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The Geochemistry of Unalloyed Copper Metallurgical Group Indicates Copper Ore Sources in the Late Bronze and Early Iron Ages of the Urals

Trace elements in copper artifacts from Late Bronze and Early Iron Age sites in the Urals, formerly attributed to the metallurgical group of "chemically pure" copper, were analyzed using the method of laser ablation inductively coupled plasma mass spectrometry. The metal of which artifacts included in this group are made reveals geochemical markers suggesting that "pure" copper actually falls into several subgroups. The PCA analysis of the results identifies 11 clusters corresponding to various sources of copper ores and their mixtures. At least seven principal associations can be linked to copper deposits of different geological types and origin: Au-Te-Bi, Au-Se-Te-Sb, Fe-Co-Ni-As-Sb, Fe-Co-Ni -Zn, Se-Co-Fe, Ag-Pb-Ni, and Sb-Pb-Zn-As. Also, several mixed associations reflect the fusion of copper items and metal scrap initially obtained from different sources: Sn-Pb, Fe-Co-Ni-Zn + Sn, Fe-Co-Ni + Au-Te-Bi-Ag, Fe-Co-Ni + Au-Te-Bi + Sn. A separate association, for which the ore source remains unknown, consists of artifacts characterized by a low content of trace elements, jointly making up less than 0.01 wt%. The largest sample in the Late Bronze Age "pure copper" group falls within the Sn-Pb cluster representing a mixture of local copper and imported Sn-containing copper scrap. Judging by trace elements, the main sources of ore in the "pure copper" group of the Itkul and Sarmatian cultures were the Gumeshki mine and another unidentified source. Both could have been used already in the Final Bronze Age.

Keywords: *Copper geochemistry, trace elements, deposits, metallurgical group, Urals, Late Bronze Age, Early Iron Age.*

Introduction

The chemical composition of copper items has been a subject of active research in world archaeometry for over sixty years. The first essential studies in Russia were carried out by E.N. Chernykh (1966, 1970) and were subsequently continued by other scholars (Chernykh, Kuzminykh, 1989; Degtyareva, Kuzminykh, 2003; Degtyareva, 2010; and others). The fundamental work by E.N. Chernykh (1970) summarized the results of many years of research on chemical composition of metal, slag, and ores in the Urals. He was the first scholar who did a comprehensive study of metallurgy of the Bronze Age metal-bearing cultures and established the main metallurgical groups typical of this region, such as "pure" copper, tin bronze, and arsenic-antimony bronze. Since then, the division into metallurgical groups which can be easily identified by various methods of chemical analysis has been widely followed in Russian archaeological and archaeometric studies. To distinguish the sources of copper raw materials, a dozen of chemical groups of copper (cuprous sandstones, Tashkazgan, Elenovka-Ush-Katta, Volga-Kama, Volga-Ural, Sosnovo-Mazinsk, Altyn-Tyubinsk, Seima-Turbino, etc.) were proposed and compared with various communities and habitation areas.

Such classification of chemical groups based on the distribution of specific elements is still widely used in Russian archaeology. The "pure copper" group in the Bronze Age is often correlated with cuprous sandstones of the Cis-Urals (Kargaly, 2007: 94), and in the Early Iron Age, with the Gumeshki mine (Beltikova, 2005). Although arsenic copper of the Trans-Urals is often correlated with the Tashkazgan group (Chernykh, Kuzminykh, 1989: 172), this ignores similar high-arsenic deposits whose use during the Bronze Age is confirmed by radiocarbon dating (Ankusheva et al., 2022). The tables indicating the chemical composition of copper and bronze artifacts provided in the studies in most cases are not interpreted in any way or are considered subjectively, without their correlation with the known sources and mines.

The above classification of the chemical groups of copper is often insufficient to accurately identify sources of copper raw materials, and its implementation is complicated by a number of factors:

1. The content of trace elements in copper depends on the type of the ore. Pure carbonate (azurite-malachite), carbonate-silicate (+chrysocolla and relicts of host rocks), or sulfide (chalcocite-covellite) ores from the secondary enrichment zones and their mixtures even from the same deposit at different operational sections may give different concentrations of impurities in copper alloys.

2. In a case of similar genesis and ore formation of deposits, their geochemical features are difficult to distinguish without additional (e.g., isotopic) analysis methods.

3. Technological features of copper smelting, such as alloying and flux addition, greatly distort the original geochemical picture of ore sources by introduction or depletion of some elements.

