# Arsenic Bronze An archaeological introduction into a key innovation

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# Introduction

The alloying of metal was a decisive step in the development of metallurgy, and it is worthwhile trying to understand the circumstances and the consequences of this key innovation. The most important early alloy was arsenical copper. For more than two thousand years it was the way to improve the properties of the copper: in hardness, elasticity and colour.

With arsenic bronze crucial innovations in arms appeared. The production of long dagger blades was only possible by adding an alloying material that reduced the formation of bubbles in the molten metal. Namely, every cavity in the blade would make it more prone to breakage. Here we understand that alloying was the technical precondition for the production of functional tools and of lethal weapons.

# Knowledge

In the 18<sup>th</sup> and early 19<sup>th</sup> century artisanal techniques were considered the precursors of scientific knowledge. Histories of inventions were an own type of scientific literature during this time, a period that was coined by many technical key innovations like steam engine and railway, lightning conductor and sextant, or even new elements of cuisine like the potato.<sup>1</sup> In particular, the invention of and workmanship in metal were recognised as the cause for the emergence of the arts and craftsmanship as well

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as science.<sup>2</sup> Metals were identified as the driving force of practical inventions.<sup>3</sup>

The classical type of history of innovations found its climax and determination in Ludwig Darmstädter and René de Bois-Raymond's monumental work "4000 Jahre Pionierarbeit in den exakten Wissenschaften". It showed the constant growth of technical inventions during history as the work of scientific pioneers.<sup>4</sup>

A new understanding of knowledge production arose from Ludvik Fleck's "*Denkstil*" and Thomas Kuhn's "paradigm".<sup>5</sup> Michel Foucault figured out the characteristic "episteme" of a certain epoque that defines the "empirical order" with which each human being has to do.<sup>6</sup> This knowledge is not developed in a steady rising way, but by new constellations of thinking which are developed by a few researchers and then confirmed and differentiated by many others. Whereas the production of knowledge was investigated within the narrow frame of western scientific tradition, today the history of knowledge and innovation must be conducted in a global measure.<sup>7</sup>

The exploratory significance of this direction in research has become apparent in recent scholarly works, which are labelled as global or deep history. So, Yuval Noah Harari's observations on global history and his pointed judgments based on a history of innovations have been a global success. Already in 1999 Jared Diamond attempted to understand the economic imbalance between the five continents,

- <sup>4</sup> Darmstädter/de Bois-Raymond 1904. 5 Elock 1025 (1006) Kubp 1062 (1067)
  - Fleck 1935 / 1994; Kuhn 1962 / 1967.
- <sup>6</sup> Foucault 1971/1995, 22.
- <sup>7</sup> Renn/Hyman 2012.

<sup>&</sup>lt;sup>1</sup> E. g. Beckmann 1788; Poppe 1837.

<sup>&</sup>lt;sup>2</sup> Plessing 1787, 182.

<sup>&</sup>lt;sup>3</sup> Orell 1786, 497.

basing on a history of innovations and thereby spanning the time from the Neolithic to the beginnings of metallurgy. Our considerations here follow this approach in the sense of outlining the emergence and transfer of knowledge precisely during a time that contributed fundamentally to what was called "technological difference"<sup>8</sup> or "Eurasian miracle".<sup>9</sup> These technologies shaped Europe and Eurasia as a common sphere of technical knowledge at an early time in the 4<sup>th</sup> millennium BC. Therefore, it is highly important to examine how these techniques evolved and diffused. The historical and social context plays a crucial role in the development of techniques. The comprehension of the development and introduction as well as the dissemination of techniques and the resultant social processes in prehistoric and ancient times is yet only in its initial stages and must still become established as a field in research.

The importance and the far reaching consequences of an innovation were probably never recognized at the moment of invention. The intentions of experimentation and invention are quite diverse, and many inventions have never been realized. But it should not be denied that there were *heureka-moments*, also in the history of early scientific practice.

## Metal

Improving metal objects with various alloys transformed the production of prestigious items into that of common commodities. This technical development was embedded in a wider field of technical innovations and the cataclysms of the social world. New forms of social domination, political organisation and economic inequalities arose.

Metallurgy is one of the key innovations, which have been the precondition for every modern machine. Metallurgy still plays a prominent role in science and engineering. Metallurgy should not be considered isolated, instead embedded in a whole spectrum of technical options. It started in the context of a Neolithic economy that had developed pottery making in closed kilns, in which the temperature was not only increased but also could be controlled.<sup>10</sup> Mining for copper was attested first in Ai Bunar, but mining for flint was already known from the Neolithic.<sup>11</sup> The volume of the rock mass during the development in Ai Bunar amounted to astonishing 20,000-30,000 tonnes, the extraction of the ore to at least 20,000-30,000 tonnes, and the presumed smelting of the copper to 500-1,000

tonnes. After the extraction work, the heaps of the waste rock were refilled in the pits, probably for cultic reasons.

The huge number of metal items known from the 5<sup>th</sup> millennium BC in Southeast Europe stands in a certain contrast to the very limited number of object types: flat axes, hammer axes, spiral pins and awls. There is hardly a stylistic development to be recognized.

The so called Copper Age in Southeast Europe had already developed strong asymmetries in power and wealth. In the cemetery in Varna near the Bulgarian Black Sea coast many graves held only few gifts or none at all, while by contrast some burials were lavishly furnished with gifts, there among, objects made of copper and gold. Jean-Paul Demoule has noted that the graves in Varna would historically mark the beginnings of social inequality.<sup>12</sup> The persons interred in graves 4 and 43 were furnished with 1.5 kg of gold, respectively. According to available radiocarbon dates, the graves in Varna cover a time span of at least 100 years (4550-4450 cal BC).13 Labour division and social inequalities are detectable in settlements of this time, e.g. in Pietrele, Romania on the Lower Danube River.14

A substantial part of technical innovations that marked Europe's development well into the modern age and constituted its special role were developed within only a few centuries' time in the 4<sup>th</sup> millennium BC. Indeed, it was a time of radical changes and transformations. In the 4<sup>th</sup> millennium BC the density of innovations increased on a hitherto unknown scale. Among the most important innovations were the wheel and the wagon, the breeding of the woolly sheep, the domestication of the donkey and horse, and the cultivation of olives and wine. Silver could be extracted from lead by means of cupellation, and this technology spread throughout the entire Near East and the eastern Mediterranean during the 4<sup>th</sup> millennium BC. And concerning pottery production, here the potter's wheel must be emphasised.

