

METALLURGICAL  
PRODUCTION IN  
NORTHERN EURASIA  
IN THE BRONZE AGE

**Stanislav Grigoriev**

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# Introduction

Copper is the first metal which had really played a large part in human history. It is considered that Latin *cuprus* from which chemical name of copper originated was connected with the island of Cyprus, with the meaning ‘*copper island*’. But actually it is not so. The Greek word κύπρος has uncertain etymology. For copper the Greeks had a word χαλκός; the term “Chalcolithic” goes back to this word. Latin language had another word: *aes*. The combination *aes cyprium* meant “Cyprian copper”. Then *cyprium* was replaced by *cuprum*. All European words connected with it do not go back to a common Indo-European base. The Latin base is closer to them (Muhly 1973, p. 174, 175).

This work is devoted to history of metallurgical production in Northern Eurasia during the Bronze Age. It should be noted that archaeometallurgical studies include a huge range of works in various directions reflecting different fields of activity of ancient metallurgists. Very often all they are united by the term ‘metallurgy’. A starting point of copper production is ore extraction. And this phase cannot be designated as ‘metallurgy’, it is ‘mining’. To date this aspect of production activity in Northern Eurasia is studied extremely poorly. Significant studies have been performed by E.N.Chernykh on the Kargaly mines in Orenburg area (Chernykh 1997, 2002, 2004, Chernykh *et al.* 1999; Černych 2003). In the Transurals the mine of Vorovskaya Yama was investigated (Zaykov *et al.* 1995; 2000). It is supposed that it was exploited already in the Middle Bronze Age, however revealed materials belong to the Late Bronze Age. In Kazakhstan and the Altai a number of works was devoted to study of ancient mines (Zhaulymbaev 1984; Margulan 1973, 2001; Chernikov 1949). S.I.Tatarinov studied mines in the Donetsk area (Tatarinov 1977, 1978, etc.). At the same time, many archaeological works contain information about ancient mines; however evidences about their use in antiquity are usually questionable. Unfortunately, these modest successes of Russian archeology in studies of ancient mining reduce possibility of studying metallurgy itself because it is often not clear what kind of ore was used, as well as volumes of production, main mining areas, etc.

Studies devoted to morphological analysis of metal artifacts are numerous. Very important research field is study of microstructure of copper artifacts and reconstruction of both forging and casting technologies on this base (Ryndina 1971; Degtyareva 2009). Another way of these reconstructions is experimental works (e.g. Savrasov 1998).

Very extensive and important studies of ancient Eurasian metallurgy were done by the Laboratory of natural sciences of the Institute of Archeology (Russian Academy of Sciences) headed by E.N.Chernykh. During long time this laboratory studies chemical compositions and typology of many copper-based artifacts of the Bronze Age of Northern Eurasia that allowed system ideas about metallurgy of this period within the huge area to be formulated (Chernykh 1970, 1977, 1992). The most outstanding result of these works is a theory of territory of ‘metallurgical provinces’, huge areas with similar chemical compositions of metal and types of artifacts. References to this thesis are common in many works on the Bronze Age, but they are not always correct. So, it is often possible to find a statement that “this culture was formed as a result of complicated processes accompanying disintegration of the Circumpontic Metallurgical Province” or something similar. Actually, this phrase is absolutely senseless as metallurgical provinces were not any really existing communities. It is only a cogitative construct for synthesis of characteristics of metallurgical production, though reflecting a certain ancient reality. And such statements reflect only misunderstanding of origins of this or that archaeological culture and attempt to come out of this situation. In works devoted to cultural genesis I tried to use in these instances another terminology, for example, “the south of the Circumpontic zone”, etc. And numerous facts of distant migrations and very similar alloys and types of artifacts of remote territories belonging to different metallurgical provinces generated my doubts in absolute

legitimacy of this theory which, however, weren't published. However, a system of metallurgical provinces is not only some production traditions or a set of similar traditions of various groups. As any complicated system, a province consists not only of elements, but also of system relationships, processes and channels/space of their behavior. Respectively, any group with its technological skills, getting to another metallurgical province, is forced to be built in available system. But when I was working on this book and generalizing results of slag analyses from huge territories, I have found that this generalization and description is correct and possible only within the theory of 'metallurgical provinces'.

In this work I consider problems of proper metallurgy, i.e. extracting metal from ore. A number of accompanying operations is closely connected with it, such as charcoal-burning, ore dressing, furnace constructing, and preparation of crucibles. In some instances I should touch upon these operations; however the main topic of the work is smelting process. Closing stage of the metallurgical production is metalworking including various casting and forging operations, and also auxiliary operations: making of crucibles, casting molds, stone tools for metal forging. These problems are, as a rule, out of frameworks of this research.

Problems of copper ore smelting in Northern Eurasia are poorly studied. Certainly, archaeologists, who excavated sites with metallurgical complexes, touched upon problems of copper production (see e.g. Kadyrbaev 1983; Kadyrbaev, Kurmankulov 1992; Tatarinov 1977, 1978; Chernikov 1949). However these works are very rare; and credibility of reconstructions is often doubtful as it demands serious analytical studies of production remains, above all, slags. Similar works took place, but they were very local, based on single analyses and had no further development (Satpaeva 1966; Terekhova 1980; Kuznetsova *et al.* 1988; Zharkova, Sunchugashev 1975). A very interesting research of metallurgical production on the Kargaly mines was executed by Salvador Rovira, and subsequently in this book we will repeatedly use results of this research (Rovira 1999; 2004). In the European archeology number of works devoted to analyses of ancient metallurgical production is extremely large and the first summarizing publications appeared many years ago (e.g. Coghlan 1951; Forbes 1958 and many others). It is possible to say that in archeology a new field was formed: archaeometallurgy. These studies always used the most modern analytical methods; however usually number of analyzed materials was very insignificant. Usually these studies are limited by careful analysis of one or several sites. Taking into account a large number of these studies, being based on them it is possible to make idea of nature of ancient metallurgy, but it is difficult to do this in a uniform system.

As materials of Northern Eurasia were not analyzed, within this work it was necessary to conduct studies of slags from the huge territory. The research task initially was to reconstruct various technological schemes in this area, history of their formation and distribution, and to determine, whenever possible, ore sources. However slag is a rather complicated system demanding application of various methods, often complex and expensive. Therefore, taking into account the huge volume of materials and high cost of scientific analyses, it was necessary to develop an optimum research scheme allowing, both to reconstruct an overall picture, and to solve individual problems.

The project of slag studies of the Bronze Age was started in 1986 and with some breaks proceeds hitherto. The first years the main emphasis was placed to slag analysis of Sintashta culture in the Southern Transurals, but simultaneously collection of materials from the huge territory from the Don River to the Altai and south of Central Asia was carried out. Perhaps, today it is the largest collection of analyzed ancient slags in the world. However, even this collection is not enough representative for this enormous territory. The most studied by various analyses is metallurgy of Sintashta culture, and, with certain reservations, it is possible to confide in conclusions drawn on the basis of these analyses. Other materials have not been analyzed by the whole complex of the methods. Such a study would be impossible not only to any single scientist, but also to a large scientific organization. Therefore the main task was to bring to light the most general regularities that will give a chance to future researchers of individual areas to consider their materials in wider context and to decide which problems should be solved. But the conclusions made in this book about metallurgy of

the Late Bronze Age have to be subjected either to inevitable updating or to full refusal as they are based on unrepresentative probes selection and a limited set of analytical methods. However, the research scheme developed on the materials of Sintashta culture can be quite applied in other territories by research groups including both archeologists and scientists.

As a rule, archeologists are poorly familiar with methods of natural sciences, therefore they either ignored analytical studies or (as it often takes place with radio-carbon analysis) choose those data which are most acceptable. On the other hand, often archeologists confide in conclusions of scientists with an excessive confidence. Especially it is unjustified in those instances if analyses are done by people who do not work in archaeometry. Sometimes we see another situation: archaeologists wait from scientists an unambiguous result or consider his conclusions as that. However any analytical research is a process approaching gradually to the result. This work is also only a stage in this process, which is more satisfactory for materials of Sintashta culture and less satisfactory for all others.

### **Chemical processes of copper ore smelting**

To do the subsequent text and research procedures clear, it is necessary to touch upon briefly physical and chemical processes which take place in the course of ore smelting. Many archeologists believe that smelting process is limited by temperature impact. However in reality it is much more complicated. The ore fusion is not able to bring to separation of metal from rock. The main role in metallurgical processes is played by chemical reactions. Temperatures create rather a condition of their successful behavior. In this book we will discuss various technologies of ore smelting caused by difference in ore base. Therefore it is necessary to discuss briefly types of copper ores and, respectively, those chemical processes which take place at their smelting.

Copper ores can be divided into two main groups: sulphidic and oxidized. The sulphidic ores can be subdivided into primary sulfides (unoxidized sulfides: chalcopyrite or copper sulfide –  $\text{CuFeS}_2$ ), and the secondary sulfides (bornite –  $\text{Cu}_5\text{FeS}_4$ , covellite –  $\text{CuS}$ , chalcocite –  $\text{Cu}_2\text{S}$ ). Oxidized ores can be divided into oxides (cuprite –  $\text{Cu}_2\text{O}$ , tenorite –  $\text{CuO}$ , chrysocolla –  $\text{CuSiO}_3\cdot\text{H}_2\text{O}$ ) and carbonates (malachite –  $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ , azurite –  $\text{Cu}_3(\text{CO}_3)(\text{OH})_2$ ). It is also necessary to mention native copper ( $\text{Cu}$ ), but it was a significant source only at the earliest stages of metallurgical development. There are many other copper minerals, but those mentioned above are the main source for ancient metallurgy.

Formation of primary ores is connected with magmatic processes, respectively, in many ore deposits these ores are situated in the deepest zones. Above, in the so-called “zone of cementation”, lie the richest ores, mainly secondary sulfides. At last, in the top parts of the deposits the oxidized ores are situated. Therefore ancient miners initially exploited the oxidized ores, and then, in process of deepening the mines, they reached the secondary sulfides, and subsequently the primary sulfides. Said above is, of course, a classical scheme because primary ores can be found on the surface, and in the zone of cementation both oxidized minerals and primary sulfides are situated. Nevertheless, in general this tendency is true. Respectively, smelting of ores with so various chemical compositions cannot be done using a single technological scheme.

Chemical reactions of these types of ores reduction are different. Here it is necessary to mention one more important point, namely, role of charcoal in this process. It is well known that charcoal is a source of thermal energy in metallurgical production. However its role as a chemical component reducing copper is also very important. But charcoal chemically is not so active to reduce copper. The main reagents are gases which form as a result of charcoal combustion: carbon monoxide ( $\text{CO}$ ) and carbon dioxide ( $\text{CO}_2$ ). The carbon monoxide is the reducing agent in metallurgical reactions. But carbon monoxide is stable only at high temperatures, above  $710\text{ }^\circ\text{C}$ , therefore it is the minimum of temperature from which metallurgical reactions begin (Charles 1980, p. 156).

Reactions between gases and solid carbon depend on oxygen content and are described by the following formulas:

$C + O_2 \rightarrow CO_2$  – full combustion of charcoal; reaction takes place at surplus of oxygen. Respectively, in case of this reaction metal reduction does not occur.

$2C + O_2 \rightarrow 2CO$  – reaction of formation of carbon monoxide.

$2CO + O_2 \rightarrow 2CO_2$  – reaction of formation of carbon dioxide from carbon monoxide in case of oxygen surplus.

