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Social Processes in Ancient Eurasia and Development of Types of Alloys in Metallurgical Production

S.A. Grigoriev

Institute of History and Archaeology, Ural Branch, Russian Academy of Sciences, Chelyabinsk, Russian Föderation; e-mail: stgrig@mail.ru

Abstract

The article is devoted to the main regularities in changes of types of alloying in the Eurasian Bronze Age. The aim of the article is to show the reasons and mechanisms of these changes. The article is based on researches by the author of the Eurasian Bronze Age slags which showed direct link of use of particular alloys with types of ore and gangue. Deviations from this rule are rare. Social processes stimulating expansion of metal consumption were a cornerstone of these changes. It led to change of the ore base that resulted in emergence of appropriate technologies of ore smelting, technologies and types of alloying and, eventually, morphology of metal artifacts. The mass transition to arsenic copper or to use of copper-arsenic ore became possible with transition from smelting rather pure pieces of malachite to smelting ore with fragments of gangue. This type of alloying was possible in case of low-temperature smelting of oxidized ores. After the abrupt territorial expansion of metallurgical technologies and increase in amounts of metallurgical production at the beginning of the Late Bronze Age, the mass use of ores from refractory rocks and coper-iron sulfides begins. It resulted in increase of smelting temperature and made impossible the alloys with arsenic because arsenic vaporized. Therefore a necessity to look for other alloying component was created. And it was tin. But, as its deposits were rare, specific conditions for its wide circulation and organization of trade and exchange network were necessary. Such conditions in Northern Eurasia were provided by migrations from east to west at first of the Seima-Turbino, and then of the Andronovo tribes. But the same processes took place in Europe and the Middle East, stimulating new social realities.

Keywords: Bronze Age, Northern Eurasia, tin, arsenic, metallurgical technologies, alloying, ore smelting, social processes.

Introduction

The problem of technological changes associated with the choice of one or another type of alloys used in copper metallurgy is one of the basic problems in archaeometallurgy. In principle, if to ignore some rare alloys, the use of pure copper was replaced by the period of use of arsenic, and then of tin alloys. But the reasons for this ubiquitous transition from arsenic to tin alloys remain not completely understandable (Pernicka, 1998, pp. 135-136).

At the end of the Middle Bronze Age (MBA) in the Urals, Sintashta and Abashevo cultures arose (Fig. 1), which were the basis of cultural genesis in the Late Bronze Age (LBA) and are considered within the first phase of the Eurasian Metallurgical Province (see about the metallurgical provinces in Eurasia: Chernykh, 2014). And in this period arsenic alloys were used. The second phase began with the westward movement in the south of the forest zone of Seima-Turbino tribes, and they brought tin alloys to the region (see Chernykh, 1966; 1970; Chernykh, Kuzminykh, 1989a). On the base of Sintashta and Abashevo cultures in the steppe and forest-steppe of Eastern Europe, Srubnaya culture formed, and to the east of the Urals did Petrovka and Alakul cultures. Then people of Fyodorovka (or Andronovo) culture move from the east. At the end of the Bronze Age in the whole region, the Cordoned Ware cultures, in particular, Sargari, appeared. And metal of these cultures contains already very high tin concentrations (see more about the cultural genesis of the region: Grigoriev, 2002). Thus, in Northern Eurasia the trend of replacement of arsenic by tin entirely corresponds to that we see in other parts of Eurasia, this means that it reflects universal processes.

Figure 1. Map of Eurasian Metallurgical Province and its basic cultures

1. Stages of technological developments: Cu → Cu+As → Cu+Sn

1.1. Copper-arsenic alloys

In the Eneolithic and Early Bronze Age in Northern Eurasia, with rare exceptions, pure copper dominated. The same is true for the Eneolithic Balkans and Anatolia, although in the latter the first arsenic alloys appeared. It is noteworthy that in all these regions there is almost no metallurgical slag, although traces of mining works are well known. A slag fragment from the settlement of Durankulak (Bulgaria) is an exception, but it was very small (Glumac, Todd, 1990). There are a find from Tepeh Hissar (Thornton, Rehren, 2009, pp. 2701-2707), and slagged crucibles from some other places. This global absence of slag can be explained by the use of relatively pure pieces of oxidized ore. In some instances the ore could contain admixtures of arsenic, but it was not able to create a steady technological tendency, only occasional presence of arsenic in the metal.

In Northern Eurasia copper-arsenic alloys appeared extensively in the Middle Bronze Age (MBA) in Catacomb culture of the steppe of Eastern Europe. In Anatolia and Iran this happened earlier, already in the Early Bronze Age (EBA). The appearance of the arsenic alloy is quite understandable, because there is a series of copper deposits with the ore containing high admixtures of arsenic and/or impregnation of arsenic-containing minerals. The latter are especially important. Only with the beginning of smelting malachite together with gangue, these arsenic-containing minerals began to fall into the furnace charge and their significance for properties of metal was understood.

In areas with deposits of copper-arsenic minerals, for example, the Iberian Peninsula and Iran, arsenic bronzes were typical, and persisted for a long time (Hunt Ortiz, 2003, pp. 323, 329-332; Palmieri, Sertok, Chernykh, 1993, p. 596; Zwicker, 1989, p. 192). But there was also a special selection of ore and its mixing with arsenic ores (Thornton, Lamberg-Karlovsky, 2004a, p. 267; Thornton, 2009, p. 317).

The fixing of this alloy as a technological tradition had, of course, quite rational reasons. This admixture has a beneficial effect on metal quality: after casting its hardness is the same as that of pure copper. But after cold-working it is noticeably harder; and the melting point of the metal decreases. After cold-working the hardness of copper with 2.6% arsenic grows from 65-70 Hv to 150-160 Hv (Scott, 1991, p. 82). In addition, arsenic plays a role of deoxidant, it improves the mechanical properties of articles (Ravich, Ryndina, 1984, pp. 117-120; Budd, Ottaway, 1990, p. 95). Smelting oxidized ores in relatively small furnaces had a serious problem: it was difficult to create a reducing atmosphere. The solution of the problem was provided by a number of measures: blowing air into the furnace without pressure, and air reacted longer with charcoal; use of a mixture of oxidized and sulfide ore; preference of ores without admixtures of refractory gangue; and this use of arsenic admixtures.

It is likely that after some time metallurgists paid attention to the fact that smelting was more successful, and the metal had better properties after the addition of arsenic minerals to the ore, and they began to add them into the furnace already deliberately. Therefore, this line between the artificial alloys and use of ores with arsenic admixtures is rather fuzzy. It depended on a concrete situation. In Anatolia, for example, both copper-arsenic and arsenic ores were used. In Northern Eurasia metallurgists of Sintashta culture added arsenic minerals at the stage of ore smelting, and arsenic is present in the Sintashta slag (for more details, see Grigoriev, 2015, pp. 152-158).

But regardless of how this alloying was realized, intentionally or accidentally (as smelting copper ore with arsenic, as mixture of ores or additions of arsenic minerals), ***all these operations were carried out at the stage of ore smelting***.

This understanding of arsenic as a reagent that changes the quality of metal is clearly visible in metal of Sintashta culture, where the correlation between the type of object and the arsenic content is found (Grigoriev, 2015, p. 159) (Tab. 1). The average value of arsenic content increases in those objects that were subjected to larger dynamic load. Exceptions are bracelets, but their higher arsenic content could be caused by either technological (better flexibility and castability) or esthetic reasons. At the same time, all types of objects show essential dispersion of these concentrations, since the alloying was carried out at the stage of ore smelting; besides, the arsenic content fell after re-melting.

The same situation is recorded in Eastern Anatolia. On the Arslantepe settlement the direct correlation between the types of artifact and contents of arsenic is observed. So, spearheads contained 2.5-3% arsenic and swards 4.5-5% (Palmieri et al., 1994, p. 447). Consequently, metallurgists could empirically determine the properties of the metal, even with such minor differences in the arsenic content.