Amidst all these innovations the production of new weapons played an important role. Here, the development of the daggers, swords and halberds must be mentioned. These weapons changed the way of war-like conflicts. The alloying of copper was without doubt a turning point in metallurgy. It was the decisive step from the production of 'prestigious objects' into that of the functional use of metal objects.

<sup>&</sup>lt;sup>8</sup> Childe 1958/2009.

<sup>&</sup>lt;sup>9</sup> Goody 2010.

<sup>&</sup>lt;sup>10</sup> Hansen Streily 2000.

<sup>&</sup>lt;sup>11</sup> Ai Bunar: Černych 1988. – Neolithic: Bosch 1979.

<sup>&</sup>lt;sup>12</sup> Demoule 2007, 78–89.

 <sup>&</sup>lt;sup>13</sup> Chapman et al. 2007, 174; see also Krauß et al. 2014, 385
Fig. 12; Krauß et al. 2016, 285,

<sup>&</sup>lt;sup>14</sup> Hansen 2018.

# Copper Alloy as a technical innovation

It was the pioneering work of Evgenij N. Černykh, who basing on metal types and chemical analyses described the Copper Age metallurgy in the Balkans as a Carpatho-Balkan Metallurgical Province (CBMP) and the succeeding Early Bronze Age as the Circumpontic Metallurgical Province (CMP).<sup>15</sup> Whereas in the CBMP pure copper was predominant in the CMP the arsenical bronzes were prevailed.

Generally, it has been assumed that the use of naturally occurring copper and arsenic ores were the background for alloyed metal objects.<sup>16</sup> However, there are good arguments suggesting that arsenic and other ingredients were intentionally added to copper, which were meant to change the properties of the metal material. The addition of another element can change the properties of copper. By adding arsenic, copper gains a silvery colour, whereas the addition of tin to copper lends a golden hue to the object.<sup>17</sup> By means of the corresponding alloy, the otherwise soft copper gains hardness, while brittleness and elasticity can be altered. The flow of the molten metal is greatly improved, because the additional elements serve as antioxidants that reduce the formation of bubbles in the metal, and in this way help to produce a homogenous, solid object. In principal arsenic has the same effect as tin.<sup>18</sup>

The mental step of mixing different sorts of metal with one another is quite comprehensible in view of the ceramic know-how.<sup>19</sup> Indeed, the addition of various organic or mineral agents can render a successful firing of pottery, hindering cracks and fissures during firing or drying. The kind of temper utilised, however, can change the properties of the particular vessel: the weight of the vessel, the porosity of the walls, or the colour of the clay could be manipulated. So, alloying copper was most likely the adaption of a well-known concept in pottery-making. The addition of another element can change the properties of the main element (clay or copper). The favoured recipe has to be found out through experimentation. These recipes had to become a routine and an active knowledge which had to be transferred from one generation to the next. Needless to say, probably hundreds of failed trials had been taken place before one one felicitous experiment was achieved.

Alloying reaches back to the 5<sup>th</sup> millennium or even into the late 6<sup>th</sup> millennium BC. At present it does not seem possible to define the "oldest" copper alloyed metal find. But proof of early alloying can be found in the middle of the 5<sup>th</sup> millennium BC, or slightly after, in a wide geographical expanse, from present day Pakistan to Bulgaria. I have argued that the knowledge of metallurgy spread over large areas within relatively short time spans. This was the result of mobile people connected with raw material sources. The wide spread of information helped, to preserve this knowledge over generations.

An early copper alloy awl dated to the late  $6^{th}$  millennium was recently found in Tel Tsaf (Israel).<sup>20</sup> In Iran copper-arsenic alloys came into use in the  $5^{th}$  millennium.<sup>21</sup> The small wheels found in Mehrgarh, Pakistan (late  $5^{th}$  millennium BC) can be added to these finds. They were made of a mixture of copper and lead, the lead content being 30-40%.<sup>22</sup>

The currently oldest alloyed product in Southeast Europe known so far was recently identified by Verena Leusch and Ernst Pernicka: a disc-ring pendant (**Fig. 1**) from grave 271 in Varna I, consisting of 50% gold, 14% silver and 36% copper.<sup>23</sup> These golden pendants have a symbolic meaning and were distributed among the Copper Age cultures in the Carpathian Basin, the Lower Danube region and Thrace.<sup>24</sup>

In 1961 a large number of metal objects (Fig. 2; 3) was found in Nahal Mishmar, located west of the Dead Sea.<sup>25</sup> A total of 429 objects including 416 metal items wrapped in a reed mat had been concealed in a cave. Beside 240 maceheads approximately 100'standards', 'crowns', a sceptre with two ibex figures and two metal vessels represent outstanding products of the late 5<sup>th</sup> millennium BC.<sup>26</sup> In a series of compositional analyses of 28 objects, Miriam Tadmor's team was able to distinguish three kinds of metal: objects made of pure copper, copper objects with high arsenic and antimony content, and objects with high nickel and arsenic content. Only a small number of pure copper objects were identified, including simple tools like axes and hammers. A few objects contain high amounts of nickel. Yet the most numerous objects by far in Nahal Mishmar are antimony-arsenic bronzes containing between 1 % and 25 % antimony and 0.4 % to 15 % arsenic.<sup>27</sup> Nahal Mishmar can be considered as a kind of laboratory, in which several experiments were executed.

- <sup>22</sup> Roux et al. 2013, 65–68.
- <sup>23</sup> Leusch et al. 2014,175 fig. 11a.
- <sup>24</sup> Hansen 2007.
- 25 Bar-Adon 1980.
- <sup>26</sup> Gilead/Gošić 2014.
- <sup>27</sup> Tadmor et al. 1995,129–131 tab. 2; cf. Shalev/Northover 1993, 43 tab. 1; 2.