$CO_2 + C \rightarrow 2CO$  – at higher temperatures and in case the gas phase passes through a charcoal layer, a back reaction of formation of carbon monoxide from carbon dioxide takes place. The content of carbon monoxide grows in the furnace at temperatures from 600 °C to 1000 °C. Starting from 700 °C it is quite fast process which leads to copper reduction (Zimmerman, Gunter 1982, p. 319; Charles 1992, p. 12).

Respectively, for formation of quantity of carbon monoxide sufficient for metal reduction both temperatures and time are necessary. Besides, oxygen blowing has to be carried out through a charcoal layer, otherwise carbon monoxide is not formed too, and smelting will not be successful. Because of this simple reason (and not because of impossibility to reach high temperatures at all) it is impossible to reduce copper in an open fire. In the open fire it is impossible to create conditions for the carbon monoxide formation.

Thus, the achievement of positive balance  $CO/CO_2$  was one of the most important problems in ancient metallurgy.

This problem was closely connected with types of smelted ores.

In case of rather developed metallurgy based on slag reactions, an example of this process can be following.

Classical type of slag has fayalite composition. It will be repeatedly discussed on pages of this book. Its formation can be described by two formulas:

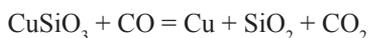
$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$  – reaction of hematite with carbon monoxide and formation of wüstite and carbon dioxide.

$2FeO + SiO_2 \rightarrow 2FeO \cdot SiO_2$  – reaction of wüstite with quartz and fayalite-type slag formation.

Thus, to form a fluid fayalite slag, in addition to necessary components, it is required to form wüstite, which is impossible in case of oxidizing conditions in the furnace and absence of necessary quantity of carbon monoxide.

Smelting of oxidized ores is carried out according to a rather simple scheme (Tafel 1951, S. 242-245, 249).

At a temperature of 550-600 °C in reducing atmosphere some of these ores (chrysocolla,  $CuSiO_3 \cdot 2H_2O$ ) can easily reduce, losing water:



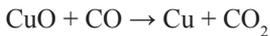
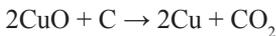
But in this case metallurgists inevitably had a problem with such refractory component as quartz that it was possible to solve, either forming fayalite slag by additions of iron oxides, or increasing the temperature. The

latter, however, could lead to the back result as intensification of blowing caused an intensive oxidation of copper.

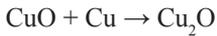
Malachite ( $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ ) and azurite ( $2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ ) already at a temperature of 220 °C lose carbon and water, forming tenorite ( $\text{CuO}$ ). At usual long heating it starts disintegrate with formation of cuprite already at a temperature of 800 °C according to reaction



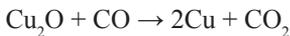
At contacts with charcoal or carbon monoxide tenorite is quite easily reduced above the temperature of 550 °C:



However, after reaction with copper, tenorite can form cuprite again:



In case of high temperatures and sufficient volume of carbon monoxide a standard reaction starts according to the scheme:



But cuprite is a rather refractory mineral; therefore the second reaction requires a high temperature. Here we meet a standard problem of early stages of metallurgy. Increasing blowing and temperature increases also oxygen volume in the furnace. Respectively, the  $\text{CO}/\text{CO}_2$  balance comes down. As it follows from the formulas above, surplus of oxygen will hampers the copper reduction. Therefore, despite a common opinion that smelting of oxidized ores is much simpler, chemically it is not so, that often causes considerable losses of copper in form of cuprite.

It is paradoxically, but smelting of sulfide ores is often simpler.

In the case of chalcopyrite smelting ( $\text{CuFeS}_2$ ) a reaction takes place (Zimmerman, Gunter 1982, p. 352):

$2\text{FeS} + 3\text{O}_2 \rightarrow 2\text{FeO} + 2\text{SO}_2$  – reaction of iron sulfide with oxygen and formation of wüstite and sulfur dioxide.

$2\text{FeO} + \text{SiO}_2 \rightarrow 2\text{FeO} \cdot \text{SiO}_2$  – reaction of wüstite with silicate components with formation of fayalite slag. Wüstite that did not participated in formation of fayalite slag, disintegrates into magnetite ( $\text{Fe}_3\text{O}_4$ ) and metal iron (Fe).

As we see, a reducing agent in this case is not the carbon monoxide, but sulfur containing in ore and reacting with oxygen. It is accompanied by exothermic reaction of sulfur burning that promotes temperature increase. Another advantage of primary ores smelting is that the ores contain all components necessary for slag formation; and after this process the copper content raises because the iron oxides go into slag.

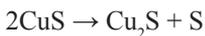
The next stage is reactions of copper sulfides. Similar reactions take place also in direct smelting of chalcocite:

$2\text{Cu}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$  – reaction of copper sulfides with oxygen and formation of cuprite and sulfur dioxide.

$2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \rightarrow 6\text{Cu} + \text{SO}_2$  – reaction of cuprite with copper sulfide and formation of copper and sulfur dioxide.

In this case sulfur acts as a reducing agent too. In addition to this there can be reactions which are described for smelting of oxidized ore.

Another copper sulfide, covellite ( $\text{CuS}$ ), already at a temperature of  $358^\circ\text{C}$  forms chalcocite (Tafel 1951, S. 237):



This is the reason why it rarely participates in metallurgical processes; and its detection in slag may be explained by any other reasons: rapidity of the process, repeated additions of ore.

Thus, sulfides react at first with oxygen, and then with oxides, restoring copper directly. Therefore chemically this process is simpler as in this case there is no need in long maintenance of positive balance  $\text{CO}/\text{CO}_2$ .

There is one more important peculiarity of ores: they contain inclusions of gangue. As we saw from the formulas of fayalite slag formation, for this formation two components are necessary: iron oxides and silicates.

Usually the types of ore and gangue depend on genesis of copper-ore fields. Volcanogenic massive sulfide ore deposits are formed as a result of magmatic processes. As the main copper mineral there is chalcopyrite, ores of these deposits are rich in iron component. Iron oxides even form in the upper part of these deposits so-called “iron caps” or gossans. Deposits in sulfide quartz veins are formed as a result of hydrothermal processes when hot solutions rise along the cracks forming copper mineralization in quartz veins. Respectively, silicate component is well presented in these fields. Porphyry copper deposits had similar genesis. However in this case hydrothermal solutions can rise in basic rocks, rich in iron or magnesian components. For ancient metallurgy copper deposits in sandstones were also important. These sedimentary rocks can have copper mineralization from destroyed deposits. More often the sandstones have silicate composition, and oxidized minerals are more typical for them, secondary sulfides are rarer. However in different areas deposits of this type can differ that is explained by the breaking down of different rocks and different primary deposits.

There are many other types of copper deposits, however given above are the main types used by ancient metallurgists.

Silicate rock is very refractory. Contrary to it, basic rocks melt at various temperatures depending on oxide type. Melting temperature of iron oxides is lower in oxides with lesser oxygen content. So among  $\text{Fe}_2\text{O}_3$  (hematite) –  $\text{Fe}_3\text{O}_4$  (magnetite) –  $\text{FeO}$  (wüstite), hematite will be most refractory, and wüstite will be least refractory. Thus, for successful smelting of minerals from these rocks it is necessary to achieve the reducing conditions in the furnace.

However, it is ideally to form slag. So, fayalite slag, consisting of iron oxides and silicates, has melting point much lower, than the components from which it was formed. Therefore metallurgists were trying to form

slag by special selection of ore, addition of iron oxides to ores from silicate ores or silicates to those from iron-rich rocks.

However some ores, for example, chalcopyrite, contain iron, irrespective of nature of ore-bearing rock. Besides, other components, for example molten sulfides or compounds of calcium, participate in slag reactions also. All this, taking into account many possible combinations, turns metallurgical process into the most complicated system which cannot be identical in different territories and during various epochs.

The situation becomes more complicated also by that, along with technological parameters of smelting caused by character of ore and ore-bearing rock, there were parameters caused by cultural traditions. The situation is simpler when any technological tradition develops in the same area, i.e. it was the local tradition. However in case of a migration of bearers of this tradition and transition to new types of raw materials we have a new situation with either possible borrowing of a local technological tradition ore attempts to adapt and transform their own.

All this causes variety of slags. So, the slags received at smelting according to the same technological scheme, can look very contrast because of sharp distinctions in ore base. Respectively, study of slag from either any individual area or a site is not able to reflect nature of metallurgical production of the period. On the other hand, the multiple character of the process forces to use quite wide range of analytical methods, without what it is impossible to do its relatively correct reconstruction.

## Methodology

The methodology of this research was developed in the first years of this project (Grigoriev 1993), however subsequently it has being constantly changed due to attraction of new scientific methods and statistical procedures. As it was already said above, slag is rather complicated system, and its study demands use of a number of various methods. Use of a spectral analysis, traditional for archaeometallurgical studies in Russia, gives, in this case, very limited information. However, on the other hand, careful studies of small series of material can also lead the research to a dead-lock, as slag, unlike metal, is inhomogeneous. Moreover, in different zones of ancient metallurgical furnaces different thermal conditions and different balance of CO/CO<sub>2</sub> influencing the smelting atmosphere could be formed. As a result, very careful modern analysis can depend on a human factor: a sample chosen for studying (Rehren *et al.* 2007, p. 215). It was necessary to avoid this problem.

Therefore even the study of slag from a single settlement requires rather representative number of probes. Empirical experience allows me to believe that a minimum desirable number of probes from a single settlement are about 20. Any accurate figures are impossible here, as it depends on degree of uniformity of the analyzed series itself. But also within one, even rather small area, it is impossible to be limited by materials from one or two settlements, because metallurgists of different settlements could use different ore sources that could inevitably influence on microstructure and chemical composition of slag. Besides, a series of large-scale projects, carried out by E.N. Chernykh, showed that even such an imperfect method as emission spectral analysis applied widely and supplement by a series of statistical procedures, allows to receive rather adequate pictures of ancient metallurgical production.

Taking into account all said above, an optimum research way is to divide the research into two stages. At the first stage the cheapest analytical methods, allowing to study the most number of slag probes and to receive maximum information are applied. This allows different mineralogical and chemical groups of slag to be distinguished and to do their statistical comparisons. After this it is possible to study selected samples inside the groups more carefully by more expensive and perfect methods to solve individual problems.

The basic method of the research is analysis of polished slag sections under microscope in reflected light that allows the main phases rather surely to be diagnosed. This analysis was done at magnification 50-200×, although in exceptional cases larger magnification with use of oil immersion were also applied. The main questions which can be solved by means of this method are: identification of initial raw materials and possible ore base, identification of smelting temperatures and smelting atmosphere, relative rate of smelt cooling. As it will be shown below in more detail, within discussion of individual problems, answers even these questions cannot be quite unambiguous.

Now it is known about 150 slag minerals (Perepelitsin 1987, p. 215). In particular increase of number of these minerals is caused recently by the use of electron microscopy. The process of all phases' identification in slag is rather expensive and labor-consuming. It is certainly needed in case of analysis any concrete, rather local material. However, in case of the analysis of large slag collections it is almost impossible to do it. Therefore this research was limited by the main slag minerals.