As we see, the dispersion of arsenic concentrations in Sintashta object is more expressed than that on Arslantepe. Perhaps the Sintashta metallurgists were also able to determine the arsenic content in copper more accurately, but they were forced to use metal that was available, as they had much lesser choice than their Anatolian colleagues had. In this period a market production already existed in Anatolia, with great volumes. This facilitated the selection of metal for specific products.

Table 1. Diapason of arsenic contents and its average value in different types of artifacts of the Sintashta-Abashevo time.

Type	Diapason As (%)	Average value (%)
rod	0.009	0.009
wedge	0.046	0.046
hook	0.005-0.32	0.163
fishing hook	0.202	0.202
ingot	0.005-0.39	0.21
clip	0.082-0.72	0.334
facing of vessel	0.81	0.81
sickle	0.005-3.2	0.836
bracelet	0.67-1.11	0.89
drift	0.011-4.9	1.042
chisel	0.005-3.6	1.328
awl	0.063-6	1.838
harpoon	1.94	1.94
adz	0.34-4.9	2.421
knife	0.01-5.4	2.85
spearhead	2.85	2.85

But arsenic vaporizes. Additions of nickel to metal contribute to its preservation. Study of a chemical thermodynamic model for ancient recycling demonstrated that the ternary As-Cu-Ni system provided saving of arsenic compared with the binary As-Cu system (Sabatini, 2015). And very often nickel accompanies copper-arsenic alloys. Therefore, we have assumed that the alloying was done by some arsenic-nickel mineral, with a ratio of arsenic to nickel as 10:1 (Grigoriev, 2015, p. 155), but it is impossible to determine how purposeful it was, although the typical nature of this type of alloy testifies it. It is widely presented on sites of Anatolia, Levant, Syria, Egypt, Luristan and Mohenjo-Daro (Tylecote, 1981, pp. 45, 50; Yener, Geckinly, Özbal, 1994, p. 378; Schmitt-Strecker, Begemann, Pernicka, 1991; Riederer, 1991, p. 89).

Meticulous studies of Maikop metal of the EBA in the North Caucasus makes it possible to speak definitely about the purposeful nature of this alloy. It was produced by additions of nickeline, nickel arsenide, to the ore. This kept arsenic in the metal. There is no significant difference in the hardness of arsenic and arsenic-nickel alloys, and the latter require some different methods of working (Ryndina, Ravich, Bystrov, 2008; Ryndina, Ravich, 2012, pp. 5-9). In this case, the same situation is likely: a long empirical experience led to understanding of some relationships, possibly not adequately interpreted.

It should only be noted that not the arsenic itself evaporates, but its oxides, it depends not only on the temperature, but also on the oxygen pressure. In oxidizing conditions arsenic is oxidized, and its trioxide evaporates (McKerrell, Tylecote, 1972; Sabatini, 2015).

1.2. Tin bronzes

The first admixtures of tin in copper are found in different regions of Europe and in the Urals already in the Eneolithic context (Chernykh, 1970, pp. 28, 108; Krizhevskaya, 1977, pp. 96-104; Radivojević et al., 2014, pp. 235-256; Grigoriev, 2015, pp. 68, 73, 74), but a source of this alloying, as well as its deliberate nature, is unclear.

Charles assumed that originally ones started to use tin sulfide, stannite (Cu_2FeSnS_4), confusing it with copper ore with arsenic impurities (Charles, 1980, p. 172). Some pieces of stannite can be actually confused with chalcopyrite. And other authors agree that the first tin bronzes were made from stannite (Roberts, Thornton, Pigott, 2009, p. 1017). I suppose this hypothesis is true, for the reason that this episodic appearance of tin coincided with the episodic chalcopyrite smelting (Grigoriev, 2015, pp. 80-83), although after the emergence of this innovation, in some places it could be used quite deliberately.

But initially the alloys with tin were not widely distributed. And the problem is not that the invention of the last type of alloy required the experience in production of arsenic copper. Tin alloys were unclaimed by society. Perhaps, only in Anatolia this tradition hardly existed, having begun to develop only in the EBA, and already on the basis of smelting of cassiterite into metallic tin (Yener, 2000, pp. 88, 100-123, Yener et al., 2003, pp. 181-186). But the rapid development of tin alloys in the Middle East took place already in the MBA (Avilova, 2008). In Northern Eurasia, the spread of tin alloys occurred at the beginning of the LBA, in the early 2nd millennium BC, with the migration of the Seima-Turbino tribes, and then this process intensified in Andronovo time (Chernykh, 1992). In Europe, tin bronzes were known occasionally in the context of the 3rd millennium BC, but their mass distribution occurred already in the first half of the 2nd millennium BC, and this coincided with the appearance of bronze artifacts going back to the Seima-Turbino tradition. This coincidence is explained, apparently, by migration from the east, from the Altai. Moreover, the appearance of the Seima-Turbino tradition in the Altai was caused by migrations from the south (Grigoriev, 2002, pp. 207-210; 2015, pp. 495, 500-502).

Therefore, at first sight this process of replacement of arsenic alloys by tin ones is explained by the natural course of technological development in the advanced areas of the Middle East, and the subsequent spread of more advanced technology by migrating tribes, or in the form of technological influences and borrowings. But the situation was more complicated. Alloying with tin was not at all a development of arsenic alloying, and its significant advantages are doubtful.

1.3. Tin versus arsenic

Technologically these types of alloys were not related: arsenic alloying was carried out at the stage of ore smelting; and metallic tin was added into copper (see, for example, Rehren, 2003, p. 209). In our huge collection of the LBA slag from Northern Eurasia there are, practically, no samples with higher concentrations of tin. First the metallurgists produced metallic tin and copper, and then they re-melted them together. Actually, for Iran a method of alloying of copper with speiss, iron arsenide, is reconstructed (Thornton, Lamberg-Karlovsky 2004b, pp. 51, 53; Thornton, Rehren, 2007, p. 316). But it was hardly widespread. It should not be excluded that this method led to the appearance of this principle of alloying “metal with metal”, which was characteristic of alloying with tin. But it is more likely that this technology was developed from smelting with stannite; when metallurgists drew attention to admixtures of cassiterite, etc.

Sometimes it is even assumed that the replacement of arsenic with tin, probably, happened not for technological, but for medical reasons, because vapors of arsenic badly affected the health (Muhly, 1976, p. 90). Let us remember that Dr. Semmelweis insisted on need to wash hands before surgeries only 150 years ago, and his colleagues mocked at him. It is possible to imagine ecological and hygienic competence of people of the Bronze Age! And in Northern Eurasia the smelting operations in dwellings are just more typical for smelts with arsenic. Its smell did not disturb them. Only after beginning of smelting sulfides the smell became unbearable and the operations were removed from dwellings. But nobody changed technologies or raw materials for this reason.

Tin bronzes are somewhat harder than arsenic ones, but the difference is not as noticeable as to compare them with pure copper. But in case of re-melting the objects gradually lose the arsenic content, and their hardness gradually decreases. However, this metal could be used for other types of object; and for objects requiring hardness it was possible to use “fresh” metal, smelted from ore.