Fig. 1. Varna, Grave 271. Disc Pendant; scale 1:1 (photo: B. Armbruster / V. Leusch /VI. Slavchev).

<sup>&</sup>lt;sup>15</sup> Е. Н. Черных 1966; Е. N. Chernykh 1992.

<sup>&</sup>lt;sup>16</sup> Schubert 1981, 448.

<sup>&</sup>lt;sup>17</sup> Pernicka 1998.

<sup>&</sup>lt;sup>18</sup> Schubert 1981, 448.

<sup>&</sup>lt;sup>19</sup> Hansen 2017.

<sup>&</sup>lt;sup>20</sup> Garfinkel et al. 2014.

<sup>&</sup>lt;sup>21</sup> Thornton et al. 2002; Thornton 2010.



Nahal Mishmar. Complex metal alloys (after Bar Adon 1980).



**Fig. 3.** Nahal Mishmar. Complex metal alloys (after Bar Adon 1980).

The connection of metallurgical experiments in the sphere of ideological objects can be understood in the frame of early metallurgy as a "magical" process. Cast metal was the result of a process of transformation, through which – simply said – stone was changed into metal. Humankind had already gathered experience with the conversion of matter for a longer time. Mircea Eliade wrote: "*The alchemist like the smith and before him the potter is a master of the fire. By using fire he caused the transformation of matter from one condition into another*."<sup>28</sup> Today the alchemist is acknowledged as the forerunner of chemistry as a science.

# **Technical Innovations and History**

There can be no doubt that metallurgy played a crucial role in the technological development of Eurasia in a significant way ever since the 5<sup>th</sup> millennium BC, which is different from all other continents. In Australia native people started using metal after colonization.<sup>29</sup> Sub-Saharan Africa never had a Bronze Age. The earliest metal production was that of iron in the 1<sup>st</sup> millennium BC.<sup>30</sup> In South and Mesoamerica metal first came into use only at the beginning of the 2<sup>nd</sup> millennium BC. Nine cold-hammered native gold beads were found in a burial in the southwest part of the Lake Titicaca basin in Peru, dated by <sup>14</sup>C to 2155–1936 calBC.<sup>31</sup> The gold necklace was associated with a burial at Jiskairumoko, a small site occupied by a hunting and gathering people, suggests that status-display using gold artifacts in this region began long before the appearance of more complex societies capable of generating surpluses. This can be well compared to the early use of native copper in Pre-Pottery Neolithic societies in eastern Anatolia.

At present, the earliest evidence for smelting activity in southern South America comes in the form of copper slag from the Wankarani site in the highlands of Bolivia, dating between 900 and 700 BC.<sup>32</sup> This fits well with recently published evidence for copper emission based on ice-core records from the Illimani glacier in Bolivia, proving largescale copper smelting activities in South America during the Early Horizon period 700–750 BC.<sup>33</sup> There is no evidence in North America that prehistoric North American copper workers ever melted,

- <sup>31</sup> Aldenderfer et al. 2008, 5004.
- <sup>32</sup> Cooke et al. 2009, 1659.
- <sup>33</sup> Eichler et al. 2017.

<sup>&</sup>lt;sup>28</sup> Eliade 1980, 83 (The master of the fire).

<sup>&</sup>lt;sup>29</sup> Harrison 2002.

<sup>&</sup>lt;sup>30</sup> Parzinger 2014, 369. – Early modern copper trade: Cassitti 2016.

smelted, alloyed or casted the metal. Metalworking was limited to native copper, cold hammering (with some hot hammering) and annealing it into shape.<sup>34</sup> But in the Eastern Woodlands, indigenous copper-working goes back well over 6000 years. Native copper from the Lake Superior region was heavily exploited from about 4000 BC.

From a comparison between Eurasia and the Americas no general conclusions about the development of metallurgy or the social context of innovations in general can be drawn. There was no "complex" society necessary to develop metallurgy, and there is no direct path from metallurgy to social complexity. Christopher P. Thornton and Benjamin W. Roberts are obviously right. There is no strict connection between metalworking and elites. Metalworking was not necessary to generate elites, and elites are not necessary to produce metal.<sup>35</sup> These formulas bring Lenin's famous but puzzling sentence to mind: "*Communism is Soviet power plus the electrification of the whole country*".<sup>36</sup>

Indeed, the connection between technical progress and changes in societies is much more complex than these simple links between technology and society. Actually, the interlinkages between technologies and society are very close. Vere Gordon Childe's aim was to show, why European societies could produce European science: *"The explanation must of course be sociological not biological. Science, like technology, is the creation of societies not races; its precepts and results are transmitted by social tradition, 'not in the blood'".*<sup>37</sup>

For Childe this was the starting point of a distinctively European way: "The history of Europe poses two fundamental questions that prehistoric archaeology should be able to answer. Four or five thousand years ago the natives of Europe were on precisely the same level, as far as equipment and economic organization are concerned, as the natives of eastern North America – a very similar environment – were on only 400 years ago and as some native tribes in New Guinea are today. Why then did they not remain illiterate Stone Age barbarians as the Red Indians and the Papuans did? On an answer to this first question prehistorians are agreed: the proximity of Egypt and Mesopotamia. In the Nile valley and the Tigris-Euphrates delta alone could be created the economic and political organization necessary to get a metallurgical industry started.

And there that first step in the 'progress' that has differentiated the Old World from the New was actually taken five thousand years ago. European barbarians profited by that achievement and so left the Stone behind.

But this answer at once raises the second question: How could European barbarians outstrip their Oriental masters as they have done? For the essential features of the economy and polity needed to nurture the infant metallurgical industry have persisted in the Orient through the Bronze Age empires of Egypt and Mesopotamia have been replaced by others – the Persian Empire, the Hellenistic monarchies, the Khalifate, the Ottoman Empire and so on. Incidentally the technological differentiae between the first and the last expressions of the primary pattern – iron water-wheels, alphabetic writing, pure mathematics etc. – were inventions introduced or imposed by barbarians and often European barbarians at that."<sup>38</sup>

Childe discussed metallurgy in terms of world history, which was in line with the histories of knowledge that have been mentioned above. It is not necessary to stress the topicality of these questions. Technical innovations are decisive factors in world economy. Copper is still an indispensable raw material in the digital world, even though rare earth metals have become so famous.