4. Refining copper, its remelting, mixing scrap copper from various sources, or using sophisticated furnace charge ultimately complicate the identification of original sources of copper raw materials.

When analyzing metal composition of ancient artifacts, little attention is usually paid to the metallurgical group of "pure" copper, although it occurs in all archaeological cultures of Eurasia, and in some places predominates. In most cases, "pure" copper was also smelted in primary ore-processing, which is important for analyzing the products of ancient metallurgy (slag, primary ingots, etc.). In archaeometallurgical studies, "pure" copper is often referenced as metal with small amount of trace elements which, in most cases, are difficult to determine because of the limited resolution of instruments for non-destructive analysis (X-ray fluorescence, microprobe, etc.). High-precision destructive methods (spectral, mass spectrometry, etc.) have the advantage of determining significantly lower concentrations, which is important to identify the sources of copper ore, as well as correlations and markers of mixing ores or metal from several sources.

This study is intended to establish indicator associations of trace elements in the "pure copper" group, which mark a specific source of copper ore in the Urals. This enables the division of copper artifacts from the Late Bronze Age and Early Iron Age into geochemical groups reflecting the use of ore from various geological and genetic types of deposits. The novelty of this work is a new method for identifying copper sources and determining the level of mixing copper alloys during the secondary melting of copper scrap, which has been proposed for the first time in the Russian archaeometric research.

Materials and methods

This study analyzed copper items, ingots, splashes, and drops from various sites of the Bronze Age (2nd millennium BC) and Early Iron Age (1st millennium BC), associated with the Sintashta, Petrovka, Alakul, Srubnaya, Cherkaskul-Mezhovo, Fedorovka, Sargara-Alekseevka, Itkul, and Sarmatian cultures (Fig. 1; see *Table*). The "pure copper" group included copper artifacts that contained <0.5 wt% impurities of As, Sn, and Fe, suggesting that the alloying components must have not been intentionally added. The final sample included 117 specimens.

The samples were prepared by selecting small fragments (up to 1–3 mm) through drilling or sawing off, which were then placed in epoxy resin blocks and polished with diamond pastes. To establish

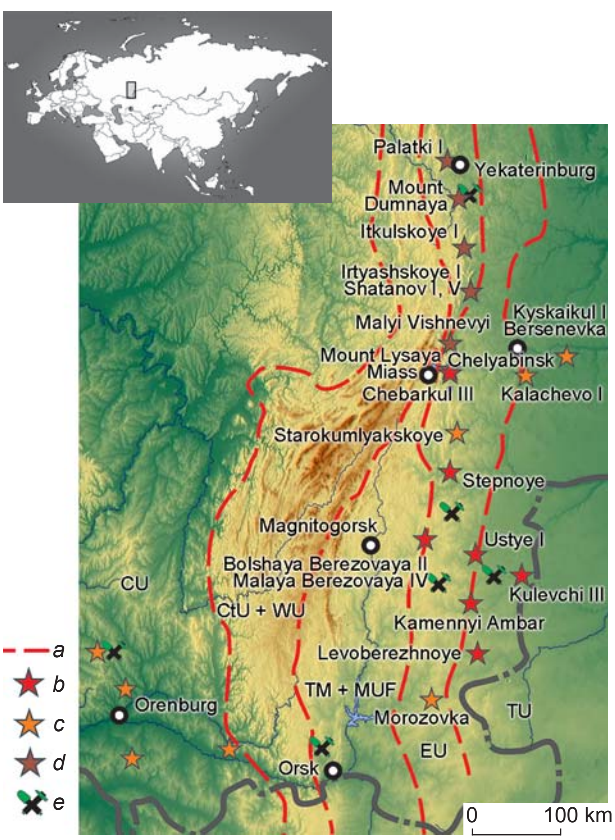

Fig. 1. Referential sites of the Bronze Age and Early Iron Age of the Urals with the examined artifacts.
a – boundaries of the main geological structures in the Urals: CU – Cis-Urals, CtU+WU – Central Uralian and West Uralian megazones, TM+MUF – Tagil-Magnitogorsk megazone and the Main Uralian Fault, EU – East Uralian megazone, TU – Trans-Urals; *b* – settlements of the Late Bronze Age; *c* – locations of artifacts of the Late Bronze Age; *d* – settlements of the Early Iron Age; *e* – known ancient mines of the Bronze Age and Early Iron Age.

geochemical features of trace elements in copper artifacts, laser ablation inductively coupled plasma mass spectrometry was used. All measurements were taken using an ultraviolet Nd:YAG laser (213 nm; flux density of 4.0–5.5 J/cm^2; frequency of 10 Hz). He was used as carrier gas in the cell with flow rate of 0.6–0.7l /min. Ar with flow rate of 0.9–0.95 l/min was the carrier gas in the mass spectrometer.