And the hardness of tin bronzes should be discussed. At low contents of the alloying component, arsenic copper is harder. But its hardness gradually increases with increase in the arsenic content only up to 3%. Beyond this, the hardness of arsenic copper almost does not increase and the tin bronze with tin content of more than 4% is already harder than arsenic copper. But even at 8% of alloying agent the hardness of arsenic copper after cold-working (50% reduction) is 150 HB, and the hardness of tin bronze is 195 HB (Scott, 1991, p. 83). This is already a noticeable difference, but it is however insufficient to be a reason for the drastic change in the system of production and exchange. In addition, during the early stages the high-tin bronze did not dominate, and the most part of this metal had no advantages in comparison with arsenic copper. For example, in Alakul culture of the Transurals 63.5% of bronzes contain 0.5-6% tin (Tigeeva, 2013, p. 33). The same situation we see in the Aegean. In the MBA, most of the bronzes had a tin content lower than 8%, bronzes with the tin content higher than 8% dominated only in the LBA (Papadimitriou, 2008, pp. 280, 287).

In the early period, when mass tin supply over huge spaces was not organized, this was a doubtful advantage. Consequently, hardness could not be the cause of the rapid spread of tin bronzes.

Certainly, tin makes it possible to better control the degree of alloying and to obtain a metal with precisely specified properties. In the process of smelting arsenic minerals with copper ore, it was practically impossible to do this (Northover, 1987, pp. 111-114), although, of course, ancient smelters roughly appreciated the degree of alloying. But I would not exaggerate this factor in choosing a type of alloy, since most of the used metal was re-melted, certainly, from metal scrap. And after its re-melting, or even after repeated hot annealing, the arsenic content in the product decreased. But even in case of melting together of different pieces of tin bronzes, the content of tin did not remain unchanged. And this problem was solved by another way. Surely, there were some empirical ways to understand for which types of products one or another piece of metal was optimal.

In principle, tin made it possible to make more complicated foundry goods. For arsenic bronzes the frequent re-melting is undesirable, since the arsenic content is reduced. That is why we see that when working with arsenic bronzes, metallurgists preferred annealing at lower temperatures, and casting was relatively simple, and it was applied in a limited way (Degtyareva, 2010, pp. 121, 123, 134, 138). In the long run, this was one of the reasons why laminar objects dominated in Northern Eurasia in the MBA and at the transition to the LBA, i.e., during the dominance of arsenic copper; and with the appearance of tin, a more complicated casting was disseminated. And we see this gradual increase in the role of casting operations in metalworking from the earlier to later LBA complexes (Tigeeva, 2011, pp. 72, 77; Degtyareva, Kostomarova, 2011, p. 35). Of course, the arsenic loss in casting could be reduced if the metal is protected from oxidation, since only its trioxide evaporates (see above). It could also be worked at low temperature. This limited the possibilities of shaping the product, but this was not a critical problem.

However, this arsenic sublimation was also a problem in ore smelting. At high temperatures, arsenic did remain neither in metal nor in slag. Tin, which was alloyed with metal, had no such problems.

Thus, all the above-mentioned reasons (somewhat better properties, the possibility to better control the degree of alloying, unpleasant smells from vaporizing arsenic, more noble color of tin bronzes) took place, of course, and played some role in this mass transition to tin, but they were insufficient for global processes. The only serious limiter was the high temperature and oxidizing conditions in ore smelting, as it could not be circumvented, and it was impossible to reconcile with it. It acted as a technological inevitability. All other minor advantages of tin were eliminated by the fact that it was a rare metal on our planet. In Northern Eurasia, its significant deposits are situated in Eastern Kazakhstan, and the transportation of this metal over long distances was a serious enterprise. However, in this case the advantage of tin was its possibility to be transported in a smaller volume, as the metal was transported, but in the case of arsenic, it was possible to transport finished copper-arsenic ingots, rather than ore, or arsenic minerals over a relatively short distance. So, this factor was significant, but only in the case of tin transportation over vast spaces.

Thus, the essential conditions for replacement of arsenic by tin were:

1) a rigid technological necessity of the transition to this type of alloy
2) social conditions that made possible the large-scale extraction of tin in relatively small areas as well as organization of its stable supplies throughout Eurasia.

2. Technological background of the victory of tin

Because of the complexity and high cost of slag studies, its study is usually limited to several samples from a single (or several) monuments and slags of a relatively large region have never been investigated. Therefore there was a feeling that these slags depended on type of ore that was nearby. In addition, a broad generalization of data from different analyzes has never been done, since they were often done using different procedures and are not always comparable. But in Northern Eurasia for many years the laboratory headed by E.N. Chernykh has studied more than 40,000 metal objects of this region, and their chemical composition was determined. And then the author carried out a project of slag studies. Within its framework 2,300 samples of slag and ore have been studied and 2,600 different analyzes have been made (Grigoriev, 2015). This allows us to compare the metal and slag statistically and to reveal for Northern Eurasia one more coincidence.

Above we have discussed that in the Eneolithic and the EBA mostly pure ore was used. In the Sintashta time (the transition from the MBA to the LBA), mainly the oxidized ore from ultrabasic ore-bearing rock was used in the smelting, and this coincided with the arsenic alloying (for more details see below). It is necessary to understand that the ore in these rocks is poor. In the LBA we see a significant growth of the ore base, and the main ores are the richer and refractory ores from quartz veins and sandstones, as well as sulfide ores.

At the comparison of technology we see again one striking difference: in the Sintashta time smelting was conducted at temperatures about 1200-1300 °C; in the LBA smelting temperatures often shift to the range of 1300-1500 °C. The reason is that the ore from more refractory rocks was used; besides, smelting copper-iron sulfides cause the exothermal reaction of burning sulfur. In addition, probably, the duration of smelting operation increased, but it is impossible to calculate this yet. All this led to the removal of arsenic at the stage of ore smelting and made it impossible to obtain alloyed metal. Accordingly, the transition to these types of ores predetermined the end of the use of arsenic copper (this became technologically impossible) and created the conditions for the spread of tin alloys.

It is necessary to note that in case of oxidized ores from quartz veins and sandstones there was one more factor. In order to achieve liquid slag, smelters raised the temperature and intensified the blowing. As a result, almost all the slags show a strong oxidizing atmosphere (Fig. 2). Thus, two factors contributed to the evaporation of arsenic: relatively high temperatures and the oxidizing atmosphere.

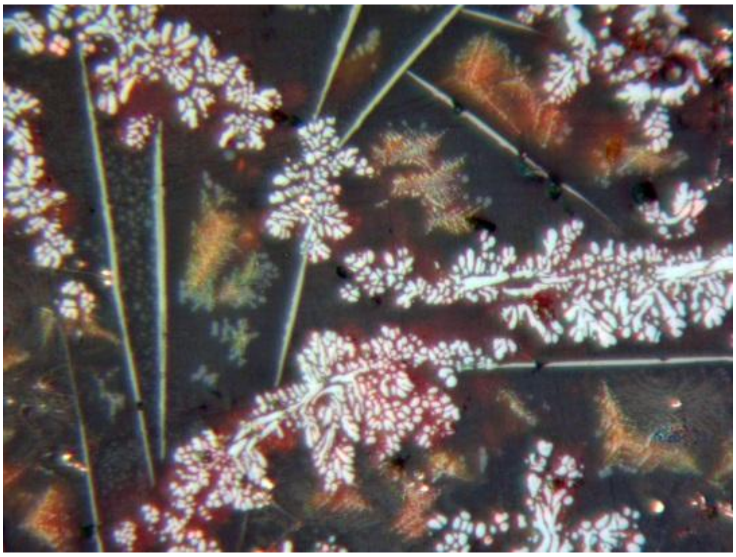

Figure 2. Slag form Pokrovskoe settlement in the Orenburg area: cuprite dendrites and needles of delafossite, marking oxidizing smelting conditions.

And we can show this strict dependence of the type of alloy on the type of initial ore on the example of materials from different areas of Northern Eurasia.