The copper ore used in antiquity belongs to three types: oxidized ores, secondary sulfides, and primary sulfides. The main ores of the first group are malachite, azurite, cuprite and chrysocolla. All of them are rather well diagnosed by means of a microscope; however they, in particular malachite, can be easily formed in slag also for a period while the slag was deposited in the settlement layer. Especially frequently it occurs not in vitreous slag masses, but in gas pores. Therefore we quite frequently see malachite inclusions round in shape. Most often it indicates its secondary character. It is possible to judge about this more confidently already using X-ray microanalysis made by means of a scanning electronic microscope (SEM). As a rule, the secondary inclusions are freer from impurity, than the ore used for smelting. However this characteristic cannot be always decisive as there are rather pure oxidized ores. Impurity of copper chlorides in these inclusions is more indicative as they could not remain in conditions of high temperatures applied in metallurgy. Compounds of copper with chlorine ( $\text{CuCl}$ ,  $\text{CuCl}_2$ ) are formed at usual temperatures. But already at a higher temperature (250-340 °C) they disintegrate, and, as a result of oxidation, turn into tenorite ( $\text{CuO}$ ). At a temperature of 500 °C copper chloride ( $\text{CuCl}$ ) vaporizes (Tafel 1951, S. 234, 235, 245, 246). Therefore the presence of chlorides is an important sign of secondary character for malachite. Unfortunately, not for all probes can be studied by SEM. Therefore the main indication is the shape of a mineral.

A similar problem is also connected with determination of character of cuprite ( $\text{Cu}_2\text{O}$ ). In some cases cuprite in slag could be formed later. However, in some instances it is a result of either of copper oxidation in the course of smelting, or as a result of smelting of oxidized copper minerals, for example, malachite. In this case, the simplest way of identification is the estimation of amount of inclusions of cuprite prills comparatively to copper prills. In principle, small copper prills must be oxidized in settlements layers much easier, than large. The density of copper is 8.96 g/cm<sup>3</sup>, and that of cuprite is about 6 g/cm<sup>3</sup>. Respectively, copper prills sink in liquid slag easier, than cuprite prills of the same size. If the cuprite prills are on the average larger than those of copper, it is possible to assume that they were formed during metallurgical reactions, and they were not a result of secondary oxidation in a settlement layer.

Secondary copper minerals (covellite and chalcocite) are quite easily diagnosed as they are anisotropic and have typical color. However, even if these minerals were the main component in charge mixture, in slag their presence can be very limited as they melt already at a quite low temperature. Besides, as a result of high temperatures and oxygen blowing, a part of sulfur leaves them, and they regenerate into isotropic copper sulfides which are very typical in this slag. As it follows from their name, they have no effect of anisotropy. Their color characteristics are quite close to cuprite, however they differ from it by absence of internal reflexes. Usually their broad presence indicates smelting of secondary sulfides. However they can be found also in slags formed at smelting of primary sulfides.

The main these sulfides are bornite and chalcopyrite. And the latter was more often used in ancient smelts. Unfortunately, its inclusions in slag can be found not so often, and they have quite small size. This results from the fact that after heating chalcopyrite disintegrates into copper and iron sulfides quickly enough. Having a low melting point copper sulfides melts, and the iron sulfides are oxidized and turn into wüstite, forming in this case very characteristic dendritic and latticed structures. The presence of these structures, accompanied by small chalcopyrite inclusions and molten isotropic sulfide, is diagnosing signs for identification of smelting of primary ores.

But in real slags the situation can be a little complicated by that various ore types could be used in smelting. Therefore the main conclusions have to become on the basis of analyses of rather large slag and ore series.

Identification of type of ore-bearing rock is also connected with some specific difficulties. In principle, it is possible to distinguish rather reliably slags formed at smelting of ores from silicate rocks, from those formed at smelting of ores from basic and ultrabasic rocks. The main sign here is the ratio of acid and basic oxides in slag and rock inclusions, especially rock associations with ore minerals. However, we have to take into account possible use of iron fluxes that increases the presence of the basic oxides in slag, but this was practiced in antiquity extremely rare. For the ultrabasic rocks an important diagnosing sign is the presence of chromspinelid grains. Sometimes it is possible to see sandstone inclusions in slag. They are visible in the form of small, extended in rows grains surrounded with ore inclusions. However, if the material is larger, such structures are not visible even in the ore from sandstones.

The use of fluxes is connected with the problem of initial ore too. At first sight, for identification of fluxes it is enough to compare compositions of ore and slag; however there are a number of objective difficulties. For example, around the metallurgical complexes of Sintashta culture we repeatedly discovered many small burned bones, and sometimes small pieces of calcite. All this allowed think about the use of these components as fluxes to add CaO in the furnace charge, promoting creation of more liquid slag. On the other hand, in slag a higher CaO content was often determined by chemical analyses in contrast to its absence in ore. This, at first sight, unambiguously indicates the use of fluxes. However, calcium contains also in ashes, and could get into slag from there. It is not possible in this instance to calculate how intensive the use of fluxes was. Similar problems rise also in case of use of iron fluxes which could be a part of gangue.

Determination of achieved temperatures is also a difficult challenge. In principle, their determination was based on studying of microstructures and of identification of molten and unmolten components whose melting point is well-known. However, in many instances it was quite difficult to distinguish the molten and unmolten inclusion. Besides, it gives not the achieved temperatures, but lower temperatures. A real temperature could be higher than it is fixed by the molten inclusions. On the other hand, sometimes the slag components melt not so much being influenced by the temperature, but by physical and thermodynamic processes in liquid slag. During the work with large slag collections it is better to use melting points of several minerals which are given in Tab. 0-1. (Zimmerman, Gunter 1982, tab. 173- 175).

Sometimes archaeometallurgists use thermal diagrams based on chemical analyses. But the diagrams using bulk (wet) chemical analysis indicate both a real temperature range and also an overstated one because the bulk chemical analysis takes into account also refractory unmelted components. So, Gale and coauthors' experimental studies demonstrated that a temperature determined by phase diagrams is always much higher than a point of this slag melting. In addition to this, the standard diagram  $\text{SiO}_2 - \text{FeO} - \text{CaO}$  is not so good, as the diagram anorthite -  $\text{FeO} - \text{SiO}_2$  (Gale *et al.* 2000, p. 89, 92). The experiments made by A. Hauptmann with slags received at smelting of the so-called self-fluxing ores demonstrated that they melt at a temperature of 1130-1150 °C. However the phase diagram demonstrated higher temperature: about 1200-1250 °C (Hauptmann 1987, p. 130). On the other hand, a possible melting point of slag is not evidence

at all that during the smelting higher temperatures were not achieved. Therefore such determinations give unreliable data and have to be verified by the whole complex of other analyses and calculations.

Use of the X-ray microanalysis of individual molten and crystallized components is more justified. But also in this case we receive melting point and temperature of solidification of any component, and the achieved temperature could be higher. Thus, this method has approximate character, but it allows us to get some ideas about the temperature. There are some instances when one of olivine inclusions showed very high temperature of melting while all other seem to be molten at lower temperatures. A possible explanation of this situation is thermodynamic processes.

Sometimes archaeometallurgists smelt slag and, by such a way, determine a probable temperature by means of measuring techniques (e.g. Mei, Li 2003, p. 114, tab. 9.4). But this method determines also only the melting point, instead of the temperature achieved.

The X-ray diffraction analysis can be used as an additional method for temperature determination too. The method identifies crystal phases in any material on the basis of study of characteristics of its crystal lattice. Crystals of various minerals differ from each other by atomic and molecular structures. In this work this method was especially useful for identification of high-temperature silica modifications (Grigoriev 2000). However, in practice this gives limited number of temperature points, namely formation of  $\alpha$ -tridymite and  $\alpha$ -cristobalite.

The behavior of quartz when heating is described by Fenner's classical diagram (Deer *et al.* 1966, 1966a, p. 221). There is no need to list all its phase transitions. It is enough to emphasize that the presence of quartz indicates a temperature below 867 °C,  $\alpha$ -tridymite – an interval 867-1470 °C,  $\alpha$ -cristobalite – over 1470 °C. The melting point of quartz is in a temperature interval of 1670-1700 °C. After cooling the molten quartz forms quartz glasses. However dissolution of quartz in slag and formation of olivine and glass starts also at lower temperatures.

In actual metallurgical slags the coexistence of two quartz modifications is possible. Let's imagine that we see in a probe both modifications: tridymite and cristobalite. It means that the temperature was above 1470 °C, but lasted at such level not too long.

Determination of smelting atmosphere is the most simple and, at the same time, the most subjective. It is a very important parameter; metal reduction depends on it. But this parameter is connected with a set of factors. The quantity of components containing oxygen is the most important. The main of these components are both air blown in the furnace and oxidized ore. Thus, metallurgists smelting the oxidized ores constantly dealt with a dilemma: at more intensive blowing temperature increases, but it resulted in oxygen surplus in the furnace that hampers the copper reduction. In many respects the success depended also on quality of charcoal. But it is not the last analytical problem, because the atmosphere in the furnace can have a local character. Experimental works showed that in different areas of the furnace the oxidizing and reducing conditions were observed. The reducing conditions usually appear at distance more than 15cm from the air blowing tuyeres (Telecote, Merkel 1992, p. 10). This results from the fact that carbon monoxide has no time to be formed closer to the tuyere. Respectively, in small furnaces it is easier to achieve high temperatures, but it is more difficult to create the reducing conditions. Probably, the size of reducing and oxidizing zones depended also on air pressure and speed of its movement in the furnace, and even on sizes of charcoal and other components of the furnace charge.

For these reasons, the smelting atmosphere determined on the basis of any analysis of slag relates only to an area where the ore was smelted. Besides, it is necessary to take into consideration that the atmosphere during the smelting was not constant. All this makes the conclusions about the atmosphere rather relative.

The presence of many cuprite inclusions in slag is the most important marker of the oxidizing atmosphere in the furnace. Other markers are: copper and iron oxide delafossite forming characteristic needle crystals. Contrary to this the markers of the reducing conditions are such minerals as wüstite, fayalite, and also in some instances inclusions of metal iron.

At slower cooling the dendrites, skeletal and idiomorphic crystals growing sometimes to large prismatic shapes are formed<sup>1</sup>. The last, however, cannot occur in case of lack of necessary components. Therefore the study of crystal shapes, being very informative, nevertheless is not fully informative, and it has to be supplemented with chemical analyses.

In this case the study of chemical composition of crystals by means of SEM is very useful. So, investigations of olivine in slag of Sintashta culture revealed that smaller crystals had started growing earlier, and they have more magnesian composition, than larger crystals. Besides, many olivines have the zonal structure visible even under light microscope. Research of different areas of the crystals demonstrated that they had been formed at different stages of smelting. More dark internal areas are more magnesian. Respectively, at different stages of smelt cooling different mineral phases are formed. Moreover, at various speeds of cooling even substance with the same chemical composition can crystallize in different phases. In case of the rapid crystallization the primary phase is spinel (Perepelitsyn 1987, p. 84).

Relative speed of smelt cooling was determined by the rate of crystallization of individual minerals, for example, olivine. In conditions of slow cooling rather large crystals can be formed. At fast cooling crystallization either does not take place at all, or crystals form small needle or dendritic structures (Textures and structures 1958, p. 67). However, sometimes lack of large fayalite crystals is not a sign of the high-speed cooling, because it was provoked by the absence of necessary components for their formation in the furnace charge. In this case the shapes of crystals were taken into consideration too. Needle crystals are formed usually at the rather high-speed cooling.