The samples were analyzed using the linear mode (laser beam diameter of 100 μm, line length of 600 μm, and beam speed of 10 μm/s), and in the point mode (with diameter of 100 μm), for small-sized samples. The mass spectrometer was calibrated with reference international standard samples NIST SRM-610 and SRM-612. The amount of molecular oxide ions ($^{232}Th^{16}O/^{232}Th$) did not exceed 0.4 %. The $^{238}U/^{232}Th$ ratio was close to 1:1. The chemical analysis was calculated using the Iolite software package (Paton et al., 2011) following standard approaches (Longerich, Jackson, Günther, 1996), and Cu^{65} as an internal standard normalized to 100 % of the total number of components. Elemental contents were calibrated using the NIST SRM-610 and NIST SRM-500 (unalloyed copper) reference materials. The calibration standard was analyzed every 10–18 points to account for instrumental laser and mass spectrometer drift. Upon spectra processing, the elements were identified, and the contents of ^{57}Fe, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{75}As, ^{77}Se, ^{107}Ag, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{197}Au, ^{208}Pb, and ^{209}Bi were calculated using NIST SRM-500 as an external standard sample. Measured concentrations of ^{118}Sn and ^{197}Au in copper are "representative", since they are not certified according to NIST SRM-500. Further, they were calculated according to NIST SRM-610.

The SAS JMP Pro software package was used for statistical processing of the final results of determining the contents of trace elements, which involved the principal component method and the factor analysis. The content of the selected 13 trace elements in copper (Fe, Co, Ni, Zn, As, Se, Ag, Sn, Sb, Te, Au, Pb, and Bi) was normalized using the logarithmic transformation of J. Aitchison (1982), making it possible to group the data that differ by several orders of magnitude. All of these elements except Fe can be used to establish the origin of metal, since they pass from ore to metal without significant decrease in concentration (Pernicka, 2014: Table 11.1). However, note that elements such as Zn, As, and Sb undergo sublimation, and their contents would decrease when copper is remelted.

Sample of artifacts made of "pure" copper from various sites of the Bronze Age and Early Iron Age in the Urals

Site / place of discovery	Period	Archaeological culture	*n*	m
Ustye I	LBA	S, P	38	25
Kulevchi III	LBA	P, A	23	20
Chebarkul III	LBA–FBA	A, ChM	12	8
Kamennyi Ambar	LBA–FBA	S, P, Sr, A, ChM	5	5
Malaya Berezovaya IV	LBA–FBA	A, ChM, SA	5	2
Bolshaya Berezovaya II	LBA–FBA	A, F, ChM, SA	4	1
Kyskaikul	LBA	A	3	2
Starokumlyakskoye	FBA	ChM	3	3
Kalachevo I	FBA	ChM	1	1
Morozovka, a.f.	FBA	ChM	1	1
Priuralye, a.f. (ingots)	LBA	Sr, A	10	10
Irtyashskoye I	EIA	I	8	8
Mount Lysaya	EIA	I	7	7
Mount Dumnaya	EIA	I	6	6
Itkulskoye I	EIA	I	4	4
Shatanov V	EIA	I	2	2
Shatanov I	EIA	I	3	1
Malyi Vishnevyi	EIA	I	1	1
Petrogrom	EIA	I	1	1
Priuralye, a.f.	EIA	Sm	12	9

Notes: *n* – number of examined artifacts, *m* – number of artifacts made of "pure" copper. LBA – Late Bronze Age, FBA – Final Bronze Age, EIA – Early Iron Age; a.f. – accidental finds.

S – Sintashta, P – Petrovka, A – Alakul, ChM – Cherkaskul-Mezhovo, Sr – Srubnaya, SA – Sargara-Alekseevka, F – Fedorovka, I – Itkul, Sm – Sarmatian.

Results and discussion

Trace elements in copper. Even the "chemically pure" copper sometimes contains various impurity elements in significant quantities, which may indicate the sources of ore, alloying impurities, fluxes, as well as smelting methods and techniques. Some of them dissolve in copper melt, integrating into the copper structure; others (e.g., Sn, As, and Pb) at high contents may form their own mineral phases and phases with copper. Some elements (Bi, S, Se, and Te) occur in copper as microinclusions of their own mineral phases, and this may lead to their increased concentrations if bulk methods of analyzing the chemical composition are applied.