2.1. Comparison of slag and metal. General regularities in the Eurasian Metallurgical Province

In addition to the results of spectral analyses of slag and metal (both ours and taken from publications), this study is based mainly on 527 mineralogical analyses of the Bronze Age slag (Tab. 2). Analyzed materials of the Early Iron Age are not included because they are out of the problem under consideration, as well as a large series of materials from the Kyzylkum desert, which were found mainly on weathered sites, and allow us to trace only the most common regional trends. It is impossible to use them in statistics. Nevertheless, this research includes some materials with an incompletely defined cultural identity, in particular, slags from settlements that have both Sintashta and Petrovka layers. In the table they are placed in a separate line, but further they are considered together with the Sintashta slags, because all they belong to the transition from the Middle to the Late Bronze Age. Slags of the Asian zone of the Eurasian Metallurgical Province are defined as “Alakul” or “Fyodorovka” if their cultural identity has been determined reliably. In case of the presence of both Alakul and Fyodorovka materials on the site, they are placed in the table as “Andronovo”; if materials of the Final Bronze Age are also present, slags are designated as LBA. But in the final tables all they are considered as LBA slags.

Table 2. Distribution of mineralogical groups of slag over cultural groups: I - oxidized ores in ultrabasic rocks, II - oxidized ores in acid rocks, III - oxidized ores in ultrabasic rocks with admixtures of acid rocks, IV – oxidized slags smelted from oxidized ores in acid rocks, V - slag smelted from the pure malachite, VI + VII - slag smelted from sulfide ores.

Mineralogical group Culture	I	II	III	IV	V	VI+VII
Sintashta	45	12	17			
Sintashta-Petrovka	36	14	29	17		
Abashevo culture of the Western Urals	8	6	3	7	4	
Total, Sintashta-Abashevo period	89	32	49	24	4	0
%	44.95	16.16	24.75	12.12	2.02	0
Srubnaya culture of the Western Urals	22	17	2	18		7
Orenburg area, LBA	10	19		39		9
Srubnaya culture of the Don area						12
Elunino culture		26		4		
Visnyovka-Odino type						7
Petrovka culture	3	1	2	15		2
Alakul culture	2	2		20		1
Fyodorovka culture				1		21
Mezhovka culture	2					32
Andronovo sites	3	5				3
Final Bronze Age	1	2		2		
LBA of the Asian zone (Andronovo/Sargari)	2	6				9
Total, LBA	45	78	4	99		103
%	13.68	23.71	1.22	30.09	0	31.31

For greater clarity, we combine I and III groups associated with ultrabasic rocks, as well as the II and IV groups associated with acid rocks. As a result, we get the following picture of the ore base in the transitional period to the LBA and in the proper LBA (Tab. 3):

Table 3. Ratio of slag smelted from different types of ore in the Sintashta-Abashevo period and in the LBA (%).

Type of ore Period	Malachite	oxidized ores from ultrabasic rocks	oxidized ores from acid rocks	sulfide ore
Sintashta-Abashevo	2.02	71.57	28.28	0
LBA	0	14.89	53.80	31.31

In general the picture corresponds exactly to the transition from the use of arsenic alloys in the Sintashta-Abashevo period, to the use of tin alloys in the LBA. But temporal and spatial comparisons allow us to see different peculiarities of this process.

2.2. Comparison of slag and ore in the first phase of the Eurasian Metallurgical Province (the MBA – LBA transition)

In the first period, we see an unconditional domination of oxidized ores from low-melting ultrabasic rocks. Their ratio to other ores is 71.57%. And, as we will see below, this ratio is duplicated in the metal of this time.

In the first publication of analyses of the Sintashta-Abashevo metal, E.N. Chernykh divided the Ural Abashevo collection (some Sintashta artifacts were included in it) into two groups: arsenic copper (55 artifacts) and pure copper (17 artifacts) (Chernykh, 1970, p. 28). Consequently, the ratio of arsenic copper to pure copper was 76.39% and 23.61%.

In the later work (Chernykh, 2007, pp. 80, 81) the Sintashta-Abashevo metal has been divided into the same two groups: the total number of analyzed samples is already 770, of which 240 are pure copper. This is 31.17%; hence the part of arsenic metal is 68.83%.

New analyses of the Sintashta metal allowed these objects to be divided into three groups: low-arsenic (0-0.3%), middle-arsenic (0.3-1%) and high-arsenic (more than >1%) (Grigoriev, 2015, p. 153) (Fig. 3). Two first groups contain 28.41% of samples, and the third – 43.18%. Respectively, 71.59% of the analyzed objects correspond to the arsenic copper. Degtyareva relates to the group alloyed with arsenic about 80% of metal, but she supposes that the lower limit of this group is 0.1% (Degtyareva, 2010, p. 83). Besides, she analyzed only objects from the Sintashta sites in the Transurals, without the Ural Abashevo, where the ratio of arsenic alloys to pure copper is lower.

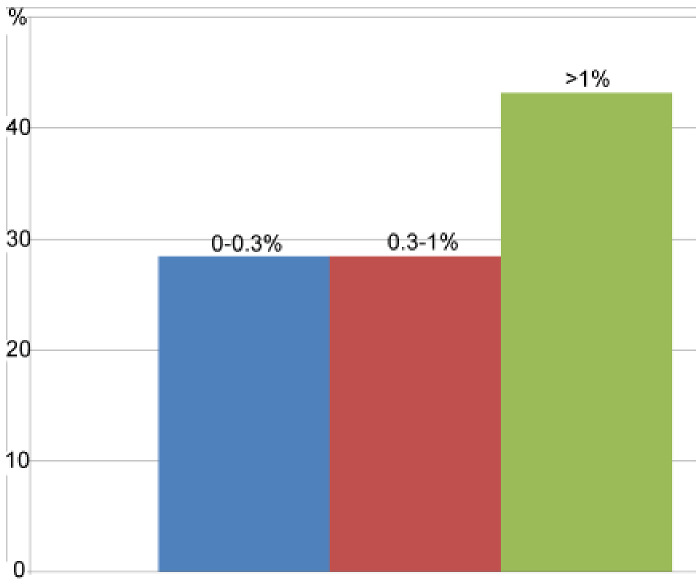

Figure 3. Distribution low-arsenical, middle-arsenical and high-arsenical metal of the Sintashta-Abashevo time.

But, in any case, this ratio of arsenic-alloyed metal is practically identical to the ratio of slag smelted from oxidized ores in ultrabasic rocks. Moreover, just this slag contains higher concentrations of arsenic, and arsenic inclusions (Fig. 4, 5; Tab. 4).

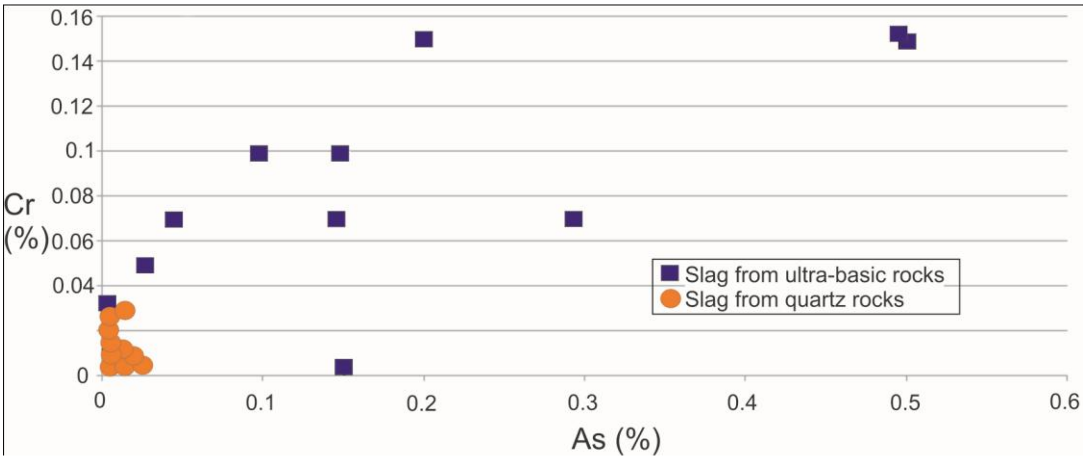

Figure 4. Arsenic concentrations in different types of Abashevo slag from the Western Urals.