Childe's considerations have been guoted at length not only because his ideas sometimes are sketched in a very simplified way, but especially because they led to the famous Neolithic paradoxon described by Claude Lévi-Strauss in his book The savage mind. "Neolithic, or early historical, man was therefore the heir of a long scientific tradition. However, had he, as well as all his predecessors, been inspired by exactly the same spirit as that of our own time, it would be impossible to understand how he could have come to a halt and how several thousand years of stagnation have intervened between the Neolithic revolution and modern science like a level plain between ascents. There is only one solution to the paradox, namely, that there are two distinct modes of scientific thought. These are certainly not a function of different stages of development of the human mind but rather of two strategic levels at which nature is accessible to scientific enquiry: one roughly adapted to that of perception and the imagination: the other at a remove from it. It is as if the necessary connections which are the object of all science, neolithic or modern, could be arrived at by two different routes, one very close to, and the other more remote from, sensible intuition."<sup>39</sup>

<sup>34</sup> Ehrhardt 2009.

<sup>35</sup> Thornton/Roberts 2009

<sup>&</sup>lt;sup>36</sup> Lenin's Collected Works, 4<sup>th</sup> English Edition (Moscow 1965) Volume 31, pages 408–426 cited after https://www.marxists. org/archive/lenin/works/1920/nov/21.htm (27.6.2019)

<sup>&</sup>lt;sup>37</sup> Childe 1958/2009, 9.

<sup>&</sup>lt;sup>38</sup> Childe 1958 / 2009, 7.

<sup>&</sup>lt;sup>39</sup> Lévi-Strauss 1966, 15; In the German language: Lévi-Strauss 1981, 27.

Whereas Childe discussed the problem from a strict historical stand point, Lévi-Strauss tried to explain the diverging development on the five continents by two different ways of thinking.

# Arsenic copper or arsenic bronze

Arsenic was long regarded as an impurity in the metal, but not as an intentional alloy. This changed with the already introduced investigations of Evgenij N. Černykh, who was able to collect data from Eastern Europe.<sup>40</sup> In 1967 J. A. Charles, basing on third millennium finds from Greece, discussed the advantages of the arsenic bronze.<sup>41</sup> Accordingly. arsenic is a useful deoxidizing agent, which lowers the bubbles in the molten copper and which leads to better results of the cast objects. Arsenical copper is also characterized by better fluidity, which improves the casting process. Irina Ravich and Natalia Ryndina provided investigations of arsenic bronzes in the North Pontic steppe and the Caucasus. They found very similar recipes in the production of daggers in Maykop, Usatovo and Mondsee.<sup>42</sup>

Heather Lechtman stressed in 1996 the fact, that "peoples in the Near East and Europe worked with arsenic bronze for almost two millennia before tin bronze became a significant competitor".<sup>43</sup> She strongly argues against the widespread opinion that tin would be the better alloy. According to Lechtman one can distinguish arsenical copper from arsenic bronze: "Arsenical copper is impure copper whose electrical properties are markedly affected by the presence of arsenic but whose mechanical properties are similar to those of copper. Mechanical properties of copper-arsenic alloys, such as hardness and malleability, begin to change appreciably with arsenic concentrations of about 0.5 weight percent. At arsenic concentrations of 0.5 weight percent and higher, copper-arsenic alloys can be considered bronzes."44

The advantages of tin or arsenic bronzes are slightly the same. According to Lechtman, tin bronze can be work-hardened to higher values than arsenic bronze, while on the other side arsenic bronzes are highly ductile and can be hot or cold worked without becoming brittle, even at extreme levels of deformation.<sup>45</sup>

It is important to note that the tin bronze technology is not superior to the arsenic bronzes.

"There is sufficient overlap in the mechanical behavior of the two bronzes that they may be used interchangeably for specific functions within rather broad alloy ranges: 2–7 weight-percent arsenic; = 2–7 weight-percent tin. Beyond these comparisons, drawn from experimental data, evaluation of the utility and performance of particular alloys depends largely on the human agents who designed and used them".<sup>46</sup>

Finally, arsenic is highly toxic, and on various occasions it was assumed that the introduction of the tin alloy was due to this fact. At Shiqmim, Israel, a 4<sup>th</sup> millennium BC site, individuals with a higher arsenic content in their bones could be identified as involved in metalworking activities.<sup>47</sup>

## Arsenic Bronzes – a short review

The history of metallurgy researched by the technical information, stored in the object itself, is limited by the find record. Metal can be recycled, and it was melted down and re-casted since the very beginning. Metal finds were preserved only when they were buried with the dead in graves or used as offerings for the imagined powers, the spirits and the gods. Therefore, metal finds from settlements are guite rare. It must be stressed here that the custom of furnishing graves with metal objects or using metal objects as votive offerings changed throughout times. Whereas the Maykop culture of the 4<sup>th</sup> millennium BC used metal in a lavish way as grave goods, the Yamnaya and Catacomb cultures of the 3<sup>rd</sup> millennium BC kept metal out of graves in general, with some exceptions. The western Bell Beaker culture used certain metal types as grave goods, but only in some regions as offerings for the imagined powers.48

Arsenic bronze was common during the 4<sup>th</sup> and 3<sup>rd</sup> millennia BC, but it was always an open question if and how the arsenic content was manipulated by the casters. Recent examinations of slag from the industrial site of Arisman in Iran have substantiated the production of 'arsenspeiss' (iron arsenic alloy). This at least proves the technical capability of adding a specific amount of arsenic as an alloy and to produce arsenical copper in a regular and well-controlled process.<sup>49</sup> Whether or not this capability had existed earlier than the early 3<sup>rd</sup> millennium BCE and elsewhere cannot be stated yet.<sup>50</sup>

<sup>48</sup> Hansen, forthcoming.

<sup>40</sup> Черных 1966.

<sup>&</sup>lt;sup>41</sup> Charles 1967.

<sup>&</sup>lt;sup>42</sup> Ravich/Ryndina 1995.