Elements completely soluble in copper include Ni, Au, Rh, Pt, Pd, and Mn, which form a continuous series of solid solutions with copper due to a similar crystal structure (Drits, Bochvar, Guzei, 1979: 5). Highly soluble elements (limited solubility in copper, atomic % is indicated in parentheses) include Zn (38.3), Ga (20.3), Al (19.7), Co (13), Ge (11.4), In (10.9), Ti (9.6), Sn (9.1), Ir (8), As (6.8), Sb (5.8), Hg (5), Ag (4.9), P (3.4), Fe (2.94), and Cd (2.1) (Diagrammy…, 1996: Vol. 1, p. 37, 135, 265, 837; 1997; vol. 2, p. 15, 240, 243, 249, 256, 259, 263, 287, 306, 323, 337, 352). Slightly soluble elements include Cr (0.89), V (0.8), Tl (0.27), Pb (0.09), O (0.036), S (0.017), Se (0.009), Bi (0.006), and Te (0.004). Mo, Os, Re, Ru, and C have negligible solubility in copper (Ibid., 1996: Vol. 1, p. 636, 713; 1997; vol. 2, p. 112, 275, 285, 287, 288, 299, 301, 311, 331, 341, 345). Most of the elements of the latter two groups most often appear in copper alloys as their own mineral microinclusions, which can be determined by optical and scanning electron microscopy. For example, high oxygen concentration will be associated with oxide phases (cuprite, tenorite); S, Se, Te, with sulfides (chalcocite, covellite); Bi, with bismuthine or native forms;

Pb, with its own immiscible phase. The content of the lithophile elements in the copper alloy, which are almost insoluble in copper, is negligible and may result from the capture of slag silicate phases by the metal. The majority of impurity elements are often present in ancient copper in significantly smaller quantities than those that could be dissolved (In, Ga, Co, Cd, etc.), which is associated with the composition of ores and weakly reducing conditions of the metallurgical process.

The division of elements into groups that reflect the sources of copper or are associated with metallurgical processing technologies is another important issue. E. Pernicka (1999) included Au, Ag, Bi, Ir, Ni, Os, Pd, Pt, Rh, and Ru into the former group, and combined Al, B, Be, Ca, Cr, Cs, Fe, Ga, Ge, Hf, K, Li, Mg, Mn, Mo, Na, Nb, P, Rb, S, Sc, Si, Sr, Ta, Ti, Th, U, V, W, Y, Zr, and rare earth elements, which most often enter silicate slag during processing of copper ore, into the latter group. A number of elements, such as As, Cd, Co, In, Hg, Re, Sb, Se, Te, Tl, as well as Sn, Zn, and Pb at low contents, may reflect both source and technologies. However, in our opinion, in the type of analysis used, poorly soluble Os, Rh, Ru, and Re should be excluded from marker elements. Conversely, Ba, typical of cuprous sandstones of the Urals (Artemyev, Ankushev, 2019), Ga and Ge as possible rare impurities in sulfide ores, U appearing in metal from the Caucasus (Ryndina, Ravich, 2012), as well as Se and Te as important markers in oxidation zones of many copper deposits, should be added to marker elements. A special role is played by the buffer elements S and Fe. On the one hand, they reflect the technological aspect of copper processing, e.g. stages, temperatures, and redox conditions; on the other hand, they indicate the use of different types of ores, such as oxide-carbonate, sulfide chalcocine, or chalcopyrite varieties.

Fe, Co, Ni, Zn, As, Se, Ag, Sn, Sb, Te, Au, Pb, and Bi were selected as indicator elements for the metal of the Urals. Zn, which is contained in "pure" copper of ancient artifacts from the Urals in small quantities, as well as Os, Hg, and Cd absent from it, are not typical of local copper ores. They demonstrate high volatility in the metallurgical process resulting in negligible quantities, and may not reflect the geochemical type of the deposit used. The contents of rare earth elements, platinum group metals, as well as U, Mn, Tl, Cr, Mo, Ge, Ti, and V, in most of the studied samples were below the detection boundary.

Principal component analysis and sources of "pure" copper

Analysis of chemical composition of artifacts made of "pure" copper using the principal component method has shown a distribution into several main groups, often intersecting along one component, but separated along others (Fig. 2).