The speed of cooling is closely connected with the slag viscosity. Usually a significant amount of copper prills in slag is a good indicator of the high viscosity. However, sometimes the slag viscosity can be calculated on the base of chemical composition.

There are different ways of viscosity calculation. Its decrease is influenced by oxides of calcium, magnesium, iron, manganese, titan, sulfides. Silicon dioxide and aluminum oxide increase viscosity. Certainly, the slag viscosity is essentially influenced not only by the chemical composition, but also by the temperature. The higher temperatures make the viscosity lower. In addition to this, the character of viscosity changes at different temperatures is not identical in slags of different chemical compound. Besides, there are unmolten components in slag. Their larger number leads to viscosity increase. For example, at calculations of viscosity for a composition basing on bulk chemical analysis it is impossible to take into account if the oxides had been molten or not. It is not always possible to say about type of iron oxides. But the melting points of wüstite, magnetite and hematite are very different. The last two oxides are present usually in slag in solid form, increasing slag viscosity. It is quite distinctly noticeable at optical studying of slags. In areas of concentration of the magnetite crystals we often see more copper prills that points to higher viscosity there.

Slag is heterogeneous, and its chemical composition can differ in different areas of an ancient metallurgical furnace. The molten copper will promote the viscosity decrease. Besides, slag viscosity is very different at different stages of smelting.

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<sup>1</sup> Dendrites are uniform two- or three-dimensional crystals with multi-branching tree-like form. Sometimes they consist of joint skeletal individuals. Skeletal crystals are imperfect hollow single-crystal individuals externally reminding contours of a crystal of the correct form. Unlike dendrites they have more perfect form (Perepelitsyn 1987, p. 84).

For all above-mentioned reasons any calculations of viscosity have very approximate character. As a rule, they are not quite correct even in a strict frame, for example, made for a certain temperature. Nevertheless, they can be useful to general estimations and comparisons of slag of different territories and cultures.

A group of German scientists suggested a formula for viscosity calculation of slag at a temperature of 1400 °C (Bachmann *et al.* 1987):

$$\eta_{1400\text{ °C}} = 4.9 / K_z - 0.45,$$

$$K_z = (\text{CaO} + \text{MgO} + \text{FeO} + \text{MnO} + \text{K}_2\text{O} + \text{TiO}_2 + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{SO}_3) / (\text{SiO}_2 + \text{Al}_2\text{O}_3)$$

In principle, groups of oxides here are close to those applied at calculations of basicity of slag (see below). However magnesium oxide (MgO) is an exception, being the basic oxide it influences on increase of slag viscosity. It forces to use a bit different formula of calculations.

It should be noted that the slag viscosity depends very strongly on initial ore. For example, the table of viscosity for ore (Tab. 0-2.) looks as follows:

Slag formed from chalcopyrite which is rich in iron and sulfur should have a very low viscosity at a high temperature if to follow a formula strictly. Even slag from the oxidized ores extracted from the ultrabasic rocks should have slightly higher viscosity.

Viscosity of chemical composition of ore from Kargaly mines is the highest, due to a lot of silicate components.

Thus, when using the sulfide ores it is simpler to receive the fluid slag. The oxidized ores of the ultrabasic fields are less difficult for smelting, and the oxidized ores from deposits in quartz are very difficult.

However, the situation for the problem ore can be improved by the use of fluxes. Otherwise high losses of metal in slag are inevitable. It was almost impossible in this case to receive a copper ingot, and metallurgists had to crush slag for extraction of individual copper prills. Another possibility is the use of very pure pieces of malachite. Basing on archaeological evidence it is very difficult to estimate a primary ratio of ore and rock in the furnace charge. And the slag reflects, mainly, chemical composition of the rock.

Similar table for slag (Tab. 0-3.) is already another:

The viscosity of Sintashta culture slag (settlements of Sintashta and Arkaim) falls in the range of 1.46-6.2 Pa·s, on the average – 3.25 Pa·s. The collection of Abashevo and Early Timber-Grave slags from the Western Urals (Tyubyak, Beregovskoye, Birsik I) is not very representative. However the variability of the viscosity fluctuations is greater: between 2.18 and 9.91 Pa·s, on the average – 5.88 Pa·s.

Slags from the Late Bronze Age settlements in Central Kazakhstan (Atasu, Myrzhik, Ak-Mustafa, Sargari) show even greater viscosity variation: from 0.47 to 22.6 Pa·s with mean value of 4.93 Pa·s. However, it is necessary to take into consideration that at such insignificant sampling this last figure is a result of the accounting of single slags with the highest rate of these values.

In the Kyzyl-Kum slag (Besh-Bulak, Ayakagitma) the viscosity lies within the range of 2.08-13.93 Pa·s, on the average – 5.92 Pa·s.

Berezovaya Luka settlement – fluctuation within 8.23-31.09 Pa·s with the mean value of 19.33 Pa·s.

Slag of the Early Iron Age from area of Irtyash Lake in the Transurals shows the low viscosity between 1.28 and 1.33 Pa·s, the mean value – 1.3 Pa·s.

On the Bronze Age settlements in the Transurals and Northern Kazakhstan (Verkhnyaya Alabuga, Vishnyovka, Novonikolskoye, Petrovka II) the viscosity fluctuates between 0.31 and 7.12 Pa·s with the mean value of 2.67 Pa·s.

The Late Bronze slag in Orenburg area (Ivanovskoe, Rodnikovoe, Gorny, Kuzminkovskoe, Pokrovskoe) demonstrates the viscosity from 1.83 to 47 Pa·s, on the average – 13.3 Pa·s.

Thus, slags of the Early Iron Age from area of the Irtyash Lake show the minimum mean values of the viscosity (1.3 Pa·s); then follow slags of the Late Bronze Age settlements in the Transurals and Northern Kazakhstan and those of Sintashta culture in the Transurals (2.67 and 3.25 Pa·s respectively); then slags of the Late Bronze Age of Central Kazakhstan, Abashevo and Early Timber-Grave slags from the Western Urals and slags from the Kyzyl-Kum (4.93; 5.88; 5.92 Pa·s). The highest viscosity is demonstrated by slags from Orenburg (13.3 Pa·s) and Berezovaya Luka (19.33 Pa·s).

This result is quite explainable. The low viscosity of the Early Iron Age slag is explained by that it was iron smelting slag rich in iron component. Besides, it is the latest slag in the analyzed series, with more perfect technology.

The low viscosity of Sintashta slag is explained by smelting ore, mainly, from the ultrabasic rocks, with the high content of components influencing viscosity decrease. The high viscosity in slag from Berezovaya Luka and Orenburg is explained by the use of ores from silicate rocks. Thus higher viscosity in the slag from Berezovaya Luka against the slag from Orenburg surprises.

The viscosity depends on two factors: a temperature and chemical composition. As well as rocks, slags can be divided into some groups with a different ratio of acid and basic oxides (Perepelitsin 1987, p. 211-214). The basic oxides are: CaO, R<sub>2</sub>O, MgO, FeO, MnO, the acid oxides: SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>. There is also a group of the amphoteric oxides (Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>) which in the basic slags behave as acid oxides, and in the acid slags they behave as the basic. Respectively, coefficients of acidity (A) and basicity (B) can be calculated:

$$A = (\text{SiO}_2 + \text{P}_2\text{O}_5 + \text{TiO}_2 + \text{B}_2\text{O}_3) / (\text{CaO} + \text{MgO} + \text{FeO} + \text{MnO})$$

$$B = (\text{CaO} + \text{MgO} + \text{FeO} + \text{MnO}) / (\text{SiO}_2 + \text{P}_2\text{O}_5 + \text{TiO}_2 + \text{B}_2\text{O}_3)$$

If  $A > 1$  ( $B < 1$ ) the slag has the acid compound and vice versa.

However it is more correct to use more detailed classification (according to V.V. Lapin), corresponding to the geological one (Tab. 0-4.).

But also here it is necessary to kept in mind that any calculations based on chemical composition have relative character as they do not take into consideration quantity of unmelted components increasing the viscosity regardless of their chemical composition.

The main difficulties in mineralogical study of slags arose from that they are rather complicated system. The same microstructure can be influenced by various factors. So, the weak crystallization can reflect as the high speed of slag cooling (and, respectively, some technological parameters), and also by the lack of components needed for crystallization, and, therefore, it reflects the ore base. The main regularities here are the following

(Perepelitsin 1987, p. 82, 214). The ultra-acid slags do not crystallize at all. The acid slags show usually slag glass. Crystal phases are presented only by minerals with high crystallization ability (spinel, magnetite, orthosilicates, etc.). In case of a slow cooling the dendritic, skeletal, and even idiomorphic crystals (of relatively perfect crystal form) can be formed. The microstructure of slags of average composition depends on the speed of cooling. At the fast cooling the glass with skeletal spinel crystals, sulfides, and orthosilicates is formed. At the slow cooling in molds the slag can obtain a holocrystalline structure. The basic and ultrabasic slag even at the fast cooling crystallizes completely, forming fine-grained structure. At the slow cooling the formation of macrocrystalline structures is possible.

### Emission spectral analysis

The second method applied in this research widely, was the spectral analysis of slag and ore. Chemical studying of metal, ore and slags from Volga-Ural region and Kazakhstan have a long history. A large work on the analysis of metal artifacts of the first region was carried out by E.N. Chernykh (Chernykh 1970), and metal artifacts of Kazakhstan was analyzed by S. A. Agapov (Agapov 1990). The spectral analysis of Abashevo and Balanbash (Abashevo culture in the Urals) metal artifacts resulted in their division into two main chemical and metallurgical groups (MP and TK) whose origins was explained smelting of ores from copper deposits in sandstones (MP) and the Ural mine of Tash-Kazgan (TK). The second group differs by the increased concentration of arsenic and is considered as a natural bronze. There is also a distinct regularity of predominance of TK copper in the Balanbash series and MP copper in the Abashevo sites (Chernykh 1970, p. 27, 28). In particular, it was supposed that the analyzed ore from the settlements of Balanbash and Urnyak was extracted from the Tash-Kazgan mine (Chernykh 1970, p. 42). Our studies of Sintashta slags demonstrated that the TK group may not be considered as the natural arsenic copper, it was artificial bronze, and the alloying was made at the stage of ore smelting (Grigoriev 2000a). It is also remarkable that diagrams of trace-elements concentration in the Abashevo and Balanbash TK metal have, as a whole, the identical configuration, but the arsenic content is much higher in the Balanbash series (Chernykh 1970, fig. 22). It is possible to explain this by the different degree of alloying only.

The main diagnosing elements used to relate the metal to some chemico-metallurgical group are As, Sb, Sn, Pb, Ni, Ag, Bi (Chernykh 1970, p. 17-31). It is necessary to kept in mind that there are positive correlations between concentrations of tin and lead with bismuth as they are geochemically connected elements which are present often in the same minerals. It is very indicative that in the diagrams of trace-element concentrations these elements behave in the same way in different chemico-metallurgical groups, showing all together both high or low contents, and often repeating the configuration of diagrams. Therefore these elements can reflect not only geochemistry of deposits, but also the alloying copper with tin (Chernykh 1970, p. 12, 21, fig. 8, 16, 20-24). Differences in diagrams of lead in the Abashevo, Balanbash and Early Timber-Grave series of the MP group (Chernykh 1970, fig. 23) are caused, apparently, by this. Deviations from this rule can be explained not only by the geochemistry of individual deposits, but also by differences in distribution of these trace-elements between slag and metal at different smelting temperatures.

