin 'tin bronze' and the alloy of copper with arsenic 'arsenical copper'.

been produced in the 5th millennium BC.[33] However, this suggestion is presently based on a single well stratified find which may be an accidental product of copper ore containing some tin. Low concentrations of tin were also recorded in three chalcolithic copper finds from Herpaly and Hodmezövasarhely-Gorzsa in Hungary[34] but the contexts are not beyond doubt. Nevertheless, this is certainly not a solid basis for postulating a "polymetallic (r)evolution of the 5th millennium BC".[35] If the archaeological contexts and thus the dating of these finds with unusually high tin concentrations should stand up against scrutiny, (none of them can be dated typologically) then one must keep in mind that these very early tin bronzes had no impact at all, neither to the metallurgical practices nor on the early societies.

Silver

The present evidence shows that silver was first used in the Near East. It is unclear, exactly where, and when it appeared, but the distribution of silver objects seems to 'conform to a pattern, similar in type to that of lapis lazuli distribution in the late fourth and early third millennia'.[36] It is worth noting that the appearance of silver objects coincides with an increasing number of lead artefacts, both in space and time, suggesting that silver may have been produced from argentiferous lead ores from the beginning, even though metallic silver does occur in nature. However, native silver is infrequently found as large lumps but rather in the form of wires with dull surfaces. This is due to the sulphide or chloride coating of the material. Consequently, its lackluster may not have attracted ancient metallurgists. Alternatively, silver could be produced from argentiferous lead ores in a two-stage process. It is a moot point to discuss, if cerussite (lead carbonate) was used, as suggested by Wertime (1973), or for that matter galena (lead sulphide). Both lead ores would have to be smelted under reducing conditions to produce argentiferous lead, from which silver would have to be separated by selective oxidation. This process, called cupellation, produces silver with a trace element pattern that is different from native silver. While cupelled silver always contains at least a few tenths of a percent lead, the concentration of this element is usually much lower than in native silver. On the other hand, native silver that is generally rather pure, often contains measurable quantities of antimony and mercury which are rarely detectable in silver derived from cupellation.[37]

The principles of the ancient metallurgy of silver are well known,[38] and it is generally assumed that cupellation was already practiced in the 4th millennium BC.[39] At least two sites, Habuba Kabira in northern Syria[40] and Fatmalı-Kalecik in eastern Anatolia, have produced metallurgical debris from workshops that provide unequivocal evidence for the process in the middle of the 4th millennium BC.[41] At the beginning of the 3rd millennium BC cupellation was performed almost at an industrial scale at Arisman in central Iran.[42]

The earliest silver object has long been held to be a silver ring from Beycesultan, level XXlV,[43] that was dated by the excavators around 4300 BC.[44] However, two radiocarbon dates from levels

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33 Radovojević et al. 2013.
34 Pernicka, unpublished analyses.
35 Radivojević et al. 2013.
36 Prag 1978.
37 Pernicka 1987.
38 Bachmann 1993.
39 E.g. Moorey 1994.
40 Pernicka et al. 1998.
41 Hess et al. 1999.
42 Pernicka et al. 2011.
43 Lloyd – Mellaart 1962, 280–283.
44 See also Wertime 1973; Prag 1978.

XXVl and XXVIII, respectively, rather suggest that the correct date should be around the middle of the 4th millennium[45] or even as late as 3000 BC.[46] Another very early find that may date to the first half of the 4th millennium[47] has been reported from Tepe Sialk, level 111:5.[48] Several dozen silver objects from Uruk,[49] as well as finds from Susa,[50] from Korucutepe,[51] Alişar Hüyük[52] and pre-dynastic contexts in Egypt[53] may be contemporaneous or slightly later. Chronological complications surround more than 233 objects from the eneolithic cemetery of Byblos that were dated to 3880–3200 BC.[54] However, these dates are disputed, and other authors have suggested later dates ranging to the late 3rd millennium.[55]

There is no securely dated silver object for the 4th millennium BC in the Aegean. There is one find of silver from the Alepotrypa cave on the Mani peninsula on the Peloponnese that is sometimes dated early on typological grounds.[56] However, the hoard (two pairs of earrings, a pendant, a cylindrical bead and a necklace consisting of 168 small flat silver beads) was recovered before the systematic exploration of the cave commenced. Although the pendant resembles those made of gold in the Chalcolithic of southeastern Europe the necklace has its closest parallel with one from Louros on the island of Naxos, which is dated to EH 1.[57] Since lead appears only in the 3rd millennium in the Aegean[58] it seems that the knowledge of silver production from argentiferous lead ores was introduced into the Aegean from the east. Furthermore, silver did not reach southeastern and central Europe before the 1st millennium BC; therefore, there is no case for an indigenous development of this rather complex two-stage technology.