Unmixed groups. Au-Te-Bi. Three artifacts from the Bronze Age sites of the Trans-Urals belong to one of the main groups of "pure" copper not "contaminated" with a metal from other geological and genetic sources of ore. The same association, combined with others, occurred in at least four other groups (see below). Thus, together with them, it is the most common variation in the sample. The group is distinguished by low content of Fe (<0.015 wt%) and high content of Bi (up to 0.1 wt%), Au (up to 70 ppm), and Te (up to 40 ppm). In a binary diagram, it can often be distinguished by higher concentrations of Au and Te, and lower concentrations of Fe. The Au-Te-Bi association could have been associated with ores of porphyry-gold deposits of the East Uralian megazone (Seravkin, Minibaeva, Rodicheva, 2011), which contain epithermal vein copper mineralization with bismuthides and gold tellurides.

Fe-Co-Ni-As-Sb. This group, corresponding to metal from a single source, includes three Late Bronze Age artifacts from the Southern Trans-Urals. The probable sources of copper for the Fe-Co-Ni-As-Sb correlation association were copper ore deposits associated with ultrabasites (for example, Ishkininskoye (Geologiya…, 2009: 168)), which still cannot be assigned to a specific geological and genetic type (pyrite, porphyry, or skarn). With a larger sample, it may be possible to identify a specific source more accurately.

Se-Co-Fe. A small group of Late Bronze Age items from the Southern Trans-Urals (5 spec.) shows high concentration of iron (which also correlates with cobalt and nickel) and selenium. High content of Se is a relatively good indicator since it rarely occurs in copper deposits of the Urals. High concentrations of Se in slags (in chalcosine, covellite, and the associated reduced copper) have been found at the fortified settlements of Kamennyi Ambar and Konoplyanka I located near each other on the Karagaily-Ayat River, and at the Sarlybai settlement in Mugodzhar Hills (Artemyev, Ankushev, 2019; Ankushev et al., 2021). The probable source of copper for the artifacts of this