Table 4. Arsenic inclusions in Sintashta slag smelted from ultra-basic rocks.

Sample	Analysis	Material	O	Cu	Fe	As
839	1	oxide	36.06	6.91	44.47	10.5
751	3	metal	6.36	9.88	38.29	44.81

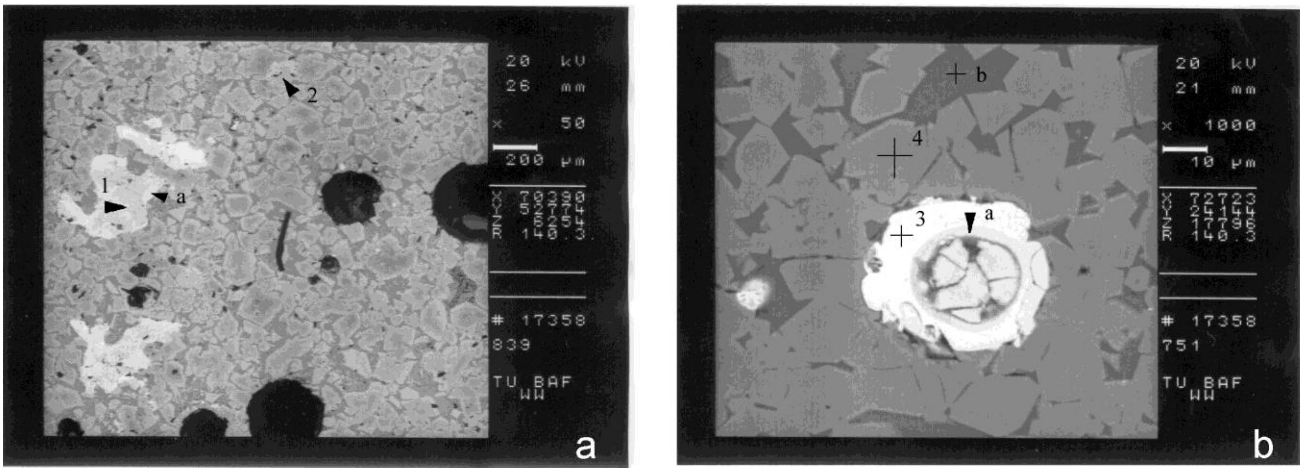

Figure 5. Arsenic inclusions in Sintashta slag: a – sample 839; b – sample 751 (see Tab. 4).

It indicates ***the rigid connection (both analytical and statistical) exactly ores from ultrabasic rocks with the production of arsenic metal.***

2.3. Comparison of slag and ore in the second phase of the Eurasian Metallurgical Province (LBA)

In the LBA, the number of slags associated with the ultrabasic rocks is reduced to 14.89%, and some of them occur from relatively early monuments that directly replaced Sintashta culture or even were synchronous with it. The part of oxidized ores from acid rocks such as quartz veins and quartz sandstones increased sharply (up to 53.8%), and sulfide ores (31.31%) were more actively used.

Unfortunately, there is no generalized data on the LBA metal for the Eurasian Metallurgical Province. Even generalizations made for individual cultures are rare. But, since the ratio of slag smelted from ore in ultrabasic rocks is low here, it corresponds to the general picture of rejection of arsenic alloying and the transition to tin alloying.

2.3.1. Arsenic and types of ore. Situation in European zone of the Province (Srubnaya culture)

More detailed comparisons can be made only for individual regions. The situation with metallurgy of Srubnaya culture (Volga and the Western Urals) is indicative. According to our data (Tab. 5), about 1/5 of the metal was smelted from ore in ultrabasic rocks. Others are oxidized ores from acid rocks and sulfide ores, and their smelting could not be crowned by the arsenic copper. It is clearly visible in the Srubnaya (Timber-Grave) slags of the Bashkir Urals (Grigoriev, 2015, p. 346), where the slag smelted from sulfide ore, as well as that from oxidized ore in acid rocks, does not contain arsenic, and in slags from ultrabasic rocks arsenic is present in 19 instances of 24, i.e., in 79% of samples. But to the west, in the Volga region, in the settlement of Shigonskoe II, there is no slag of this type containing arsenic at all; probably there was already a problem with the alloying component.

Table 5. Types of ore used by metallurgists of Srubnaya culture (%).

Type of ore	oxidized ores from ultrabasic rocks	oxidized ores from acid rocks	sulfide ore
%	21.94	60	18.06

According to date of E.N. Chernykh (2007, p. 93), in the Srubnaya metal about 9% of objects contain arsenic and antimony (Tab. 6), which is lower than the ratio of slag from ultrabasic rocks. But, if we re-calculate this data by excluding tin, i.e., having obtained only data on the metal that was smelted from ore, we will see that the Srubnaya smelters produced 85% of pure copper and 15% of arsenic one, with a limited addition of objects with arsenic and antimony. This number is closer to the one we got for slag. However, some of these objects could be produced in this period from fahlores, such as tetrahedrite (Cu_3SbS_3) and tennantite (Cu_3AsS_3). They contain a lot of arsenic and antimony, and it's easy to smelt them; and although the temperatures could be high enough, probably a part of the arsenic remained in metal, although its content, of course, was reduced. Besides, not all of the Srubnaya slags smelted from ultrabasic rocks contained arsenic.

Table 6. Types of alloy of Srubnaya culture (Chernykh, 2007, p. 93)

Type of alloy	Cu+As, Cu+As+Sb	Cu+Sb	Cu	Cu+Sn, Cu+Sn+As
%	8.2	0.7	45.6	45.4
	8.9		91	

Therefore, the ratio of slag smelted from ultrabasic rocks and the ratio of arsenic copper are also quite comparable here. And, as in the case of the Sintashta-Abashevo slag, slags from ultrabasic rocks usually contain higher arsenic concentrations, although not so often. Thus, this tradition is gradually dying out.

2.3.2. Arsenic and types of ore. Situation in Asian zone of the Province

The situation in Asian zone has been studied incomparably worse. Our study has covered a limited amount of slag, but the chemical composition of the Andronovo metal has been well studied only in the Tobol area. Only metal of the Final Bronze Age was studied in the entire Asian zone.

We see obvious sharp changes in the slag, in comparison with the previous periods: the ratio of slag smelted from ultrabasic rocks is reduced to 7%. The remaining raw materials are presented by oxidized ore from acid rocks and sulfide ore (Tab. 7).

Table 7. Types of ore used by metallurgists of the Asian zone of the EAMP.

Type of ore	oxidized ores from ultrabasic rocks	oxidized ores from acid rocks	sulfide ore
%	6.94	47.22	45.83

Therefore, in principle, we could expect that about 7% of the region's copper objects should contain arsenic, while the rest should be represented by pure copper or tin bronzes. Formally, it is so: according to the earlier data of E.N. Chernykh (1970, pp. 21, 22) 8% of Andronovo objects have arsenic-antimony impurities, but some of them had been additionally alloyed with tin. In general, 2/3 of the objects were alloyed with tin. Later studies gave a similar number 8.7% for the metal Cu+As+Sb in the Alakul culture of the Tobol area (Kuzminykh, Chernykh, 1985, pp. 346-366). This fully corresponds to the above stated slag mineralogy and, at first sight, should have the same explanation, but it is not so. As a rule, slags of this mineralogical group contain no arsenic. But arsenic impurities are present in slags smelted from sulfide ores, for example, in slags of Mezhovka culture from the settlement of Arkhangelski Priisk (Grigoriev, 2015, p. 538). Therefore, probably, this metal was smelted from fahlores or by alloying into sulfide ore. And a part of it is alloyed with tin.