<sup>&</sup>lt;sup>43</sup> Lechtman 1996, 477.

<sup>&</sup>lt;sup>44</sup> Lechtman 1996, 481.

<sup>&</sup>lt;sup>45</sup> Lechtman 1996, 506.

<sup>&</sup>lt;sup>46</sup> Lechtman 1996, 506.

<sup>&</sup>lt;sup>47</sup> Oakberg et al. 2000.

<sup>&</sup>lt;sup>49</sup> Rehren et al. 2012. For the archaeological background: Helwing 2013, 122.

<sup>&</sup>lt;sup>50</sup> Pernicka (pers. Information) could identify arsenspeiss also in Western Anatolia.



Fig. 5. Nalčik. Silver dagger (photo: S. Reinhold).



3 cm 🖵

Fig. 6. El-Amrah. "Silver" dagger with ivory handle (photo montage from Baumgartel 1960, Pl. 2.1.2). It was an earlier assumption that the high-arsenic content in metal (up to 15% arsenic) could have served as the alloying additive to copper.<sup>51</sup> This practice was already supposed by Helmut Otto and Wilhelm Witter, when they discussed an ingot containing 16.49% arsenic.<sup>52</sup> Recently it was demonstrated that under deoxidising conditions the loss of arsenic in the process of re-smelting is relatively low.<sup>53</sup>

Another strong argument for the intentional alloying was already made in the 1970s, when E. R. Eaton and H. McKerrell reviewed the evidence of arsenical coating. They emphazised the high percentage of at least 12% arsenic in the copper to produce a silver colour. There are a number of methods of effecting the required surface: "One such simple procedure is to paint a thin paste of arsenic oxide on to the areas to be coloured, then to cover the object in charcoal powder and heat briefly until bright red. After cooling and polishing the silver colour emerges clearly."<sup>54</sup> But they also pointed to an alternative method: the inverse segregation, which has been investigated recently.<sup>55</sup>

Eaton and McKerrell assumed that a number of "silver" daggers were in fact produced with a high percentage of arsenic. This is certainly true for the daggers in Usatovo (Fig. 4). The 19.5 cm long dagger from the central grave in Kurgan 3 has a shiny silvery surface.<sup>56</sup> The arsenic content is nearly 10%.<sup>57</sup> Large daggers of the "Usatovo" type – contemporaneous with the Maykop grave – were in general made of highly alloyed arsenic bronze and clad with arsenic, which gave them a silvery colour (an original way of imitating silver).

This might be true also for the "silver" daggers, which have not been investigated analytically. Indeed, there are several examples for silvery daggers known from the 4<sup>th</sup> and 3<sup>rd</sup> millennium BC.<sup>58</sup> Silver weapons appeared in the second half of the 4<sup>th</sup> millennium in a broad geographic zone between the Caucasus (**Fig. 5**) and Egypt (**Fig. 6**). In the 3<sup>rd</sup> millennium silver weapons were also in use in the Aegean and the west Carpathian Basin (**Fig. 7**). In the 2<sup>nd</sup> millennium BC golden daggers replaced the silver ones. This is quite parallel to the predominant alloying practices with arsenic and tin.

In Iran the production of arsenic bronze metal objects reaches back to the 5<sup>th</sup> millennium BC.<sup>59</sup> It



Fig. 7. Poduri, silver-copper alloy (photo: R. Munteanu).

remained the most common metal on the Iranian Plateau until the Iron Age. Also in Mesopotamia arsenic bronze was the predominant material in metalworking during the 4<sup>th</sup> and 3<sup>rd</sup> millennia BC.<sup>60</sup>

In the Caucasus the famous Maykop grave shows a full range of arsenical bronzes. The 34.7 cm long dagger (Fig. 8) with two silver rivets is especially remarkable. It is the longest dagger blade of this time period and illustrates the potential of alloying. The dagger displays the potential of alloying, although it could not be measured because of the lack of metallic substance. All the other tools from the Maykop grave were made of arsenical bronze (2.03–9.08%).<sup>61</sup> The development of axes in the fourth millennium in the Caucasus shows a plausible typological pathway from the copper axes of a fifth millennium tradition with a spiked neck into the "modern" shafthole axe of the 37th / 36th century BC.<sup>62</sup> This provides an additional typological argument for dating the Maykop grave to this

<sup>&</sup>lt;sup>51</sup> Eaton / McKerrell 1976, 178

<sup>&</sup>lt;sup>52</sup> Otto / Witter 1952, 44.

<sup>&</sup>lt;sup>53</sup> Mödlinger et al. 2019.

<sup>&</sup>lt;sup>54</sup> Eaton / McKerrell 1976, 175–176.

<sup>&</sup>lt;sup>55</sup> Mödlinger/Sabatini 2016.

<sup>&</sup>lt;sup>56</sup> Ryndina / Kon'kova 1982, 32–33 Fig. 3,7.

<sup>&</sup>lt;sup>57</sup> Vajsov 1999, 110 Fig. 4,8.

<sup>&</sup>lt;sup>58</sup> Hansen 2015.

<sup>&</sup>lt;sup>59</sup> Thornton et al. 2002.

<sup>&</sup>lt;sup>60</sup> Helwing unpublished (2007).

<sup>&</sup>lt;sup>61</sup> Data in Selimkhanov 1962, 78 No. 27–35; Черных 1966, 99, 1–4.

<sup>&</sup>lt;sup>62</sup> Hansen forthcoming (St. Petersburg).

time span. For the early development of arsenical bronzes Maykop is a key site, since in Mesopotamia the deposition of metal in graves or sanctuaries was not a common practice during this time. Evgenij N. Chernykh identified the copper-arsenic-nickel combination as particularly characteristic of the Maykop culture.<sup>63</sup> He presumes the source of this metal to be Anatolia or Iran, whereas the source of copper with low nickel content is probably the southern Caucasus.