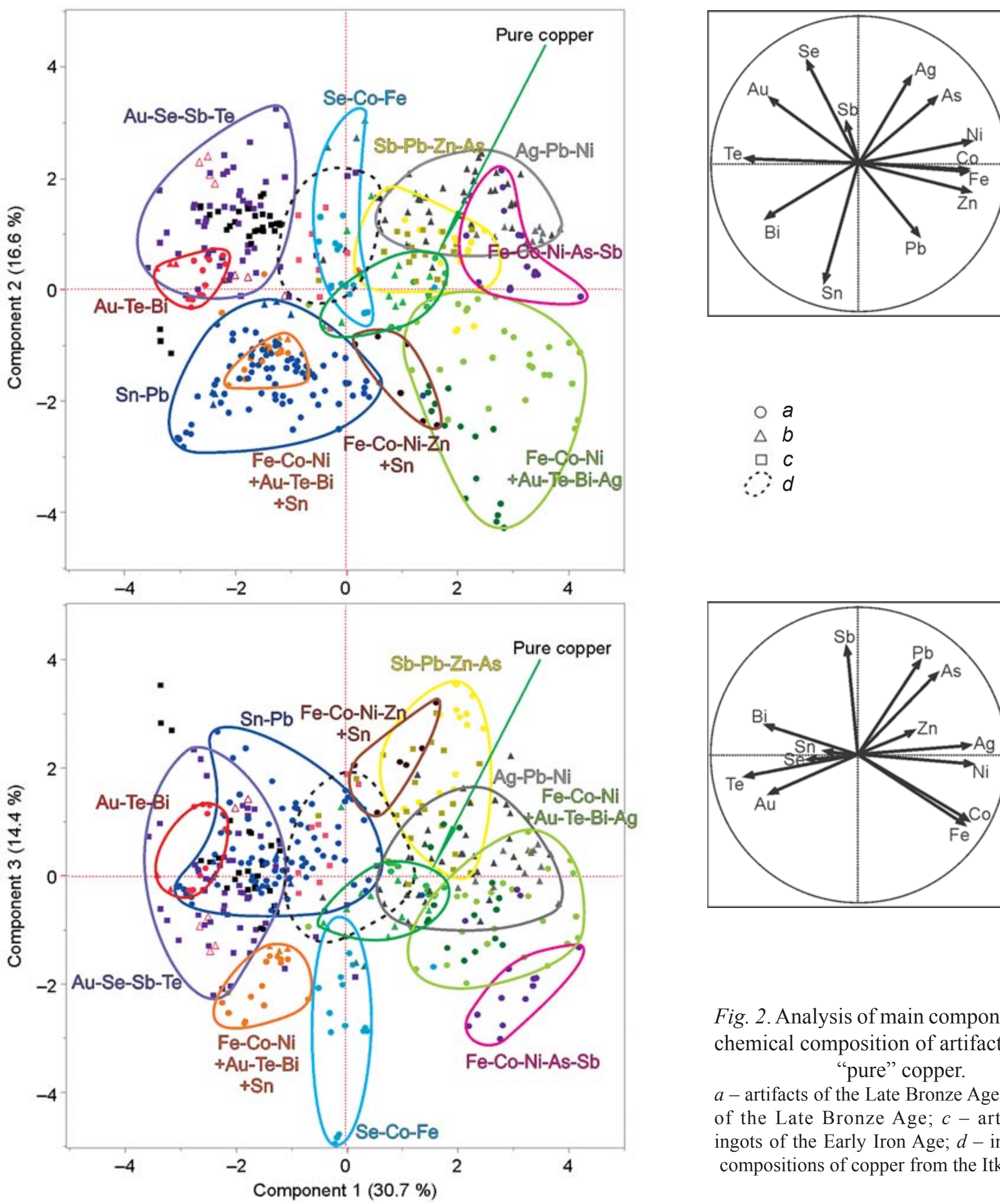

Fig. 2. Analysis of main components in the chemical composition of artifacts made of "pure" copper.
a – artifacts of the Late Bronze Age; *b* – ingots of the Late Bronze Age; *c* – artifacts and ingots of the Early Iron Age; *d* – intermediate compositions of copper from the Itkul culture.

group was the zone of secondary sulfide enrichment of the so far unidentified porphyry copper deposit in the volcanogenic strata of the East Uralian megazone. Possible candidates may be the Mikheevskoye porphyry copper deposit located near the fortified settlements or the Novonikolaevskoye copper-skarn deposit with the well-known mine of the Bronze Age (Ankusheva et al., 2022: 7–9).

Au-Se-Sb-Te. The source of copper ore—the Gumeshki copper-skarn deposit, which was actively mined in the Early Iron Age—has been reliably established for this correlation association (metal from the Itkul and Sarmatian cultures, and two ingots from Kamennyi Ambar). The metal contains high concentrations of Se and Te. This association occurs in slags and in copper artifacts from the sites of the Itkul culture, such as settlements on Mount Dumnaya (near the Gumeshki mine), Itkulsky I, Palatki I, and settlements on Lake Irtyash (Irtyashskoye I and Shatanov I). Two ingots from the settlement of Kamennyi Ambar and slags of the Mezhovo-Cherkaskul period at Levoberezhny (unpublished data) may testify to the earlier use of such metal in the Bronze Age.

This group also includes the majority of the accidentally discovered Sarmatian artifacts, which are kept in the Chesma Museum of Local History (Alaeva et al., 2023). This confirms the previous suggestion about the main role of the Itkul metallurgy in supplying the nomadic societies of the Southern Urals (Tairov, 2019: 198).

Ag-Pb-Ni. This reliably established association is typical of the copper ingots of the Urals (10 spec.), which were most often smelted from carbonate-sulfide nodules of cuprous sandstones, widespread in the Orenburg Region (Lurie, 1988: 29; Artemyev, Ankushev, 2019). Copper is characterized by significant purity; only S, Ag, and Pb are present in high concentrations, which is caused by numerous drops of sulfides with microinclusions of native silver and galena. The content of other trace elements is insignificant.

Sb-Pb-Zn-As. This correlation association may be related to stratiform deposits in sedimentary and volcanogenic-sedimentary strata. Artifacts with this association (3 spec.) were found at steppe and forest-steppe sites of the Late Bronze Age, and in the southern area of the Itkul culture. The source of copper ore has not been reliably established, but it could have been the Kolpakovskoye deposit, which has copper, polymetallic, and brown-iron ore occurrences in the Transuralian megazone (Snachev V.I., Snachev A.V., 2018). According to I.A. Talitskaya, numerous "Chud mines" were known in the valley of the Bagaryak River (1953: 291–294). These mines can be correlated with these ore occurrences. As opposed to stratiform deposits of the Urals, the metal is distinguished by low concentrations of Ag and higher concentrations of Pb, Zn, and Sb.

Mixed groups are represented by alloys obtained from smelting the copper of various origins or using the ore from several sources.