Thus, in the LBA everywhere we see the same situation: there was the rejection of use of oxidized ores in ultrabasic rocks, transition to oxidized ores in refractory acid rocks, and also to sulfide ores. This strongly correlates with the rejection of arsenic alloys and the transition to tin alloys.

2.3.3. Tin-bronzes in the Eurasian Metallurgical Province

In the Alakul culture of the Tobol area, a half of the metal is presented by pure copper and another half by the tin alloys (Kuzminykh, Chernykh, 1985, pp. 346-366, Tigeeva, 2011, pp. 69, 70). In principle, both these copper groups correspond to the situation with slag, which reflects the predominant smelting ores from acid rocks in the Alakul time. The difference in the groups is explained only by the availability of tin. But the old tradition of arsenic alloys disappeared, even in those rare cases when ore from the ultrabasic rocks was used.

And this trend continued in Fyodorovka culture, where the part of tin bronzes rose to 72.7%, and tin-lead bronzes are also presented (9.1%). The rest of the objects were made from pure copper (18.2%) (Degtyareva, Kostomarov, 2011, p. 35). This is quite normal for this culture with its eastern roots.

As we have discussed above, to the west, in Srubnaya culture, the proportion of tin bronze is 45.4%, which is close to the Alakul indicators, but is much less than number of copper-tin alloys in Fyodorovka culture. Thus, the kinship of cultures could play some role in this metal distribution. Although the distance, of course, was also important, since the ratio of tin bronzes in the Srubnaya metalworking of the westernmost Don area was noticeably lower, about a quarter (Chernykh, Kuzminykh, 1989b, p. 11). In the Final Bronze Age in the Asian zone of the EAMP, the domination of tin bronzes persists, and there are some territorial differences caused by the remoteness from the Altai sources of tin: 68.7% of metal is alloyed in Northern Kazakhstan, 80.5% in Central Kazakhstan, and 88.5% in Eastern Kazakhstan. It is also remarkable that in the Altai, where the most part of tin was mined, we see a lot of bronzes with a high tin content, about 12-26%; but in the steppes of Eastern Europe the ratio of tin bronzes is only 12.5% (Agapov, Degtyareva, Kuzminykh, 2012, p. 56) (Fig. 6).

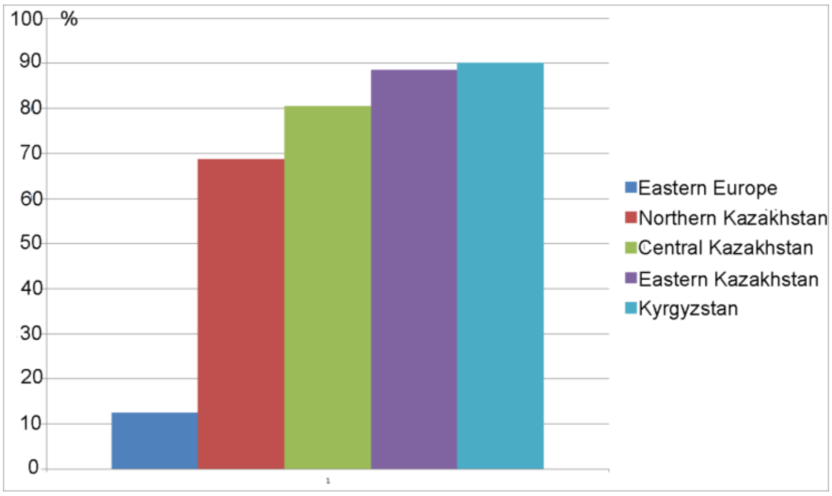

Figure 6. Tin bronzes in the Final Bronze Age in Eastern Europe and different areas of Asian zone of the Eurasian Metallurgical Province.

This means, although we see a slight decrease in the ratio of tin bronzes from east to west in the Asian zone, connected with the increase in distance of transportation, this factor was not the only significant one. A sharp drop in the ratio of tin bronzes in the European zone indicates that the efficiency of supply depended not only on distance, but also on social and ethno-cultural contexts, on the involvement of territories in some united system of relations and exchange; this means that the situation we have discussed above for the Fyodorovka, Alakul and Srubnaya metalworking, was repeated.

Thus, the ratio of tin alloys to pure copper depended on the availability of the alloying components. Therefore, the ratio of tin bronzes is reduced from east to west, but this was influenced not only by distance, but also by the presence of kindred inhabitants on the paths of tin trade, and by the degree of inclusion in this system of exchange.

3. Deviations from the trend

Of course, in its pure form this typological series "copper – arsenic copper – tin bronze" never existed. Different types of metal could coexist concurrently, even within the framework of a single archaeological culture, and their coexistence in different territories was, rather, a standard situation. And in some instances it can be explained by the availability of a particular raw material, as described above.

Situation in Europe was somewhat different from that described above for Northern Eurasia. Already in the Eneolithic metallurgists began using secondary sulfides, usually fahlores, such as tetrahedrite (Cu_3SbS_3) and tennantite (Cu_3AsS_3), whose smelting produced copper-arsenic or copper-arsenic-antimony alloys. With the spread of Beaker Culture about the mid-3rd millennium BC this tradition was distributed from Central Europe and the Eastern Alps to Northern Italy, France, Iberia, Britain and Ireland. Relatively pure ores were used, without admixture of gangue; and this was a non-slagging low-temperature process. But in this case drastic reduction in the arsenic content took place. Tennantite contained about 20% arsenic, and the copper of this period did only 1-3% arsenic (O'Brien, 1999; 2011; 2013).

Then, about 1800 BC volumes of production expanded significantly, and the number of mines and types of used ore increased. At the same time, there was a transition to smelting copper-iron sulfides, such as chalcopyrite and bornite. And this corresponds to the spread of tin bronzes everywhere and decline in extraction of fahlores (O'Brien, 2013; Craddock, 1999, p. 183). This means, in Europe we see the same logic of technological development as in Eurasia, but the stage of arsenic copper was implemented differently, although it was the low-temperature process too.

But we know also a series of paradoxes. For example, in China initially the tin alloys were used, and then they were replaced by the arsenic alloys, which contrast sharply with the main trends identified in Eurasia (Mei, 2003, pp. 31, 34; Mei et al. 2012, pp. 37-41; Grigoriev, 2015, pp. 554-556). But the same process took place also in Southern Siberia in the period of formation of metallurgy of the Karasuk, Irmen and Lugavskaya cultures, based on copper-arsenic alloys (Bobrov, Kuzminykh, Teneishvili, 1997, pp. 58, 59, 69; Grigoriev, 2015, pp. 541-543). Cultures formed on the base of previous Andronovo tradition (Elovka and Korchazhka) saved technology of tin alloying (Fig. 7).

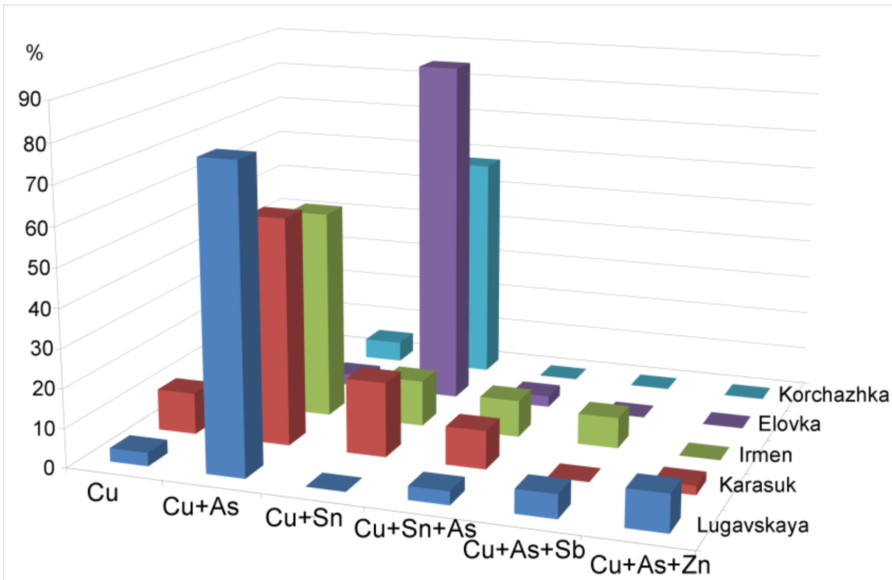

Figure 7. Types of alloys in Southern Siberia in the Final Bronze Age.