South of the Great Caucasus daggers found in kurgans 1 and 5 in Soyuq Bulaq in Azerbayčan can be mentioned, which are assigned to the contemporaneous Leilatepe culture of the 4<sup>th</sup> millennium BC. Both of the 15 and 19 cm long daggers contain arsenic.<sup>64</sup> Daggers from arsenic bronze were also produced in Iran during the 4<sup>th</sup> millennium BC.<sup>65</sup>

Grave 31 / 5 in Novosvobodnaya (Klady cemetery), some centuries younger, contained a number of daggers and, most spectacularly, a sword, one of the earliest swords in the world (**Fig. 9**).<sup>66</sup> The high percentage of arsenic in the daggers stands in clear contrast to the low percentage of arsenic in the axes. This suggests that the manipulation of the copper was within the scope of the craftsmen.

Also, in other cases, one can observe the differing percentage of arsenic in knives and daggers, on the one hand, and heavy axes, on the other. In the recently published kurgan 3 of Marinskaya (**Fig. 10**), the dagger from grave 18 has an arsenic content of 4.9%, whereas the shafthole axe has only 1.8% arsenic.<sup>67</sup>

This was recently also confirmed by the investigations on grave 3 in Kurgan 1 at Dolinka, Kr. Krasnoperekopsk, Ukraine (**Fig. 11**).<sup>68</sup> It has been attributed to the Kemi Oba culture, but has very close connections to the late Maykop culture. It was dated between 3500-3330 cal BC. Among the grave goods a chisel, a flat axe and a dagger contained 3.2-3.4% arsenic, whereas the shafthole axe was made of a pure copper.

The 9 swords and 12 spearheads found in a collapsed building in Arslantepe near Malatya (Turkey) Layer VIA belong to the earliest weapons of these types. The sheer number of swords and their craftmanship (**Fig. 12**) shows that there was a regular production of such weapons in larger quantities, which had to meet demands. The arsenic contents

<sup>69</sup> Hauptmann et al. 2002, 49 Pl. 5; Zimmermann 2011.

> Fig. 8. Majkop. Metal tools from the grave (after Korenevskij 2004, rearranged).

of these weapons range from 2.57 up to 6.08%.<sup>69</sup> Here note should also be made of the hoard from Tülintepe containing one sword and several spearheads. The short sword has a length of 44.6 cm, a width of 5.3 cm and contains 2.11% arsenic.

Large daggers and sword blades found their way also to the west or were produced in the west. The recently published hoard from Ivan'ky, Mankivka District, Region Tcherkassy in Ukraine is most spectacular. The hoard contained a copper axe without arsenic and five swords **(Fig. 13)** made of arsenic bronze (1.862–4.529%). The swords, 28.3 to 41.5 cm long, can be dated into the third quarter of the 4<sup>th</sup> millennium BC, contemporaneous with Usatovo.<sup>70</sup>

The dagger **(Fig. 14)** in grave 21 from kurgan 1 in Purcari, jud. Ştefan Vodă dates into the same time period. It was situated before the head of the deceased person. This dagger and another blade have a considerable higher amount of arsenic (5 and 8%) than the axe (3%).<sup>71</sup>

<sup>&</sup>lt;sup>63</sup> Черных 1966, 98–101 tab. 1; 2; Chernykh 1992, 74; 145.

<sup>&</sup>lt;sup>64</sup> Courcier 2017, 529.

<sup>&</sup>lt;sup>65</sup> E.g. Tepe Meymanatabad: Kashania et al. 2013.

<sup>&</sup>lt;sup>66</sup> Rezepkin 2000.

<sup>&</sup>lt;sup>67</sup> Kantorovič / Maslov 2008.

<sup>68</sup> Ivanova/Rassmann 2014.

<sup>&</sup>lt;sup>70</sup> Klochko/Klochko 2013.

<sup>&</sup>lt;sup>71</sup> Dergačev 2002, 23; 222–223 (analysis) Pl. 17,B.





Metal daggers were widely distributed in the 4<sup>th</sup> millennium.<sup>72</sup> It is striking that they did not exist in great numbers or were not deposited north of the Alps. It is not clear yet whether this distribution pattern is due to technological or other reasons. Here



Fig. 9. Novosvobodnaja, grave 31/5. Sword (after Rezepkin 2012).

a few daggers of Usatovo type can be mentioned: Aspenstedt (**Fig. 15,1**) with an arsenic content of 5.7 %,<sup>73</sup> and Kałdus (**Fig. 15,2**) with an arsenic content of 5.2 %.<sup>74</sup>

Grave 3 in Rinaldone near Montefiascone **(Fig. 16)**, Prov. Viterbo (Italy), also shows a clear relation between the functionality and the arsenic content of the objects. There two axes, three daggers, one halberd and 22 flint arrowheads were found, which can be dated to the early second half of the 4<sup>th</sup> millennium BC. The halberd has 4.1% arsenic and one of the daggers 1.7%, whereas the axes are made of nearly pure copper.<sup>75</sup>

In the case of more massive axes it was not that necessary to add arsenic to improve the casting of the object. This is the background of "Ötzi's" axe, which is made of pure copper with a low percentage of arsenic (0.4%). Recent studies have confirmed the Central Italian origin of the metal ore.<sup>76</sup> It was not necessary to add arsenic. The same is true for the shafthole axes of the 4<sup>th</sup> millennium BC, distributed in the Carpathian Basin and the eastern

<sup>&</sup>lt;sup>72</sup> Vajsov 1993.

<sup>&</sup>lt;sup>73</sup> Müller 2013.

<sup>&</sup>lt;sup>74</sup> Adamczak et al. 2015.

<sup>&</sup>lt;sup>75</sup> Dolfini 2004.

<sup>&</sup>lt;sup>76</sup> Artioli et al. 2017.





Alps.<sup>77</sup> They are mostly composed of copper with few impurities.<sup>78</sup>

As already mentioned, the visibility of metal is not very strong in archaeological sources during the 3<sup>rd</sup> millennium. In many parts of the Near East, Anatolia and Eastern Europe metal objects were used as grave offerings only in a few cases and in limited number. Nevertheless, the use of arsenic bronze is well documented there.<sup>79</sup>

The king's burial in Arslantepe is a rare case of an over-display with a larger number of weapons, dated to around 3000 BC. The daggers and spearheads were made of arsenical bronze with 2.18–3.06% arsenic content.<sup>80</sup> There is one exception: a dagger that was made from a copper-silver alloy. Copper-silver alloy was regularly employed for ornaments, with silver contents from 32 to 64%.