The combination of increased concentrations of arsenic and antimony characterizes the chemico-metallurgical group VK (Volga-Kama). The total content of these elements fluctuates usually within 0.5-2.5%. Statistical calculation showed that the presence of these elements at alloys is not casual and it is possible to speak, apparently, about an antimony-arsenic alloying (Chernykh 1970, p. 16, 17, 21). At the same time, it is necessary to kept in mind the following circumstance. Antimony often replaces sulfur in sulfide minerals of arsenic and other elements. On the other hand arsenic, along with other elements (Ag, Au, Pt, Pb, Co, Ni, Mn, Sn, Zn, Se), can be present as in the form of impurity to copper sulfide minerals, replacing sulfur, as also in the form of arsenopyrite in copper sulfide deposits (Deer *et al.* 1966, p. 182). Therefore the combination of such elements as As and Sb can reflect both exploitation of copper sulfide deposits, and the use of arsenopyrite as an alloying component. Taking into account that the increased concentrations of other

elements are peculiar to VK copper, the first variant could be, apparently, rather often. It is very indicative fact that antimony-arsenic impurities in metal appeared in the period when slag studies demonstrates the beginning of use of sulfide ores.

In this regard the 1st chemico-metallurgical group suggested for Kazakhstan bronzes is also very indicative, because its chemical characteristics are close to the VK group of Eastern Europe (Agapov 1990, p. 11). Altai copper deposits could be a source of this group. However, for Seima-Turbino sites of Asian zone connected with these deposits, these bronzes were not typical (Chernykh, Kuzminykh 1989, p. 166-170). Therefore, a final decision about their belonging to artificial alloys or to products of smelting of ores from the copper sulfide deposits enriched with arsenic and antimony, is problematic. It is not excluded that both of these reasons were a source of these bronzes.

The arsenic content is not also indicative for associating to a type of ore deposits. As we already showed in the former works (Grigoriev 1994, 2000a), TK copper group of the Middle Bronze Age in the Volga-Ural region and the Southern Transurals was not connected with the Tash-Kazgan mine, being a result of deliberate alloys of copper ores with arsenic minerals, although the use of some copper deposits with high arsenic content is not excluded. However the latter was not typical because in this period mainly oxidized ores with low arsenic content were the main source for copper smelting. Our studies also revealed a positive correlation between arsenic and nickel that allows assuming in some cases even the use of arsenic-nickel minerals for this alloying. Similar distinct connection of nickel and arsenic is seen also in metal (see Chernykh 1970, fig. 3, 4). Therefore, the growth of both these elements concentration in metal, as well as in the case with the VK copper, had different reasons: the alloys copper with arsenic and the use of copper ores with high arsenic content. In the case of TK copper the first reason is the best explanation. After the beginning of copper sulfide ores exploitation a part of the arsenic copper originated from them could increase.

Thus, the only trace-element silver is less dependent on such reason as the alloying. From this it is possible to draw a single conclusion. In most cases the chemico-metallurgical groups reflect either an alloying of metal or a type of ore (oxidized or sulfide). These groups do not reflect any concrete deposits or even a large mining area.

Possibly, MP copper is exception as being relatively pure it is characterized by the increased concentration of silver (Chernykh 1970, p. 17). Now it is supposed that in view of scarcity of forest in the area of Kargaly mines and huge scales of production, only limited local smelting was practiced there. The majority of ores was taken out to other, sometimes very remote, areas. To the north, in Bashkiria, traces of smelting of the ore from Kargaly have been found (Chernykh 1997, by p. 67, 68). Nevertheless, the statements that metal of this area is chemically comparable to the Kargaly ores (Chernykh 1997, p. 67, 68) it is not quite justified as silver is a very typical impurity for Bashkirian copper sandstones (Narkelyun *et al.* 1983, p. 12). On the basis of trace-elements comparison in copper it is, in principle, impossible to link this metal and ore from sandstones to any concrete area. This problem is outside opportunities of both emission spectral analysis and mineralogical analyses because the geochemistry of copper deposits in sandstones in the Western Urals is very uniform (Chernykh 1970, p. 37, 48). It is also necessary to take into consideration a possibility that some products smelted from oxidized ore with the increased silver concentration from deposits of other types can get to MP group. Nevertheless, taking into account this reservation, we can assume that this group is mainly connected with copper containing sandstones of the Western Urals. Unfortunately, recently the situation with MP group was aggravated, and a thesis has been formulated that all this group of metal was smelted even not from ores in sandstones, but from ores from the Kargaly mines. Moreover, even copper with obvious impurities is considered as copper from Kargaly alloyed with other metals (Chernykh 2007, p. 66). It is necessary to tell only one thing. Today we have no analytical method to do such conclusions.

One more group of copper EU in the Volga-Ural area is characterized, mainly, by the low concentration of silver. Its origin from Elenovka and Ush-Katta mines in the Mugodzhary zone is suggested (Chernykh 1970, p. 17, 22, 40). However it is not excluded that this group can reflect wider range of oxidized zones of different deposits in Orenburg area, the Mugodzhary and the Transurals.

As a whole, now many researchers are skeptical about former results of spectral analyses of metal. In the European literature it is now difficult to find references to the former works based on these analyses of copper artifacts. Many Russian archaeologists share this skepticism. Nevertheless, I would like to emphasize that the groups of metal based on this analysis have objective character, although their interpretation demands a considerable reconsideration.

All this provokes a necessity to discuss possibilities of application of the emission spectral analysis for studies of ore and slag. First of all, this analytical method is insufficiently reliable. In Russia the most reliable methodically spectral analyses were carried out by the Laboratory of natural sciences of the Institute of Archeology. However the repeated studies of Balkan copper artifacts by means of modern methods have found mistakes in some important trace-elements identified in Moscow. As a result, only some new chemical groups of copper have coincided with those suggested by E. Chernykh (Pernicka *et al.* 1997, p. 88-89, 102-106, 118). Nevertheless, the comparison of results of neutron activation analysis (NAA) and atomic absorption spectroscopy (AAS) with the old spectral analyses of the SAM project for Iberia are quite comparable (Müller, Pernicka 2009, p. 303).

In addition to the analytical problems, there are problems of the analyzed material. It is well known that trace-elements are distributed in ore very irregularly that does possible comparison of ore probes only statistically; the method is inapplicable at comparison of separate probes. We have the same situation also at the analysis of rough copper whose chemical compound is additionally influenced by fluxes. For example, a study of trace-elements in different parts of one copper object gives doubtful results as they differ; probes from deposits do not reflect character of its trace-elements in different areas; other minerals and fluxes could be added; re-melting makes its impact too (Palmieri *et al.* 1993, p. 577).

Very indicative experiments were carried out by U. Zwicker. After ore smelting the extracted copper was analyzed. As a result of this analysis it became clear that trace-elements are distributed unevenly in the metal. To receive a homogeneous metal the re-melting was required (Zwicker 1980, p.15). However, relatively correct result can be received only in case the metal was not mixed with another metal either initially or subsequently at the re-melting of scrap. But in the Middle and Late Bronze Age the part of the re-melted metal sharply increased that complicates substantially the correct determination of chemico-metallurgical groups (Chernykh 1970, p. 11, 12). Unfortunately, we do not know how many metal objects of any archaeological culture had been re-melted, but the degree of this utilization was apparently great. But the problems are not limited by this. Even smelting of ore from one deposit, with the use of the same fluxes and without next possible re-melting, can give as a result an absolutely various picture of trace-elements in metal. Very often such elements in copper as Ni, As, Sb and Ag are used as diagnosing for identification of a source of initial raw materials. However, studies of British scientists showed that they are insignificant for this problem solution, because their contents substantially depends on nature of technology (mainly, on a temperature) of metal production (Pollard *et al.* 1990, p. 135).

All above-mentioned problems limit the use of the emission spectral analysis only to determination of types of alloy. However, as it will be shown further, chemico-metallurgical groups based on this analysis have, nevertheless, quite objective character. Comparison of data on trace-elements based on spectral analysis of ancient materials from France with data based on the mass spectrometry method showed that correlation of trace-elements in ore and slag is quite good, although there are some problems (Berthoud *et al.* 1980, p. 87, 93). It is quite expected result because chemical compound of slag is based, mainly, on smelted gangue.

In this research the spectral analyses have been applied to the slag. Slag is quite seldom analyzed by this method as it is considered as heterogeneous material, therefore results of its analysis show considerable dispersion. To avoid it I selected for the analysis large probes, about 5-10g, pulverized them and only then analyzed. The analysis was carried out on the ISP-30 device, No. 740521 in the Chelyabinsk geological expedition. The received results were processed by means of the Brookhaven Data Handling Programs.

Here it is necessary to specify the legitimacy of application of this analysis. The problem of trace-elements transition from ore into slag and metal is quite important for the solution of a number of problems in ancient metallurgy. In particular it concerns a problem of correlation of slags and ores found on any concrete settlement, and also a possibility to link a slag probe with a concrete mine. At this stage this problem is almost unsolvable. Nevertheless, we need some ways to judge about the possibility of links of slag with this or that ore, based on its chemical composition. Similar studies were undertaken by E.N. Chernykh (Chernykh 1970, p. 11). He analyzed ore, slag and metal by means of the spectral analysis for the purpose of determination of regularities of trace-elements behavior in metal, slag and ore at metallurgical redistribution. The main attention was paid to their behavior in metal and ore, which is quite explainable owing to the tasks of his research. But now we will not discuss the problem of trace-elements transition into metal, because the object of this study is slag. E.N. Chernykh related to the group with decreasing coefficient of trace-elements transition into slag Ag, Sb, Au, As, and Bi, to the neutral group – Ni, Pb, Sn, Zn, and Co, and to the group with raising coefficient Mn, Ti, V, and Mo. Quite high coefficients of this transition (10-100) were suggested. My experience in Middle Bronze Age slags studies (Grigoriev 2000a), and also the latest works with slag of the Late Bronze Age showed that there are no so high coefficients of chemical distinctions between ore and slag. For the purpose to determine these coefficients the statistical work with results of spectral analysis of ore and slag from Northern Eurasia was done. I have selected only those analyses where ore and slag from one settlement were analyzed. It should be noted that on each individual settlement ore and slag if they are presented by single objects, could be not linked with each other. However, the comparison of the whole sampling has demonstrated the most general regularities. In total slag and ore from 14 sites were used: 155 analyses of slag and 106 analyses of ore (Tab. 0-5.). From the table it is well visible that overwhelming majority of sites (and, respectively, analyses), where both slag and ore were analyzed, belong to Sintashta culture (Arkaim, Ustye, Sintashta, Yagodniy Dol). It imposes some limitations on the drawn conclusions as Sintashta metallurgists used, mainly, oxidized ores and secondary sulfides. Secondly, the alloying with arsenic at the smelting stage was practiced, and an alloying mineral contained also high nickel concentrations. Therefore, the results relating to arsenic are doubtful, and those relating to nickel demand some correction towards reduction.

The data of the spectral analysis relating to individual trace-elements were summarized and divided by number of analyses. As a result, mean values of the content of each trace-element in slag and ore have been received. Comparison of these values allowed the coefficients of transition of trace-elements from ore to slag to be calculated. However, some trace-elements (Cd, Bi, W, Sn, Sb) show, as a rule, zero values, therefore the coefficients for them are statistically absolutely invalid and, probably, wrong. These elements and arsenic, introduced in these slags as an alloy, are marked out in the table (Tab. 0-6.).