References

Bachmann 1993
H.-G. Bachmann, The archaeometry of silver, in: R. Francovich (ed.), Archeologia delle attività estrattive e metallurgiche. V Ciclo di Lezioni sulla Ricerca applicata in Archeologia, Certosa di Pontignano 1991 (Florence 1993) 487–495.

Bar-Yosef Mayer – Porat 2008
D. E. Bar-Yosef Mayer – N. Porat, Green stone beads at the dawn of agriculture, Proceedings of the National Academy of Sciences of the USA 105, 8548–8551.

Begemann et al. 1994
F. Begemann – E. Pernicka – S. Schmitt-Strecker, Metal finds from Ilıpınar and the advent of arsenical copper, Anatolica 20, 1994, 203–219.

Bilgi 1984
Ö. Bilgi, Metal objects from İkiztepe, Turkey, Beiträge zur Allgemeinen und Vergleichenden Archäologie 6, 1984, 31–96.

45 Kohlmeyer 1994.
46 Moorey 1994.
47 Kohlmeyer 1994.
48 Ghirshman 1938. 16–17.
49 Van Ess – Pedde 1992.
50 Thallon 1987.
51 Brandt 1978.
52 V. d. Osten 1937, 91.
53 Prag 1978.
54 Dunand 1973, 214–216.
55 See Kohlmeyer 1994 for a discussion.
56 Zachos 1996.
57 Branigan 1974.
58 Branigan 1974.

Bilgi 1990
Ö. Bilgi, Metal objects form İkiztepe, Turkey. Beiträge zur Allgemeinen und Vergleichenden Archäologie 9–10, 1990, 119–219.

Birch et al. 2013
T. Birch – T. Rehren – E. Pernicka, The metallic finds from Çatalhöyük. A review and preliminary new work, in: I. Hodder (ed.), Substantive Technologies at Çatalhöyük. Reports from the 2000–2008 seasons, Çatalhöyük Research Project 9 (London 2013).

Brandt 1978
R. W. Brandt, The other chalcolithic finds, in: M. N. van Loon (ed.), Korucutepe 2 (Amsterdam 1978) 61–63.

Branigan 1974
K. Branigan, Aegean Metalwork of the Early and Middle Bronze Age (Oxford 1974).

Buss et al. 1992
P. Budd – D. Gale – A. M. Pollard – R. G. Thomas – P. A. Williams, The early development of metallurgy in the British isles, Antiquity 66, 1992, 677–686.

Chernykh et al. 1991
E. N. Chernykh – L. I. Aviloval– T. B. Borceva – L. B. Orlovskaja, The circumpontic metallurgical province as a system, in: J. Lichardus – R. Echt (eds.), Die Kupferzeit als historische Epoche. Symposium Saarbrücken und Otzenhausen 6.–13.11.1988, Saarbrücker Beiträge zur Altertumskunde 55.2, 593–622.

Dunand 1973
M. Dunand, Fouilles de Byblos Y (Paris 1973).

Einwögerer et al. 2008
T. Einwögerer – M. Händel – C. Neugebauer-Maresch – U. Simon – M. Teschler-Nicola, The Gravettian infant burials from Krems-Wachtberg, Austria, in: K. Bacvarov (ed.), Babies Reborn. Infant/child Burials in Pre- and Protohistory. Proceedings of the 15th World Congress UISPP, Lisbon, 4th–9th Sept. 2006, British Archaeological Records, International Series 1832 (Oxford 2008) 15–19.

Frank – Pernicka 2012
C. Frank – E. Pernicka, Copper artifacts of the Mondsee group and their possible sources, in: M. S. Midgley – J. Sanders (eds.), Lake Dwellings after Robert Munro. Proceedings Munro International Seminar. The Lake Dwellings of Europe, 22th–23th October 2010, University of Edinburgh (Leiden 2012) 113–138.

Girshman 1938
R. Ghirshman, Fouilles de Sialk 1 (Paris 1938).

Heskel 1983
D. L. Heskel, A model for the adoption of metallurgy in the ancient Middle East, Current Anthropology 24, 1983, 362–366.

Hess et al. 1998
K. Hess – A. Hauptmann – H. Wright – R. Whallon, Evidence of fourth millennium BC silver production at Fatmalı-Kalecik, east Anatolia, in: Rehren et al. (1998) 57–67.