Bronze tools and ornaments from silver and gold were found in a recently discovered tomb at Hasansu (Fig. 17) in Azerbayčan, dated to the first half of 3<sup>rd</sup> millennium BC.<sup>81</sup> Two daggers (or spearheads?) have an arsenic content of 1.63 and 2.54%. The shafthole axe and the flat axe contain only 0.98 and 1.08% arsenic.<sup>82</sup>

In Southeast Europe several hoards consist mainly of shafthole axes and flat axes. The epony-

<sup>77</sup> Hansen 2009; Szeverenyi 2013.

<sup>&</sup>lt;sup>78</sup> Dani 2013.

<sup>&</sup>lt;sup>79</sup> Bray et al. 2015, 206 Fig. 2.

<sup>&</sup>lt;sup>80</sup> Hauptmann et al. 2002, 51 Tab. 7.

<sup>&</sup>lt;sup>81</sup> Müseyibli et al. 2012.

<sup>&</sup>lt;sup>82</sup> Courcier et al. 2017, 533.



Fig. 12. Arslantepe. Sword (photo: M. Frangipane).

> mous find from Kozarac (Bosnia-Herzegovina) contained nine axes made of pure copper or a very low arsenic content.<sup>83</sup> Another find in this group from the early 3<sup>rd</sup> millennium BC contains 23 flat axes of the Griča type, one shafthole axe of the Kozarac type, and four axes whose best analogies are in the Mala Gruda kurgan in the bay of Kotor (Montenegro).<sup>84</sup> The flat axes and the Kozarac axe are made of pure copper, one case with 1.45% tin. The four other axes consist of a copper-silver alloy with silver

content of 32%, 23% up to 55% and 58%.<sup>85</sup> Similar alloys are known from the king's burial in Arslantepe and a recently published dagger from Poduri, eastern Romania **(Fig. 7)**.<sup>86</sup> It remains unclear why these copper-silver alloys were produced.

In Western Europe the second half of the 3<sup>rd</sup> millennium BC was coined by Bell Beaker metallurgy. This is clear from copper mines in the Ross Islands in Ireland or entire mining regions around Cabrières in Languedoc.<sup>87</sup> Mining activities are also known from the Iberian Peninsula.<sup>88</sup> The metallurgy of the 3<sup>rd</sup> millennium BC is also well described.<sup>89</sup>

The most significant metal product of the Bell Beaker culture is the dagger, another specific type of metal work are the Palmela points.<sup>90</sup> Halberds were in use as well as axes, but do not occur very often in clear Bell Beaker contexts. In the recently published grave U1853 in the cemetery of Humanejos near Madrid a dagger, two Palmela points and a halberd were found together; according to radiocarbon dating they were buried between 2474 and 2338 cal BC.<sup>91</sup> The Palmela points and the halberd contain 2.05–2.64% arsenic; the dagger contains 4.06% arsenic.

A similar relationship could be observed in the grave of Montilla **(Fig. 18)**. The 28 cm long dagger contains 3.83-4.17 %, and the Palmela points contain between 0.56 and 1.94 % arsenic.<sup>92</sup>

In a hoard discovered at São Brás (southern Portugal) the daggers clearly display higher arsenic contents (an average  $5.1 \pm 2.0$  wt% As) than other types. Axes and other objects have a significantly lower content (on average  $2.1 \pm 0.8$ % and less).<sup>93</sup> Moreover, in the southwest of the Iberian Peninsula the Bell Beaker daggers show a significant higher percentage of arsenic than other objects.<sup>94</sup> Valério et al. connected this result with the silvery shine of the alloy, but stressed also the aspect of hardness.<sup>95</sup>

Axes which can be connected with the Bell Beaker culture also have an enriched content of arsenic. The six axes (Fig. 19) found in the Loire river near Trentemoult (Nantes, France) together with a Palmela point had an arsenic content of

- <sup>88</sup> Hunt Ortiz 2003.
- <sup>89</sup> Rovira/Montero 2013.
- <sup>90</sup> Zimmermann 2007.
- <sup>91</sup> Blasco et al. 2016.
- <sup>92</sup> Rovira Hortalà et al. 2014, 553–554.
- <sup>93</sup> Valério et al. 2018.
- <sup>94</sup> Valério et al. 2018, 10 Fig. 4.
- <sup>95</sup> Valério et al. 2018, 11.

<sup>&</sup>lt;sup>83</sup> Truhelka 1909,54–55.

<sup>&</sup>lt;sup>84</sup> Born/Hansen 2001, 25 Pl. 1.

<sup>&</sup>lt;sup>85</sup> E. Pernicka in: Born / Hansen 2001, 269.

<sup>&</sup>lt;sup>86</sup> Munteanu/Dumitroaia 2010.

<sup>&</sup>lt;sup>87</sup> Ambert et al. 2015.



Fig. 13. Ivan'ky, Mankivka District, Ukraine. Hoard (from Klochko / Klochko 2013).











2-4%.<sup>96</sup> This is also true for the hoard of Campo de Calatrava (**Fig. 20**), which consisted of 12 axes of considerable size and weight. They are 22–24 cm long and 1,000–1,105 g in weight. Their arsenic content is between 1.1 and 2.1%.<sup>97</sup>

This short review of find complexes from the 4<sup>th</sup> and 3<sup>rd</sup> millennia BC makes obvious that the content of arsenic was related to the object. Daggers and swords have a higher amount of arsenic than thick axes and other objects. Yet, it remains an open question as to whether this alloy was achieved by using *arsenspeiss* or metal objects or ingots with a high arsenic portion, or by smelting copper ores chosen for their natural impurities with arsenic.<sup>98</sup> There were probably several possible methods. It is a matter of future research to investigate the early arsenic bronzes more closely. The basis are thousands of metal analyses which should be analysed in a wider geographical frame and augmented by lead isotope investigations.