Thus, the trace-elements with decreasing coefficient of this transition are: Ag, Sr, Pb, Ba, Ni, Zn, Co, Yb, and Y. Their content in slag descends. The coefficient of this decrease for different trace-elements fluctuates from 0.235 to 0.605. The maximum coefficient of 0.001 is revealed for silver. Relatively neutral are V, Be, Mo, Sc, and Mn. Ge, Ti, Zr, Ga, and Cr increase their values. The coefficient of the increase fluctuates between 1.31 and 2.374. Thus, we do not see considerable deviations in the content of the main trace-elements that makes comparable the chemical analyses of slag with ore analyses. However, it is needed be kept in mind that these data are correct for the oxidized ores smelting, and in case of slag relatively free of copper that was typical to Sintashta slag. The situation with slag from sulfide ores should be another, because they, on the one hand, are more polluted by impurities, on the other hand, they were smelted at higher temperature. Therefore, the

behavior of trace-elements is less predictable in these conditions. But many researchers are convinced that the behavior of trace-elements depends on ore type (Brovender, Choubin 2008, p. 2).

Possibly, these coefficients are inapplicable also to smelting of oxidized ores in oxidizing conditions that resulted usually in the high copper content in slag. For example, experiments with ore, slag and ingots from archaeological sites showed that (unlike my results and those of Chernykh) nickel and cobalt remain, mainly, not in slag and their concentration in metal ingots decreases. But it was in ingots rich in cuprite, i.e., in the oxidizing conditions. In ingots with sulfide inclusions the content of these trace-elements is higher (Zwicker *et al.* 1980, p. 140). Therefore for all these slag types it is necessary to do separate calculations. In addition to this, it is necessary to remember about conditional character of these coefficients which reflect the most general tendencies. In a real situation the coefficient of this transition depended also on a ratio of copper and gangue in ore, and this ratio on different sites could be various.

For slags (27 samples) and ores (21 samples) of the Late Bronze Age settlement of Ilyaska a bit different coefficients are received (Tab. 0-7.). However the used sampling is too small. Therefore more precise calculations of these coefficients for the Late Bronze Age slag is needed. Nevertheless, the differences are not so considerable. They are notable only for arsenic that is explained by its use as alloy in many probes discussed above.

These coefficients for slags from oxidized ores (lower temperatures and oxidizing conditions) can be not so considerable as these slags contain a lot of inclusions of copper and cuprite. Therefore their chemical compositions differ not too much from initial ore that was heterogeneous itself and can show considerable variations in different areas of any ore field. Nevertheless, the results of any analyses have quite objective character, although they cannot be considered as absolute evidence. Thus, the use of the spectral analysis of slag is quite possible. It gives quite objective groups, however their interpretation as relating to any concrete mine is absolutely wrongful.

At the same time, so insignificant coefficients show that the slag analyses, in principle, can be compared to the ore analyses. Although slag is less homogenous in comparison with metal, it has one indisputable advantage. The huge mass of metal was repeatedly re-melted and often mixed with other metals. Slag was smelted from ore only once. However slag has some specific problems, namely, the transition of trace-elements from the furnace dressing or components of charge that will be discussed at the description of experimental works. Therefore, this analysis is not also absolutely reliable for slag.

### **Problem of ore sources identification**

As it was already shown above, the method of the spectral analysis even in the slag or ore analysis (not to mention metal artifacts) gives no possibility to connect them not only with a concrete ore deposit, but even with a group of deposits in any area. In full measure it is applied to the RFA and others, more modern, types of analysis. The mineralogical analysis used widely in this work is a good way to determine a type of ore bearing rock only. However, the rock of the same type can be present in different deposits from distant areas.

In modern archaeometallurgy to the solution of this task the isotope method is widely applied. It is based on the fact that in metallurgical processes the ratio of three lead isotopes in slag, ore and metal remains invariable. It, as though, favorably distinguishes it from other chemical methods, and gives a chance for direct comparison of metal and ore. However this method has some problems too. Often individual probes in diagrams are situated along a straight line, having only different places on this line (see, for example, Gale, Stos-Gale 2002, fig. 2-4). It (purely graphically) makes impossible to distinguish probes from a large number of deposits (Fig. 0-8.).

These thoughts should not be considered as an appeal to refuse the use of this method, but its results are not a solution of the problem too. There are many works showing that this method perfectly copes with the tasks if probes of different deposits are situated in diagrams along parallel lines (see e.g. Gale *et al.* 2003). But in case of many deposits (and at large sampling of metal it is so), many of these lines coincide. Therefore, when two complexes of metal, slag and ore differ, we can **reliably state this difference**. But if lines merge, it does not always mean that we may draw a conclusion about a single source.

There are also other problems. Studies in different regions, for example, in Armenia, Serbia and Bulgaria showed that within particular deposits the isotope composition can vary, and the composition of trace-elements is constant. In copper artifacts the set of trace-elements depends also on traditions of casting and forging (Ryndina, Ravich 2012, p. 12, 13). Studies of ores in Southwest Britain also showed that the ratio of isotopes in any individual ore deposit can strongly differ in different zones, and this method is not applicable in this area (Craddock, Craddock 1996, p. 61).

Probably, it is the only thing to do in this situation to use several analytical methods and correlate its results. Study of chemical compositions of chromites by means of the scanning electronic microscope can be one of them. However this method is not universal and is applicable only to materials of Sintashta culture. Possibilities to use this method for Sintashta metallurgy are very great owing to three circumstances:

1. Unlike the Late Bronze Age metallurgy, the Sintashta metallurgy was based on ores from the ultrabasic rocks; therefore the ore and slag almost always contain chromite inclusions that is typical also of the ultrabasic deposits.
2. The chromites are very refractory and their chemical composition does not change after ore smelting because they, practically, do not interact with other slag components as our numerous analyses of the Sintashta slags have demonstrated. It differs them from all other components and from the chemical composition of ore and slag as a whole.
3. Within a particular ore deposit the chemical composition of chromites is quite close and can be considered as an important diagnostic sign.

The phase diagram  $\text{Fe}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{Cr}_2\text{O}_3$  constructed on the basis of these analyses gives a possibility to compare chemical compositions of chromites in slag and ore fields.

One more method that can help in the solution of the discussed questions is identification of specific minerals, typical of any deposit, and chemical analysis of slag. Unfortunately, after metallurgical reactions these minerals cannot keep in slag, and the chemical composition is strongly transformed. Petrochemical calculations of slag chemical compositions can help.

The studies of chemical compositions of slag are, as a whole, a way to determine chemical compositions of ore-bearing rock and its mineralogy. This determination can be made by means of standard petrochemical calculations. In this research the Minpet program was used. However it is necessary to make some reservations here. These calculations would be correct in the case when only ore was used in smelting. But if the fluxes were added we inevitably receive a doubtful result. However, our study of large slag series of the Middle and Late Bronze Age of Northern Eurasia has not found the wide use of fluxes. It is possible to say quite definitely that Sintashta metallurgists of the Middle Bronze Age almost did not know the fluxes. Nevertheless, they added fragments of bones that introduced calcium and potassium in the furnace charge, promoting creation of more liquid slag. Phosphorus containing in the bones promoted temperature increase at exothermal reaction of its burning.

This circumstance forces to doubt in identification of Ca-containing pyroxenes, such as wollastonite<sup>2</sup>. This is also a reason to doubt in identification of apatite, nepheline and leucite – the minerals containing Ca and K. Reconstruction of some other components of the furnace charge, for example olivines and pyroxenes, owing to the resemblance of their chemical composition, cannot be recognized as the satisfactory too. Therefore this method is not strict and can be used only as an addition to the main methods. It is necessary to fix one more circumstance. In the following text the identification of this or that mineral in slag by means of these calculations is mentioned. But the minerals which are really present at slag, and the normative mineral compound reconstructed on the basis of recalculation of the chemical analysis are slightly different things. The latter is only idealized mineralogy.

There is one more reservation. The mineral composition depends not only on a chemical composition, but also on the speed of slag cooling. Therefore often it does not correspond to the idealized composition, based on the petrochemical calculations. Nevertheless, the method allows with confidence a type of the ore-bearing ore to be identified.

### **Base of the research**

In the research mainly Bronze Age ores and slags of the area from the Don River to the Altai and Central Asia were included. In total 2331 slag and ore samples have been investigated (this number includes also some samples of our experimental smelts). On the whole, 2628 analyses have been done: 1184 emission spectral analyses, 738 by optical microscopy, 467 SEM analyses, 74 bulk chemical analyses, 88 RFA analyses of metal objects and 135 visual ore identifications<sup>3</sup>.

Unfortunately, these figures only seem to be considerable. Actually for such huge temporal and spatial length they are insignificant. It is connected not only with large work content of all research procedures, but, often, also with lack of materials. So, data on Eneolithic metallurgy of the region are limited to only several samples, and data on metallurgy of the Early and Middle Bronze Age are simply absent. Only the final stage of the Middle Bronze Age is well presented by Abashevo and Sintashta settlements.

The Late Bronze Age is reflected in the research very irregularly too. The most slags are found on sites of Timber-Grave (Srubnaya culture). Slags from the Transurals and Kazakhstan are presented incomparably worse. But even on this background data on production during the Final Bronze Age, taking into account a huge number of bronze artifacts of this period, look depressing, and in many areas date on the Early Iron Age are absent at all. All this is partly explained by concrete research situations, but partly it reflects any other realities, for example, partial transfer of production to mines or increase of exchange operations and territorial specialization.

### **Archaeological cultures in Northern Eurasia**

Before starting the description of cultures whose materials are analyzed in this work, and also historico-cultural processes connected with the development of metallurgical production in Northern Eurasia, it is necessary to touch upon the periodization accepted here. The studied materials belong to the Eneolithic, Early, Middle and Late Bronze Age, and the Early Iron Age. Belonging of any culture to the Eneolithic is not a special problems, although, as it will be shown below, often it can be quite controversial. However numerous problems arise with the belonging of other materials to this or that period. So, we consider Sintashta culture within the Middle Bronze Age (Grigoriev 1994, 1999, p. 34). But often scholars relate it to a transition period between the Middle and Late Bronze Age and even to the beginning of the Late Bronze Age. There are also many problems in correlation of materials from different areas. Because we will touch upon the

<sup>2</sup> Information about individual minerals is taken from Deer *et al.* (1965, 1966, 1966a).

<sup>3</sup> The author is thankful to many colleagues who helped collect slag for this research.

materials of the huge area, a question of vital importance is that in different areas the different schemes of periodization are used. In Eastern Europe a more or less harmonious system going back to V.A. Gorodtsov is developed. He suggested the following division: Early Bronze Age (Pit-grave culture), Middle Bronze Age (Catacomb culture) and Late Bronze Age (Timber-grave culture). Subsequently in both European and Asian zones of Eurasia many archaeologists started to distinguish a period of the Final Bronze Age, but many others consider it within the Late Bronze Age as its final phase. But in some areas the late Pit-grave complexes existed during the Middle Bronze Age. Besides, the Gorodtsov's periodization was not based on strict historico-metallurgical criteria, and differs from the periodization accepted in Central and Western Europe where the materials corresponding to the Eneolithic, are considered now within the Copper Age. The Early Bronze Age, if to be based on its name, should commence only since the appearance of arsenical alloys. Those in the Pit-grave complexes are known seldom, being, apparently, the Caucasian imports. In the Orenburg area, where ore smelting was practiced by the Pit-grave people, these alloys are not known. Therefore if to be based strictly on etymology of the terms, the Abashevo and Sintashta complexes should be considered as The Early Bronze Age.