Ivanov 1991
I. S. Ivanov, Der Bestattungsritus in der chalkolithischen Nekropole von Varna (mit einem Katalog der wichtigsten Gräber), in: J. Lichardus (ed.), Die Kupferzeit als historische Epoche. Symposium Saarbrücken und Otzenhausen 6.–13.11.1988, Saarbrücker Beiträge zur Altertumskunde 55 (Bonn 1991) 125–149.

Kohlmeyer 1994
K. Kohlmeyer, Zur frühen Geschichte von Blei und Silber, in: R.-B. Wartke (ed.), Handwerk und Technologie im Alten Orient (Mainz 1994) 59–66.

Koukouli-Chrysanthaki – Weisgerber 1999
C. Koukouli-Chrysanthaki – G. Weisgerber, Prehistoric ochre mines on Thasos, in: C. Koukouli-Chrysanthaki – A. Muller – S. Papadopoulos (eds.), Thasos. Matières premières et technologie de la préhistoire à nos jours. Actes du Colloque International 26.–29. 9. 1995, Thasos, Liménaria (Paris 1999) 129–144.

Krysko 1979
W. W. Krysko, Blei in Geschichte und Kunst (Stuttgart 1979).

Lechtman – Klein 1999
H. Lechtman –S. Klein, The production of copper-arsenic alloys (arsenic bronze) by cosmelting. Modern experiment, ancient practice, Journal of Archaeological Science 26, 1999, 497–526.

Leusch et al., forthcoming
V. Leusch – E. Pernicka – R. Krauß, Zusammensetzung und Technologie der Goldfunde aus dem chalkolithischen Gräberfeld von Varna I (Ein Zwischenbericht), in: V. Nikolov (ed.), Der Schwarzmeerraum vom Neolithikum bis in die Früheisenzeit (6000–600 v. Chr.), Kulturelle Interferenzen in der Zirkumpontischen Zone und Kontakte mit ihren Nachbargebieten. Proceeding of the Humboldt Kolleg in Varna, Bulgaria, 16–20 May, 2012 (forthcoming).

Lloyd – Mellaart 1962
S. Lloyd – J. Mellaart, Beycesultan I. The Chalcolithic and Early Bronze Age Levels (London 1962).

Marean et al. 2007
C. W. Marean – M. Bar-Matthews – J. Bernatchez – E. Fisher – P. Goldberg – A. I. R. Herries – Z. Jacobs – A. Jerardino – P. Karkanas – T. Minichillo – P. J. Nilssen – E. Thompson – I. Watts – H. M. Williams, Early human use of marine resources and pigment in South Africa during the Middle Pleistocene, Nature 449, 2007, 905–908.

Moorey 1994
P. R. S. Moorey, Ancient Mesopotamian Materials and Industries (Oxford 1994).

Muhly 1989
J. D. Muhly, Çayönü Tepesi and the beginnings of metallurgy in the ancient world, in: A. Hauptmann – E. Pernicka – G. A. Wagner (eds.), Old World Archaeometallurgy, Der Anschnitt, Beiheft 7 (Bochum 1989) 1–11.

Pernicka 1987
E. Pernicka, Erzlagerstätten in der Ägäis und ihre Ausbeutung im Altertum. Geochemische Untersuchungen zur Herkunftsbestimmung archäologischer Metallobjekte, Jahrbuch des Römisch-Germanischen Zentralmuseums Mainz 34, 1987, 607–714.

Pernicka 1995
E. Pernicka, Gewinnung und Verbreitung der Metalle in prähistorischer Zeit, Jahrbuch des Römisch-Germanischen Zentralmuseums Mainz 37 (1990), 1995, 21–129.

Pernicka et al. 1993
E. Pernicka – F. Begemann – S. Schmitt-Strecker – G. A. Wagner, Eneolithic and Early Bronze Age copper artefacts from the Balkans and their relation to Serbian copper ores, Prähistorische Zeitschrift 68, 1993, 1–54.

Pernicka et al. 1998
E. Pernicka – T. Rehren – S. Schmitt-Strecker, Late Uruk silver production by cupellation at Habuba Kabira, Syria, in: Rehren et al. (1998) 123–134.

Pernicka et al. 2011
E. Pernicka – K. Adam – M. Böhme – Z. Hezarkhani – N. Nezafati – M. Schreiner – B. Winterholler – M. Momenzadeh – A. Vatandoust, Archaeometallurgical researches at Arisman in central Iran, in: A. Vatandoust – H. Parzinger – B. Helwing (eds.), Early Mining and Metallurgy on the Central Iranian Plateau. Report on the First Five Years of Research of the Joint Iranian-German Research Project, Archäologie in Iran und Turan 9 (Mainz 2001) 633–705.