Understanding the technical details of this innovation should also shed light on its main application area as is visible in the archaeological record. Arsenical bronze was used for the production of effective weapons. They became harder and more elastic. The daggers and swords had fewer cavities, which were always predetermined breaking points. The sword and the halberd were developed only for killing people. Thanks to the work of Christian Horn the development of the halberd can be followed from the 4<sup>th</sup> to the 2<sup>nd</sup> millennium BC.<sup>99</sup> The silvery shine of the daggers was probably favoured not only for aesthetical reasons, but also as proof of quality. This may include the restricted access to these products to the upper classes.<sup>100</sup> Alloying made developments in weapons techniques possible, which could be decisive for one's life.

# Chronology and terminology

When Christian Jürgensen Thomsen introduced his chronological system, he based it on Danish finds, and the Bronze Age was of course defined by objects from the middle of the 2<sup>nd</sup> millennium BC.<sup>101</sup> Forty years later, in 1876, the term Copper Age was introduced by Ferenc Pulszky to describe the earliest copper tools in the Carpathian Basin,

<sup>97</sup> Pers. information by Salvador Rovira.

<sup>98</sup> Thornton et al. 2002.

<sup>101</sup> Thomsen 1836.



**Fig. 18.** Montilla (from Rovira Hortalà et al. 2014).

<sup>&</sup>lt;sup>96</sup> Baudouin 1923: Axes and Palmela point are not a closed find *strictu sensu*, but the dating is not contradictory.

<sup>&</sup>lt;sup>99</sup> Horn 2014.

<sup>&</sup>lt;sup>100</sup> Mödlinger/Sabatini 2016.



Fig. 19. Trentemoult (from Baudouin 1923, rearranged).



which can now be dated to the 5<sup>th</sup> millennium BC.<sup>102</sup> The term 'Copper Age' was later used by Hermann Müller-Karpe for describing all pre-Bronze Age societies with metal, but this concept failed because it connected very different cultures from more than two millennia.<sup>103</sup> But the term 'Copper Age' should be restricted to Southeast Europe in the 5<sup>th</sup> millennium BCE.

During the times of the "old chronology", arsenic bronze could be regarded as a short experimental phase before the introduction of the tin bronze. But already in 1967 J. A. Charles noted, that copper alloying represents a definitive phase of 300–400 years of technological development

<sup>102</sup> Pulszky 1877.

Fig. 20. Campo de Calatrava (from Monteagudo 1977, rearranged).

<sup>&</sup>lt;sup>103</sup> Korfmann 2004.





during the Bronze Age.<sup>104</sup> Ivan Vajsov argued that arsenical copper was the "signpost" to the Bronze Age, but not the Bronze Age itself.<sup>105</sup> Therefore, he spoke of a "Proto-Bronze Age". Since then the calibration of the radiocarbon data has profoundly changed the chronology of the 4<sup>th</sup> and 3<sup>rd</sup> millennia BC and, hence, we must consider an arsenic copper production for more than 2000 years in most parts of the metal producing world. This is hardly an experimental phase, nor can it be regarded as preparatory for the "real" Bronze Age with tin alloy, which moreover lasted only 1000 years before it was replaced by the production of iron **(Fig. 21)**.

The current situation in archaeological terminology is guite confusing. In Mesopotamia the 4<sup>th</sup> millennium BC is called the 'Chalcolithic', and is contemporaneous with the Early Bronze Age in the Caucasus region. Farther to the West this time period is called the 'Eneolithic' in Moldavia or 'Late Copper Age' in the Carpathians. In Central Europe at this time there is still the 'Middle and Late Neolithic'. It is obvious that the old terminology is no longer fitting. Since then it has become clear that the Corded Ware and Bell Beaker cultures cover more or less the entire third millennium; that is, they are contemporaneous with the Early States in the Near East and Egypt. The entire time period of the 4<sup>th</sup> and 3<sup>rd</sup> millennia BC is characterized by the use of arsenic copper or, better, arsenic bronze. It is a period with far reaching changes in technology and also in social organisation.<sup>106</sup> It is always very difficult to change terminologies. However, the existing terminology in chronology prevents a conceptual frame for a time period of technical change in the area between Western Europe, the Caucasus, Iran and the Near East up to Central Asia.

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<sup>&</sup>lt;sup>104</sup> Charles 1967, 26.

<sup>&</sup>lt;sup>105</sup> Vajsov 2002 173: "Die Entdeckung des Prinzips der Arsenlegierung ist jenes entscheidende Know-how, welches der Wegweiser in die Bronzezeit ist, nicht aber die Bronzezeit selbst! Diese hat sich noch auf der Basis von neuen Metall-

technologien, neuen Bezugsquellen und letztendlich auch neuen Kontakten und vielerorts auch neuen Bevölkerungsgruppen als Gesellschaftsstruktur zu konstituieren und zu etablieren. um auf der historischen Bühne aufzutreten."

<sup>&</sup>lt;sup>106</sup> Hansen 2014.

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# Summary

In this paper the scientific interest in the rise of metallurgy and copper alloys is discussed in a wider frame of the history of knowledge. Alloying is described as the turning point in metallurgy from a prestigious goods production into a production of functional objects. According to the archaeological record this change seems to be driven especially by the weapon industry. A short overview serves to show that arsenic was chosen for certain objects as an intentional alloy. It was not a natural impurity. This crucial technical innovation deserves more archaeological and scientific investigations. Furthermore, the long period during which arsenical bronze was used needs some changes in archaeological terminology. The term 'Bronze Age' should not be limited to the short time span of tin bronzes.

## Резюме

В данной статье в широком контексте обсуждается научный интерес к возникновению металлургии медных сплавов. Легирование явилось поворотным моментом в металлургии, в результате которого от производства престижных изделий был совершен переход к производству функциональных предметов. Согласно археологическим данным, это изменение в первую очередь было связано с производством оружия. Краткий обзор показывает, что для определенных объектов в сплав в качестве добавки был выбран мышьяк. Он применялся преднамеренно, а не являлся природной составляюшей металла. Это важнейшее техническое нововведение заслуживает дополнительных археологических, атакже специальных исследований. Крометого, длительный период использования мышьяковой бронзы требует некоторых изменений в археологической терминологии. Термин «бронзовый век» не должен ограничиваться коротким промежутком времени, связанным лишь с оловянистой бронзой.