Sn-Pb. This is the largest group of the examined artifacts made of "pure" copper (23 spec.). These items are typical of the Bronze Age sites in the Southern Urals, belonging to the Petrovka, Alakul, Cherkaskul, and Mezhovo cultures, such as Kulevchi III (8 spec.), Ustye I (6 spec.), Starokumlyakskoye (3 spec.), Chebarkul III (2 spec.), Bolshaya Berezovaya (1 spec.), Malaya Berezovaya (2 spec.), and Kalachevo I (1 spec.). Copper shows the increased content of Sn and Pb (from 0.01 to 0.3 wt%) and their mutual correlation, which may reflect unintentional mixing of scrap of tin bronzes and copper while remelting metal items. Tin content is quite high for all known Uralian copper ores (in the metal obtained from them and in copper metallurgical slags, it usually does not exceed 10 ppm, and only in isolated cases, 50–80 ppm), but not enough to significantly affect the physical and mechanical properties of the finished metal and to indicate deliberate introduction of a tin-containing component.

The principal components of chemical composition of items in this group were analyzed, except for Sn and Pb, which had the greatest impact on clustering. As a result, four subgroups were identified. Three of them have parallels in copper items of other groups (Fig. 3). The Au-Te-Bi association, as mentioned above, corresponds to copper ores of epithermal porphyry-gold deposits of the East Uralian megazone. The Au-Ni-Co-As association is typical of orogenic gold deposits in ultrabasites of numerous suture zones of the Southern Urals, with the largest being the Main Uralian Fault zone. The Fe-As-Co-Ni association is related to the previous one, but differs by the absence of gold and increased iron content. It may reflect the use of ores from copper-iron-skarn deposits in ultrabasites, where magnetite concentrations are always high. The Fe-Zn-Ag association is not typical of copper ores of the Urals. It reflects the geochemical markers associated with admixture of tin bronzes imported from other regions (the Altai or Central Kazakhstan) (Berdenov, 2008).

Fe-Co-Ni-Zn + Sn. This group (two items from the Kulevchi III settlement) is distinguished by a mixture of copper associated with oxidation zone of copper pyrite deposits, with a small amount of tin-containing alloys. The presence of zinc may indicate the volcanogenic-sedimentary genesis of copper ores. The fact that the relative amount of zinc is higher than its content in the majority of other artifacts reveals that metal was not remelted too often, since zinc actively sublimes during the process. Copper pyrite deposits widely appear in the Urals structures. The best known Bronze Age mine in basaltoids was described at the Bakr-Uzyak deposit (Chernykh, 1970: 40).

Fe-Co-Ni + Au-Te-Bi + Sn. This group includes artifacts from the settlements of Chebarkul III (3 spec.) and Ustye I (3 spec.). Because of high tin content, their chemical compositions are similar to the Sn-Pb group, although include additional correlation associations (Fe-Co-Ni and Au-Te-Bi). The intersection of Fe-Co-Ni and Au-Te-Bi associations may indicate mixing of the metal from at least three sources associated with copper-skarn and porphyry-gold-copper deposits. This metal shows high Fe content (up to 0.9 wt%).