And, judging from the presence of the Karasuk artifacts, the situation in China was simply a reflection of the situation in Southern Siberia. Furthermore, there is a hypothesis about southern roots of the Karasuk-Irmen cultures (Chlenova, 1972, pp. 131-135, Grigoriev, 2002, pp. 288-294), and in Iran the use of arsenic copper dominated until the Early Iron Age, and arsenic minerals are typical of Iranian deposits (Pigott, 2004, p. 29; 2009, p. 371; Oudbashi, Emami, Davami, 2012, p. 158). Accordingly, ***the type of alloying depended not only on the availability of one or another raw material, but also on the processes of cultural genesis, and on some other traditions***. Information on ore smelting of this time in Southern Siberia is still too limited, but the available data indicate a return to smelting oxidized, relatively pure ores.

It is significant that for the simultaneous Sargari monuments of Kazakhstan this ligature was not characteristic even in those areas that are closest to the Karasuk-Irmen territory. Tin alloys were preserved there, although tin-arsenic alloys are found in some sites (Sitnikov, 2006, p. 157, Agapov, Degtyareva, Kuzminykh, 2012, p. 49). And then, at the beginning of the Early Iron Age, alloys with tin returned up to the Urals, but not from Kazakhstan. Most likely the process was started in the east, in the Baikal region, where the vicinity of developed Chinese metallurgical centers facilitated preservation of tin alloys.

Thus, if we exclude these deviations in the Final Bronze Age, the main trend in Northern Eurasia was, nevertheless, the following: 1) smelting relatively pure oxidized ore and production of pure copper in the Eneolithic – EBA; 2) smelting oxidized ore with low-melting ultrabasic gangue and production of copper-arsenic alloys (MBA-LBA transition); 3) smelting sulfide ores and ores from quartz and other refractory rocks, and alloying with tin brought from afar (LBA). And this trend was typical of the ancient metallurgy.

4. Historical and social processes and consequences

Transitions to new alloys coincided with the territorial expansion of metal production (Chernykh, 1989, pp. 17, 18). In addition, it coincided with the growth of metal consumption. In the Middle East with the transition to each subsequent period, the amount of metal increases five times more, and in Anatolia in the MBA 100 times more (Tab. 8) (Avilova, 2008). At the same time, in the Middle East in the early 3rd millennium BC we see a general transition to slagging technologies, which means the expansion of ore base (Craddock, 1999, p. 183). In Northern Eurasia, similar processes started in the early 2nd millennium BC, when metal consumption increased; the area covered by metal-consuming cultures expanded; metal objects become more massive, and they are more often present in layers of settlements. And this coincides with the change of ore types and expansion of ore base. As a matter of fact, the same processes are reconstructed in Europe: in the 2nd millennium BC the dependence on metal grew, types of ore were changed and tin bronzes were introduced. In Ireland 2,500 copper objects are known only for the period between 1600 and 1300 BC (O'Brien, 2011, p. 346; 2013, p. 433).

Table. 8. Number of finds of metal in different areas of the Middle East and Eastern Europe in the Eneolithic, Early and Middle Bronze Age (based on Avilova, 2008).

	Eneolithic	EBA	MBA
Eastern Europe	60	878	4,678
Anatolia	71	360	36,586
Mesopotamia	6	580	14,307
Levant	4	701	4,795
Iran	160	952	2,174

This growth in number of metal objects corresponds to the change of types of alloys (Tab. 9, Fig. 8).

Table 9. Types of alloys in different areas of the Middle East and Eastern Europe in the Eneolithic, Early and Middle Bronze Age (based on Avilova, 2008).

%	Eneolithic			EBA			MBA		
	Cu	Cu+As	Cu+Sn	Cu	Cu+As	Cu+Sn	Cu	Cu+As	Cu+Sn
Eastern Europe	100	0	0	46	54	0	10	90	0
Anatolia	62	31	2	15	74	8	13	51	32
Mesopotamia	100	0	0	14	74	8	16	38	45
Levant	0	0	0	39	57	1	20	38	39
Iran	44	53	0	29	70	1	1	69	28

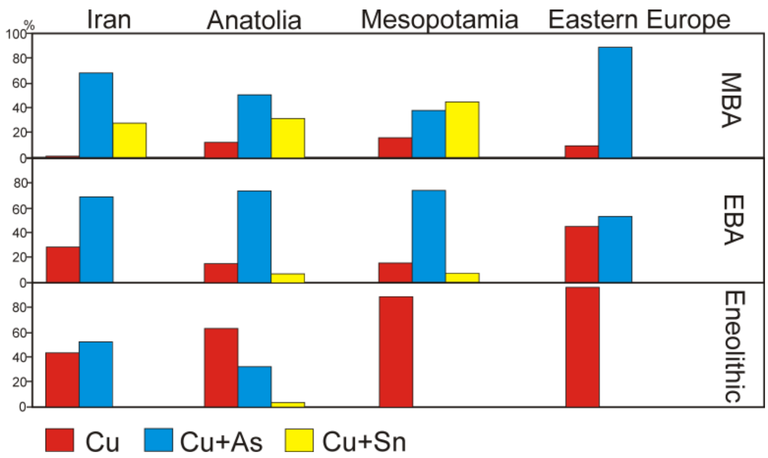

Figure 8. Types of alloys in different areas of the Middle East and Eastern Europe in the Eneolithic, Early and Middle Bronze Age.

Thus, everywhere the introduction of tin alloys coincides with the drastic increase in metal consumption, change in the ore base, expansion of the area of metal consuming cultures, and the emergence of the system of trade and exchange. This was a general situation, but it showed itself especially clearly in the cases when early civilizations and complex hierarchical societies arose. In the Middle East the distribution of tin alloying since the 3rd millennium BC coincides with the most impressive growth of metal consumption. At this time, Anatolia begins to act as an important manufacturing center supplying metal to Mesopotamia. In the early 2nd millennium BC over a 50-year period about 80 tons of tin could have been transported to Mesopotamia from the east. From this quantity it was possible to obtain about 800 tons of bronze (Muhly, 1980, p. 33). Very remote sources are proposed in Iran or Uzbekistan (Pigott, 2004, pp. 29, 34; Thornton et al., 2005, p. 395). This variant conflicts with the fact that in Iran, through which these transportations had to be carried out, tin alloys widely spread only in the Early Iron Age.

But there are also possible closer Luristan sources in Western Iran (Pigott, 2009, pp. 371-374). And the above mentioned conflict is not insoluble, both variants are possible, but in any case we must discuss the creation of a complex system of trade and exchange, which covered huge spaces.

In Jezkazgan, in Central Kazakhstan, the mines were several hundred meters long, about 10,000 tons of copper were produced there (apparently, this is an exaggeration, but the scale of production was enormous), and the commercial character of production is indicated by finds of ingots weighing up to 5 kg (Margulan, 2001, pp. 50, 52, 54, 60, 65, 75). And, if the tin supply were absent, this most powerful metallurgical center of Northern Eurasia would not function successfully. In this case the tin trade and exchange was carried out over long distances too, from Eastern Kazakhstan. And processes in Europe in this period were the same.