However, it is a universal problem. So, in the Pre-Pottery Neolithic of Mesopotamia single metal objects are already known (Ryndina, Yakhontova 1989, p. 306, 308). Their number grows in the Neolithic. But, certainly, native copper was used for their production. The division of the Copper Age and Eneolithic is very problematic. Moreover, in the Urals and Western Siberia the Eneolithic complexes contain usually no metal finds. We simply know that metal was known in the region during this period. However, basing on flint and other finds it is very difficult to distinguish Eneolithic and Neolithic materials. Only experts familiar with the typology of ceramics of the region are able to do it. In Kazakhstan and Siberia the used schemes of periodization are not linked to those in Eastern Europe, against comparability of materials. The terms "Early Bronze", "Middle Bronze", "Developed Bronze", "Late Bronze", and "Final Bronze" are used, and this division is rather arbitrary in each territory. A situation in contact areas, especially in the forest zone, is even more complicated when near the Late Bronze Age cultures there are Neolithic cultures. And the designation of an epoch for the region turns into a question of preference.

Citation of similar paradoxes can be continued indefinitely, however there is no special need in it as from everything told it is clearly that available schemes of periodization have no enough rigid universal criteria; besides, development of these criteria is hardly possible, they will always have conditional character. It should be understood, and not to absolutize any of criteria. It seems more reasonable to adhere to the generally accepted terminology. Therefore, in spite of the fact that it is more correct to refer the Pit-grave culture to the Copper Age, all Russian archaeologists prefer the term "Early Bronze Age" (EBA). Similarly, it is more correct to refer the Abashevo and Sintashta complexes to the Middle Bronze Age (MBA). It corresponds also to historico-metallurgical criteria as during this period tin alloys were almost not known, and the arsenical alloys were widespread. Besides, chronologically these complexes correspond to the late Catacomb culture that allows them to be considered within the second phase of the Middle Bronze Age (MBA II). But chronologically they correspond also in Siberia to Elunino and Krotovo sites of the Late Bronze Age (LBA). Considering their connection with Seima-Turbino sites of the Late Bronze Age, Sintashta and Abashevo cultures of the MBA can be synchronized with the LBA cultures of the Asian zone. This is explained by that the stereotypes of the Late Bronze Age spread from the east to the west together with the movement of Seima-Turbino tribes (Chernykh, Kuzminykh 1989). Similar division of the material will be kept also in this book.

My former experience in the field of ancient metallurgy allows me to claim that any features of the technology and ore base, used in antiquity, were closely connected with global cultural and historical processes occurring on our continent. The essence of these processes was stated earlier (Grigoriev 1999, 2000a, 2002), however, it is necessary to give them the most general description here.

Although the earliest metal objects in Northern Eurasia are dated to the Eneolithic, there is not enough evidence of smelting for this period. There are no reliable data also on the ore smelting during the Early Bronze Age although copper deposits in sandstones of the Southern Urals were exploited at this time (Chernykh 2002). However the lack of settlements in this zone hinders studying of this problem. Most likely, the late Pit-grave complexes in this region continued to exist also during the MBA II. But the data on metallurgical production of this time are not present too.

Essential changes in Northern Eurasia started in the MBA II. In the 18th century BC (in the radiocarbon chronology, it is the late 3rd millennium BC) there was a migration of tribes from the Syro-Anatolian region to the Southern Transurals. It led to formation of Sintashta culture in the Transurals, and then to the appearance of Potapovo sites in the Volga region. Synchronously, in Eastern Europe several Abashevo cultures is formed. Possibly, with some lag from the described process, in the 17th century BC (the early 2nd millennium BC in radiocarbon chronology) the essential cultural transformations happened also in the east of the described region. The penetration of tribes bearing the Seima-Turbino traditions in metalworking to the Altai leads to emergence of Elunino culture here, and subsequently, with spread of this process westward, to formation of several cultures in the southern areas of Western Siberia: Krotovo, Tashkovo. Other cultural complexes (Vishnyovka, Odino-Krokhalevka) were connected with this process. The spread of the Seima-Turbino complex to the Western Urals led to the appearance of the Seima-Turbino burials and sites of Chirkovo culture in the Volga-Kama area. This migratory process influenced on Sintashta and Abashevo cultures. The disintegration of Sintashta system and migration of people to Eastern Europe began. As a result, in forest-steppe and the steppe areas of Eastern Europe Timber-grave culture is formed on the base of Sintashta Abashevo, Poltavka and late Catacomb populations. Similar process took place in the Southern Transurals: the formation of Alakul culture. At the heart of this process the Sintashta complexes lay. The spread of Alakul culture to the east resulted in assimilation of the related Petrovka tradition that had been formed in Northern Kazakhstan earlier on the base of the same Sintashta culture. As a result, in the 16th (17th ) century BC a very large Timber-grave-Alakul cultural block arose. Thus, Sintashta culture was the main cultural component participated in these processes.

Some Alakul and Timber-grave populations penetrated the south of Central Asia. The Timber-grave penetration is limited to East Caspian area, and Alakul people penetrated in the east, up to Kyrgyzstan. However, it is impossible to say that this penetration was mass and reached Iran and Afghanistan although such belief can be met in Russian archeology.

In the 16th (17th ) century BC new processes began. They were connected with the appearance of the Fyodorovo tribes in the Altai. From the Altai these tribes started spread by a wide stream to the west. The area of their movement included the steppe, forest-steppe and the southern part of the forests. In the steppe and forest-steppe these tribes actively interacted with the Alakul tribes that lead to formation of a series of syncretic types. In the forest zone these tribes interacted with bearers of former cultural traditions, including Seima-Turbino. As a result, the formation of Cherkaskul, and then Mezhovka culture of the Urals began. This process was continued also in Eastern Europe, with Fyodorovo and Cherkaskul-Mezhovka penetrations caused the formation of Suskan-Lebyazhinka and Prikazanskaya cultures.

In the 14th -13th centuries BC in the steppe and forest-steppe of Northern Eurasia cultures of the final bronze formed, characterized by vessels with an applied cordon below the neck. In the European part it is the Ivanovskoe (Srubno-Khvalinsk in another terminology), and in Asian part the Sargari. The formation of these cultures was based on Timber-grave and Alakul cultures, however, in the previous period penetrations into the steppe populations from the northern forest-steppe and the forest zone (Fyodorovo, Mezhovka, Suskan-Lebyazhinka) took place.

At last, in the early 1st millennium BC in the steppe archaeological sites almost disappeared. An exception is the Belozerka culture of the North Pontic area that was a continuation of its Sabatinovka predecessor. The latter originated being influenced from the Northeast Balkans and therefore these cultures were not connected with the cultures of Northern Eurasia described above. On the Lower Volga the rather sparse Nur sites are known, and the unexpectedly great number of the Dongal sites in Central Kazakhstan proceeded the Sargari tradition. The former cultural tradition remained also in the Western Urals where new cultures formed, as a whole, on a local basis, but it interrupted in the Transurals. However we, practically, have no slag materials of this time.

It is necessary to stipulate once again that the sampling is very limited for so vast area and so long period. It reflects even not quite adequately a real picture of development of metallurgical production in Northern Eurasia. In some areas excavators did not collect slag materials because their informative opportunities were not understood. In other areas archaeological works simply were not carried out. Therefore the available collection is capable to reflect only the most general tendencies of production development in this territory.

And, these tendencies are very important at reconstruction of historico-cultural processes, in particular, the migrations. It is possible to discuss doubtful opportunities of borrowings of types of ceramics and architectural styles over long distance, or even more doubtful possibility of borrowings of funeral rites, ideology and mythological system. But any discussions of borrowings of metallurgical technologies are in most cases absolutely senseless. First, these technologies cannot be passed without training. As we saw, metallurgical production is a very complicated process. This is also true for the change of alloys which were, as we will see, closely connected with type of ore. For example, the transition to new types of ore caused the transition to tin alloys, and the need of search and smelt the tin ore, cassiterite, thin-walled casting into closed molds, the lost wax casting, new techniques of forging operations and so on. So, the metallurgical technologies are a very difficult, interconnected system. Direct contact with experienced metallurgists is necessary for its borrowing. Close neighbors could borrow these technologies, but over barren areas, without ore deposits, it was impossible. If it occurred, it is a reliable indicator of migrations.

Any cultural processes depend on two major factors – culture of a former population and either influences or migrations from outside. The processes of cultural interactions of different forms provided formation of similar stereotypes within rather large areas. However, the former traditions disappear completely seldom. As a rule, they show themselves to some extent in the culture of derivatives. The technology of metallurgical production is not an exclusion. Moreover, if any other productions and features of material culture are dependent, above all, on traditions of composing components, the metallurgical production depends also on the ore base. Therefore the local components can be expressed as in borrowings of local technological traditions (and it is a standard cultural process depending on a concrete situation of cross-cultural interactions), as also in transition to local ores that is a forced transition.

This circumstance causes new difficulties in the system of description of Northern Eurasian metallurgical technologies. On the one hand, there are chronological regularities caused by technological changes in huge territories. However, they show themselves not always and not everywhere that is caused already by local specifics. Therefore, at first sight, it seems to be more logical to consider production of the whole region by phases. But, unlike ceramics, slag has no accurate cultural or chronological indications; often only comparative and statistical procedures allow slags of different periods in multilayer settlements to be distinguished. It forces to consider at the same time slags of different periods of any particular area. And from this point of view, the territorial approach has to dominate when slags from different areas are described successively that leads already to the loss of chronological approach. In the end, it is necessary to search for any compromises.

In particular, the starting point for consideration of the Bronze Age slags is Sintashta and Petrovka cultures of the Transurals that causes also discussion of some materials from Kazakhstan. Further, the materials of the Late Bronze Age of the European zone are considered. However, partially the Western Ural materials are considered also in the context of Sintashta culture. Chemical analyses of slags from the settlement of Tyubyak are considered as in the context of Sintashta as in the context of Timber-grave culture, which is caused by the necessity to do a comparative analysis.

Some of the discussed problems will be covered in different chapters in more detail. But, it would be desirable to emphasize that a task of this book is a development of any research standard and the most general model of development of copper production in this territory. This will do possible in the future to organize more detailed studying of individual areas and cultures. There is one more problem demanding a special discussion. It is the chronology used here. For the most part of the interval included in this work, it is possible to use as the traditional dating linked to the Middle Eastern chronology, as the radiocarbon dating. The last system of dating unconditionally dominates recently, but it is created not for all regions. On the other hand, there are serious problems with the radiocarbon dates, about which usually ones keep silence. Attempts to compare these two systems give while few hopes that it is possible, because for different periods the difference between them makes from 200 to 900 years (Michael 2004, p. 18). It is also obviously that the radiocarbon method works today only at a statistical level that does not allow it to be surely used in case of small series of dates (Müller 1998, S. 66). And for many cultures of Northern Eurasia these series are insignificant yet. I do not know how to regard with this problem, and how correct the calibration of radiocarbon analyses is. But it is just necessary to give the calibrated data. That means that irrespective of these dates correctness, they are used here for identification of relative time of discussed processes and their sequence. In addition to this, sometimes, I give dates in system of traditional chronology.

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Tab. 0-1. Melting points of some slag minerals.