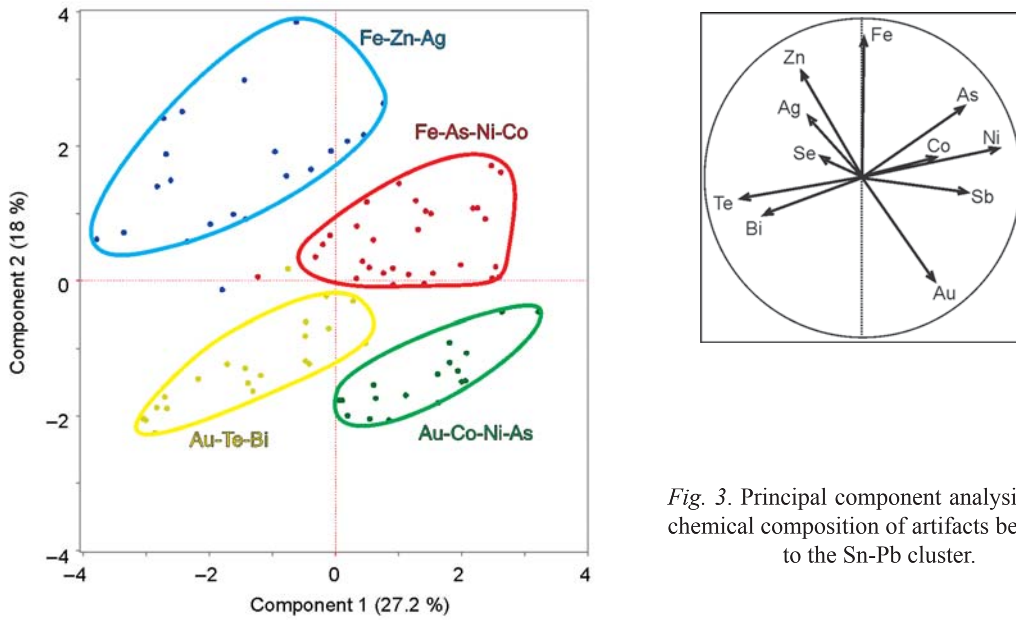

Fig. 3. Principal component analysis of the chemical composition of artifacts belonging to the Sn-Pb cluster.

Fe-Co-Ni + Au-Te-Bi-Ag. In terms of correlation series, this group is similar to the previous one. It includes 12 items from the settlements of Kulevchi III (2 spec.) and Ustye I (10 spec.). In the latter case, a large number of artifacts of this group at a single site with well-developed metal production (Drevneye Ustye…, 2013) shows the proximity of the copper ore sources that have such correlation series. As mentioned above, one of them may be associated with numerous porphyry-gold-copper epithermal deposits in volcanites and ultrabasites (beresite-listvenite formation).

Pure copper. The metal of this group has a relatively high purity as compared to the entire studied sample. The contents of trace elements do not exceed 0.01 wt%, while those of microtrace elements (Co, Zn, Sb, Se, Te, Au, Bi) do not exceed 0.001 wt%. This group includes ingots and artifacts from Late Bronze Age settlements in the steppe Trans-Urals (7 spec.). The copper purity most likely resulted from the use of sorted carbonate (azurite-malachite) ores, which have a smaller isomorphic capacity with respect to many impurity elements as opposed to silicate and sulfide components of ore charge. Such metal is difficult to correlate with specific ore sources.

Conclusions

Chemical composition of artifacts from the Bronze Age and Early Iron Age sites of the Urals, which belonged to the metallurgical group of "pure" copper, has geochemical markers allowing for the identification of several geological and genetic groups of deposits, i.e. sources of copper ore. We could identify seven main correlation associations: Au-Te-Bi, Fe-Co-Ni-Zn, Fe-Co-Ni-As-Sb, Se-Co-Fe, Au-Se-Te-Sb, Ag-Pb- Ni, and Zn-Pb-Sb-Ni.

Most of the Late Bronze Age artifacts under study contain a mixture of copper from deposits of different types. The largest sample is the Sn-Pb cluster indicating a mixture of local copper alloys and imported tin copper or bronze. Copper smelted from the ores of the Uralian deposits usually contains no more than 0.005 wt% of tin. In a number of the examined copper artifacts, it is higher, but still not enough to change the physical properties of the resulting metal (0.01–0.5 wt%), meaning that tin was not intentionally added. This likely reflects the fusion of copper and bronze scrap when smelting copper from different sources.

The As-Sb-Co-Ni-Au-Te-Bi correlation typical of arsenic bronzes of the Sintashta-Abashevo period is rare in our sample, and may indicate their fusion (in the form of scrap) with the higher-purity copper.

Two main sources of copper ore have been determined using the composition of "pure" copper of the Early Iron Age Itkul culture. One source may be correlated with the Gumeshki deposit, while the other source has not yet been established. The use of Gumeshki ores is also confirmed by inclusions of garnet (andradite) in copper slags discovered on

Mount Dumnaya and at the Itkulskiy I settlement (Stepanov et al., 2023). Chemical composition of the Itkul copper corresponds to that of the metal found among the Sarmatian nomadic communities of the Southern Urals, and finds geochemical parallels in the evidence from the sites of the Late Bronze Age.

We can see the prospects for further studies in expanding the sample accompanied by creation of a database linked to geographical locations of the examined sites and the corresponding copper artifacts, which would make it possible to predict location of sources of copper ore in the deposits of various geological and genetic types more accurately. One of the methodological conclusions is the expected low effectiveness of searching for possible sources of copper ores using lead isotopes, caused by a large share of artifacts made of smelted scrap copper originating from a variety of ore sources, as demonstrated in our study. High lead concentrations particularly severely distort the signal from a copper ore source.

Acknowledgments

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