Thus, the introduction of tin alloys coincides with the sharp increase in metal consumption, the expansion of area of metal-consuming cultures, and the emergence of trade and exchange systems covering huge spaces.

The historical background of this transition from arsenic to tin alloys in Northern Eurasia is also quite obvious. When metallurgical technologies spread together with Sintashta culture or its descendants far beyond the primary area, in some places initially metallurgists were forced to use unalloyed copper. A vivid example is the metallurgy of Petrovka culture, where the ratio of pure copper to alloyed metal reached 60% (Vinogradov, Degtyareva, Kuzminykh, 2013, Fig. 5).

But then, after the Seima-Turbino migration and, especially, after the appearance of Fyodorovka culture, the eastern centers producing tin begin to function. And, in Northern Eurasia social conditions develop that allow the supply of tin to be organized over vast spaces, since these spaces are populated by related tribes.

But the deliveries of tin over vast spaces created a possibility to exploit those rich deposits, whose exploitation previously could be very limited, since smelting their ore would not be crowned with alloyed metal. As a result, colossal mining centers are being formed, for example, in Kargali and in Central Kazakhstan. And they are also included in the complex relationship of this exchange.

Thus, these features of Eurasian cultural genesis and new social structures had an effect on the nature of production in the huge region. On the other hand, these metallurgical technologies and metallurgical trade relations, having been formed, provided additional cementing influence on these structures, but they also became factors for further development of these structures. Probably, something similar happened in Europe, where tin was mined mainly in the British Isles, from where it was transported not only to Continental Europe, but even to the Mediterranean. On the other hand, in the Eastern Mediterranean, on Cyprus, a powerful center of copper production appeared. The metal of this center penetrated far to the west. And if the supplies of tin had not been established, these powerful mining and metallurgical centers could not function successfully, since they could not produce alloyed metal.

But something had to be received in exchange for tin and copper. And if earlier the trade relations were optional in most regions (except for Mesopotamia and other centers of ancient civilizations), then the transition to tin bronzes led to the inclusion of other goods in the trading network formed by metal, and to the further development of regional specialization. The best example of this first world trade system is the Uluburun shipwreck sank ca. 1300 BC near the Anatolian shore (Pulak, 2000). Its cargo contained 10 tons of copper ingots, one ton of tin (from two different sources), one ton of terebinth resin in ceramic jars, disc-shaped glass ingots, hippopotamus teeth and elephant tusk, ostrich eggshells and ebony logs. Here artefacts of 9 or 10 cultures have been found: Cannanite, Mycenaean, Cypriot, Egyptian, Nubian, Baltic, Northern Balkan, Old Babylonian, Kassite, Assyrian, eastern Near East, and possibly Sicilian.

As a result, the whole of Eurasia was permeated with a complex network of trade and exchange, which became an additional (though not the only) factor in the formation since this time of complex hierarchical societies.

Conclusions

Concluding the article it is necessary to outline the main factors influenced on the technological and partly social development in the Bronze Age. Technological aspect of the problem is fundamental, because the primary choice of the type of ore stimulated the technology of its smelting, technology and type of alloying, technology of metalworking, and, in the long run, the morphology of final metal objects (Fig. 9). But the sequence of changes of alloys discussed above is correct only in context of the most general processes. Within each individual area significant deviations from this scheme could be, influenced by some regional factor that suddenly turned out to be particularly significant: availability of raw materials and trade communications, local cultural and technological traditions, internal innovations and technological borrowings. These are also the peculiarities of cultural genesis, which we have discussed above for China and Southern Siberia, or the factor of distance from tin sources, as in Eastern Europe, and some other.

But in general, we can discuss the following regularity: in case of smelting oxidized ores and ores from low-melting rocks, it was possible and technologically necessary to add arsenic minerals at the ore smelting stage.

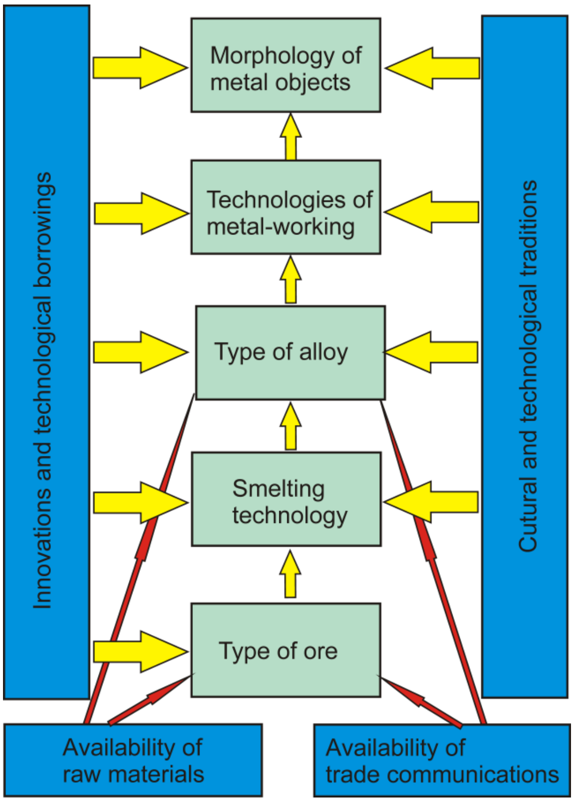

Figure. 9. Factors of technological developments.

After the widening of ore base and the transition to sulfide ores and ores from refractory rocks, the possibility to produce copper-arsenic alloy disappeared. It necessitated the use of tin alloys, whose distribution was soon provided by migrations of eastern tribes with the corresponding technology. Of course, to some extent this process was based on the fact that the oxidized ores lie higher and the sulfide ones do lower, which forms this chronological sequence (Strahm, Hauptmann, 2009, pp. 122, 123).

Nevertheless, these processes should be considered in the socio-cultural context (Roberts, Thornton, Pigott, 2009, pp. 1016-1019) (Fig. 10).

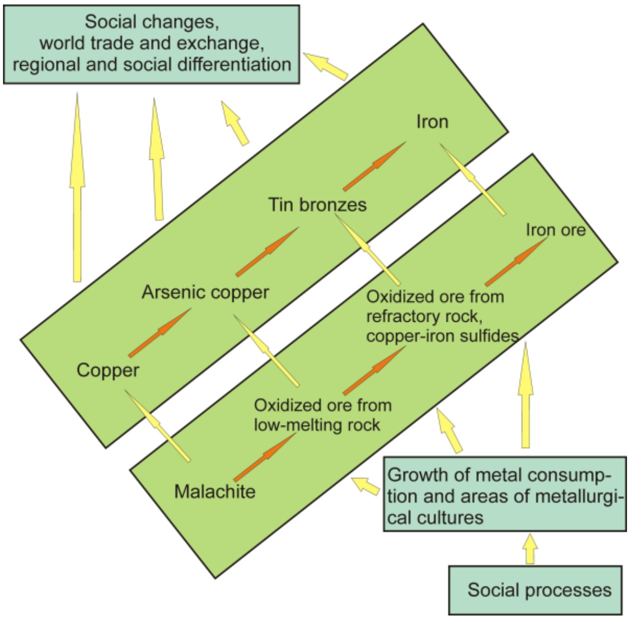

Figure 10. Social processes and stages of metallurgical technologies.

A stimulus to technological changes was the growth of metal consumption, i.e., social processes. But these technological changes then had a significant effect on these social processes. As a result, in many instances it forms a new social reality, the first world trade system and intensification of social and regional differentiation.

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List of abbreviations

EAMP – Eurasian Metallurgical Province
EBA – Early Bronze Age
LBA – Late Bronze Age
MBA – Middle Bronze Age