Cu	Cu <sub>2</sub> S	Cu <sub>2</sub> O	CuO	FeO	Fe <sub>3</sub> O <sub>4</sub>	Fe <sub>2</sub> O <sub>3</sub>
1084°C	1127°C	1232°C	1336°C	1360°C	1530°C	1570°C

Tab. 0-2. Relative viscosity calculated for ores of different chemical compositions.

№	Site	Material	Kz	η 1400 (Pa·s)
2158	Experimental smelting № 9	Chalcopyrite	25.21	-0.26
2195	Experimental smelting № 12	Chalcopyrite	21.81	-0.23
2126	Experimental smelting № 5	Oxidized ore of the Dergamysh deposit in ultra-basic rocks	1.25	3.46
2161	Experimental smelting № 10	Oxidized ore of the Ishkinino deposit in ultra-basic rocks	0.99	4.5
2106	Experimental smelting № 4	Oxidized ore of the Nikolskoe deposit in quartz rock	0.58	7.95
2103	Kargaly	Oxidized ore of the deposit in copper sandstone	0.03	149.73

Tab. 0-3. Viscosity calculated for slags of different chemical compositions.

№	Site	Kz	η 1400 (Pa·s)
66	Verkhnyaya Alabuga	35.83	-0.31
2173	Experimental smelting № 11	25.39	-0.26
2193	Experimental smelting № 11	17.28	-0.17
2186	Experimental smelting № 11	16.61	-0.15
2116	Experimental smelting № 3	13.39	-0.08
1781	Arkaim	1.83	0.00
2145	Experimental smelting № 6	9.29	0.08
2121	Experimental smelting № 2	6.37	0.32
21	Atasu	5.35	0.47
26	Myrzhik	4.8	0.57
2123	Experimental smelting № 4	4.77	0.58
2212	Uzhovoy Island	2.83	1.28
2207	Guseva Gora	2.76	1.33

## METALLURGICAL PRODUCTION IN NORTHERN EURASIA IN THE BRONZE AGE

№	Site	Kz	$\eta$ 1400 (Pa·s)
19	Atasu	2.6	1.44
1792	Arkaim	2.57	1.46
27	Myrzhik	2.45	1.55
54	Vishnyovka	2.4	1.59
Gor-E09/3	Gorny	2.15	1.83
483	Ayakagitma 234	1.93	2.08
1923	Tyubyak	1.86	2.18
1789	Arkaim	1.86	2.19
46	Novonikolskoye	1.79	2.29
1799	Sintashta	1.53	2.76
2144	Experimental smelting № 6	1.51	2.8
590	Besh-Bulak 1	1.45	2.94
588	Besh-Bulak 1	1.44	2.96
18	Atasu	1.44	2.96
1937	Beregovskoye	1.42	3.00
1946	Sintashta	1.23	3.52
1285	Kuzminkovskoye	1.16	3.78
1798	Sintashta	1.14	3.85
2129	Experimental smelting № 5	1.07	4.15
1303-1	Ivanovskoye	1.03	4.31
1925	Tyubyak	0.98	4.56
44	Sargari	0.92	4.89
1333-1	Rodnikovskoye	0.9	4.97
1318-1	Pokrovskoe	0.89	5.09
1787	Arkaim	0.77	5.94
1304-1	Ivanovskoye	0.75	6.09
Gor-E29/7	Gorny	0.74	6.21
1344	Rodnikovskoye	0.72	6.33
2169	Experimental smelting № 10	0.69	6.66
13	Petrovka II	0.65	7.12
Gor-E10/1	Gorny	0.64	7.17

№	Site	Kz	$\eta$ 1400 (Pa·s)
Gor-E26/7	Gorny	0.64	7.21
Gor-E01/5	Gorny	0.63	7.3
580	Besh-Bulak 1	0.6	7.68
Gor-E11/3	Gorny	0.58	8
Gor-E12/1	Gorny	0.57	8,13
Gor-E27/5	Gorny	0.57	8,21
2063	Berezovaya Luka	0.56	8,23
Gor-E28/6	Gorny	0.49	9,48
1941	Beregovskoye	0.48	9,75
1942	Birsk I	0.47	9,91
Gor-E06/1	Gorny	0.44	10.58
Gor-E23/5	Gorny	0.39	11.97
Gor-E18/5	Gorny	0.39	12.09
Gor-E25/6	Gorny	0.37	12.8
Gor-E08/1	Gorny	0.36	13.13
2037	Berezovaya Luka	0.34	13.83
Gor-E20/3	Gorny	0.34	13.86
567	Besh-Bulak 4	0.34	13.93
1355	Rodnikovskoye	0.34	14.04
Gor-E30/4	Gorny	0.29	16,26
1356-2	Rodnikovskoye	0.29	16,4
Gor-1-5	Gorny	0.26	18,42
2146	Experimental smelting № 7	0.23	20.98
2047	Experimental smelting № 7	0.22	22.24
53	Ak-Moustapha	0.21	22.6
Gor-E22/5	Gorny	0.21	23.04
2044	Berezovaya Luka	0.2	24.15
Gor-E13/5	Gorny	0.19	25,06
Gor-E19/8	Gorny	0.17	28,41
2048-1	Berezovaya Luka	0.16	31.09
Gor-E21/5	Gorny	0.12	41.9

№	Site	Kz	$\eta$ 1400 (Pa·s)
Gor-E24/5	Gorny	0.1	47
2030	Experimental smelting № 5	0.05	108,4
2029	Experimental smelting № 5	0.04	113.3
2074	Experimental smelting № 11	0.02	323

Tab. 0-4. Coefficients of basicity and acidity used for the classification of slag.

Group of slag	Coefficient of acidity	Coefficient of basicity
Ultra-basic	0-0.5	> 2.5
Basic	0.5-1	2.5-1.5
Average	1-1.5	1.5-1
Acid	1.5-3	1-0.5
Ultra-acid	> 3	< 0.5

Tab. 0-5. Quantity of analyses of ore and slag used for calculations of regularities of the trace-elements transition.

Site	Slag	Ore
Arkaim	55	12
Burli	1	1
Ilyaska	27	12
Itkul	1	1
Myrzhik	1	1
Novobaryatino	3	1
Petrovka	2	1
Rodniki	3	1
Sergeevka	2	3
Sintashta	16	38
Tash-Kazgan	2	4
Ustye	41	30
Yagodniy Dol	1	1
Total	155	106

Tab. 0-6. Coefficients of trace-elements transition from ore to slag. Statistically doubtful trace-elements are marked out with red.

Group		
decreasing	neutral	increasing
Ag 0.001	V 0.91	<b>As</b> 1.31
<b>Cd</b> 0.1	Be 0.93	Ge 1.335
<b>Bi</b> 0.125	Mo 1.186	Ti 1.571
Sr 0.235	Sc 1.217	Zr 2.1
Pb 0.238	Mn 1.22	Ga 2.25
Ba 0.353		Cr 2.374
Ni 0.375		<b>Sn</b> 12
Zn 0.392		<b>Sb</b> 13
Co 0.489		
<b>W</b> 0.5		
Yb 0.594		
Y 0.605		

Tab. 0-7. Coefficients of trace-elements transition from ore (settlement of Ilyaska).

Group		
decreasing	neutral	increasing
Ag 0.08	Cr 1.083	Mn 1.595
Pb 0.091		V 2.1
Sr 0.105		Sc 2.17
Ni 0.157		Zr 2.41
Ba 0.187		Ti 2.779
Co 0.253		Be 3.482
Zn 0.267		Mo 7.799
Ge 0.296		
As 0.4		

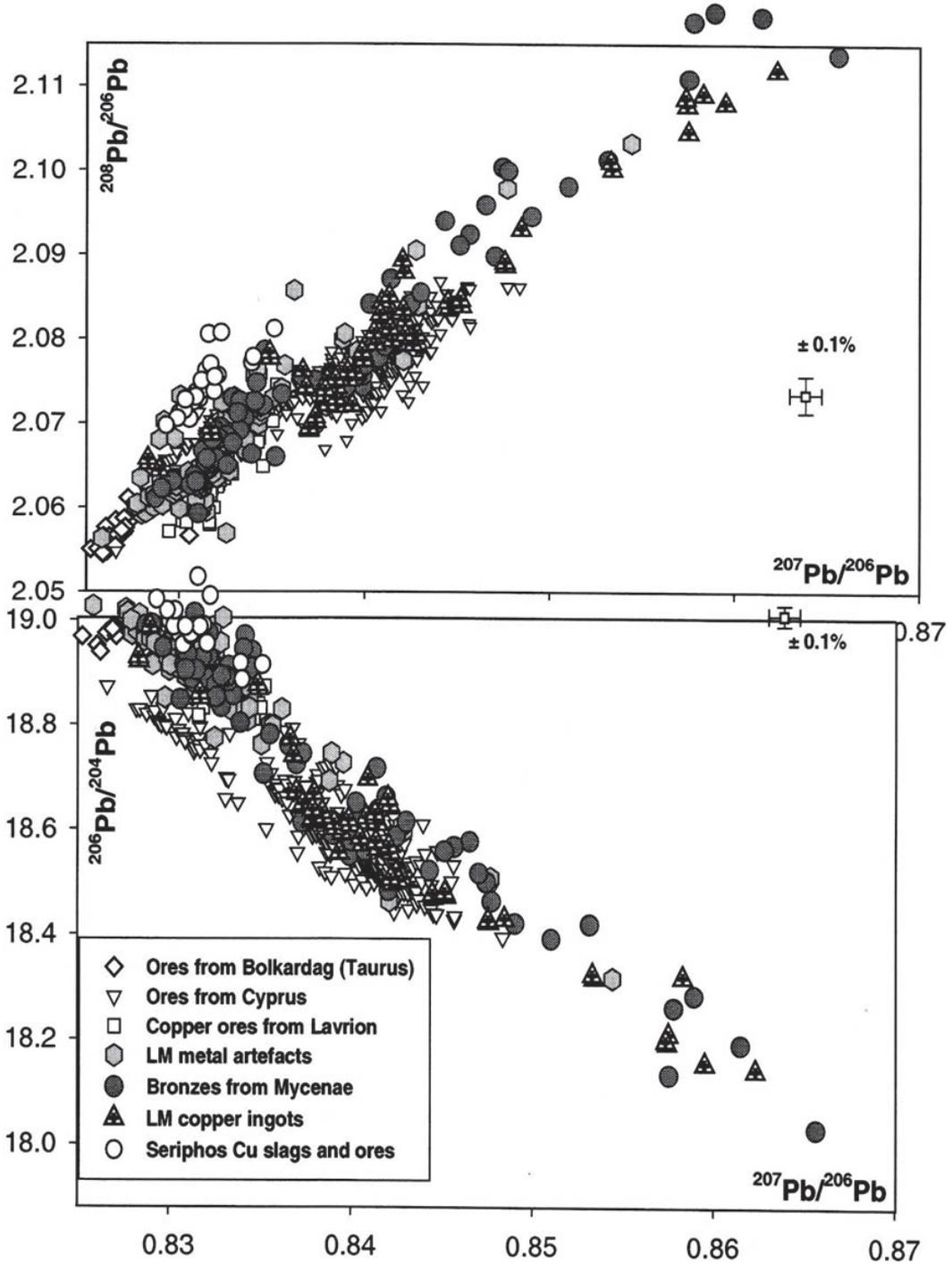


FIG. 0-8. DIAGRAM OF CORRELATION OF LEAD ISOTOPES (AFTER GALE AND STOS-GALE, 2002).