Prag 1978
K. Prag, Silver in the Levant in the fourth millennium B.C., in: P. R. S. Moorey – P. J. Parr (eds.), Archaeology in the Levant – Essays for Kathleen Kenyon (Warminster 1978) 36–45.

Radivojević et al. 2010
M. Radivojević – T. Rehren – E. Pernicka – D. Šljivar – M. Brauns – D. Borić, On the origins of extractive metallurgy. New evidence from Europe, Journal of Archaeological Science 37, 2010, 2775–2787.

Radivojević et al. 2013
M. Radivojević – T. Rehren – J. Kuzmanović-Cvetković – M. Jovanović – J. P. Northover, Tainted ores and the rise of tin bronzes in Eurasia, c. 6500 years ago, Antiquity 87, 2013, 1030–1045.

Rehren et al. 1998
T. Rehren – A. Hauptmann – J. D. Muhly (eds.), Metallurgica Antiqua. In Honour of Hans-Gert Bachmann and Robert Maddin, Der Anschnitt, Beiheft 8 (Bochum 1998) 279–289.

Rehren et al. 2012
T. Rehren – L. Boscher – E. Pernicka, Large scale smelting of speiss and arsenical copper at Early Bronze Age Arisman, north-west Iran, Journal of Archaeological Science 39, 6, 2012, 1717–1727.

Renfrew 1969
C. Renfrew, The autonomy of south-east European Copper Age, Proceedings of the Prehistoric Society 35, 1969, 12–47.

Roberts et al. 2009
B. W. Roberts – C. P. Thornton – V. C. P. Roberts, Development of metallurgy in Eurasia, Antiquity 83, 2009, 1012–1022.

Sangmeister 1971
E. Sangmeister, Aufkommen der Arsenbronze in SO-Europa. Actes du VIIIe Congrès International des Sciences Préhistoriques et Protohistoriques 1 (Belgrade 1971) 131–138.

Schubert 1981
E. Schubert, Zur Frage der Arsenlegierungen in der Kupfer-und Frühbronzezeit Südosteuropas, in: H. Lorenz (ed.), Studien zur Bronzezeit. Festschrift für Wilhelm Albert v. Brunn (Mainz 1981) 447–459.

Sperl 1990
G. Sperl, Urgeschichte des Bleies, Zeitschrift für Metallkunde 81, 1990, 799–801.

Strahm 2012
C. Strahm, Kupfer: Netzwerke und Expansion, Archäologie in Deutschland 2, 2012, 28–30.

Thallon 1987
F. Tallon, Metallurgie susienne I. De la fondation de Suse au XVllle siècle avant J.-C. Notes et Documents des Musées de France H (Paris 1987).

Thornton et al. 2002
C. P. Thornton – C. C. Lamberg-Karlovsky – M. Liezers – S. M. M. Young, On pins and needles. Tracing the evolution of copper-base alloying at Tepe Yahya, Iran, via ICP-MS analysis of common-place items, Journal of Archaeological Science 29, 2002, 1451–1460.

Thornton et al. 2009
C. P. Thornton – T. Rehren – V. C. Pigott, The production of speiss (iron arsenide) during the Early Bronze Age in Iran, Journal of Archaeological Science 36, 2009, 308–316.

Van Ess – Pedde 1992
M. van Ess – F. Pedde, Uruk. Kleinfunde Band 11, Ausgrabungen in Uruk-Warka, Endberichte 7 (Mainz 1992).

Wertime 1964
T. A. Wertime, Man's first encounter with metallurgy, Science 146, 1964, 1257.

Wertime 1973
T. A. Wertime, The beginning of metallurgy, a new look, Science 182, 1973, 875–886.

Yalçın 1998
Ü. Yalçın, Der Keulenkopf von Can Hasan (TR). Naturwissenschaftliche Untersuchung und neue Interpretation, in: Rehren et al. (1998) 279–289.

Yalçın – Pernicka 1999
Ü. Yalçın – E. Pernicka, Frühneolithische Metallbearbeitung am Aşıklı Höyük, Türkei, in: A. Hauptmann – E. Pernicka – T. Rehren – Ü. Yalçın (eds.), The Beginnings of Metallurgy, Der Anschnitt, Beiheft 9 (Bochum 1999) 45–54.

Zachos 1996
K. Zachos, Metal jewellery, in: G. A. Papathanassopoulos (ed.), Neolithic Greece (Athens 1996) 166.