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Trace Elements of Cu-(Fe)-Sulphide Inclusions in Bronze Age Copper Slags from South Urals and Kazakhstan: Ore Sources and Alloying Additions

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Abstract

In the paper, the results of an investigation into trace elements found in slag sulphides from 14 archaeological Bronze Age settlements of the Cis-Urals, Trans-Urals and North and Central Kazakhstan are presented. The study used Cu-(Fe)-sulphides as indicator minerals. Cu-(Fe)-S minerals in slags are primarily represented by covellite and chalcocite, as well as by rarer bornite and single chalcopyrite grains. Slag sulphides formed relic clasts and neogenic droplets of different shapes and sizes. Supergenic ores in the Bronze Age in Urals and Kazakhstan played a significant role in the mineralogical raw material base. In sulphides, the main indicator elements Fe, Co, Ni, As, Se, Te, Sb, Ag, Pb, and Bi are important markers of copper deposit types. Sulphides from olivine Cr-rich spinel containing slags of Ustye, Turganik, and Kuzminkovskoe 2 are characterised by As-Co-Ni assemblages and confined to copper deposits in ultramafic rocks. Olivine sulphide-containing slags from Kamenny Ambar, Konoplyanka and Sarlybay 3 are characterised by Co-Se-Te assemblage and confined to mafic rocks. Glassy sulphide-containing slags from Katzbakh 6, Turganik, Ordynsky Ovrag, Ivanovskoe, Tokskoe, Bulanovskoe 2, Pokrovskoe, Rodnikovoe, and Taldysay are characterised by Ag-Pb-(Ba)-(Bi) assemblage and confined to cupriferous sandstone deposits. High As, Sb, Sn and Ba contents found in slags can be seen as indicators of alloying or flux components in primary copper smelting. These include samples from Ustye, Katzbakh 6, Rodnikovoe, and Taldysay sites, where high Ba and As slag contents are identified. The compilation of a database with a broad sample of sulphide compositions from Bronze Age slags and mines in the Urals and Kazakhstan will permit the further identification of ore types and raw materials associated with a particular deposit.

Keywords: copper slag; sulphide; chalcocite; covellite; bornite; LA-ICP-MS; South Ural; Kazakhstan; Bronze Age

1. Introduction

During much of the Bronze Age, the South Urals, including the southern tip (Mugodzhary) and Central Kazakhstan, was the most significant mining and metallurgical regions of Central Eurasia [1]. This region, which comprises over 1 million square kilometres containing numerous copper deposits, is characterised by forest, forest-steppe, steppe and semi-arid zones suitable for pastoralism. Since at least 5000 BCE, several successive cultural and historical predominantly pastoral societies occupying this territory were consistently involved in copper ore extraction, smelting and copper production. The first evidence of metal working in this region is referred as the pastoral societies of the Early Yamna culture of Volga Region and Cis-Urals [2]. Although these cultures initially used metal imported from the Caucasus, from 4000 BCE onwards, locally produced copper started to become widespread [2,3]. Possibly as a consequence of their nomadic way of life and small number of known settlements, there is little evidence of the use of Cis-Urals copper sandstones by the Yamna culture between the middle of the fourth and the beginning of the third millennia BCE. However, it can be assumed that all pure copper of the Volga-Ural region is associated with the Cis-Ural copper deposits [2]. The earliest

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information about the smelting of metals from Uralian ores is from slags in cultural layers of the Turganik settlement dated to 3900 BCE [4,5]. In the Trans-Urals, the first metal-bearing communities were the Eneolithic Kysykul-Surtandin tribes who apparently used a native copper [6]. In this region, the heyday of metallurgy occurring during the third millennium BCE is associated with the transition of the Abashevo communities through the Urals Mountain and formation of the Sintashta culture in the forest-steppe zone of Trans-Urals [7]. The consistent transformation of the Sintashta culture into the Srubna-Alakul society resulted in the expansion of metallurgical activity to the north, south and east. By the middle of the second millennium BCE, the boundary of the metallurgical area has been expanded up to the Middle Urals in the north (Gumeshevo mines) and to the south into Mugodzhary (Mugodzhary mines) [8,9]. Some of them reached the Central Kazakhstan to exploit the cupriferous sandstone deposits [9]. At the end of 2000 BCE, the Alakul community is slowly disintegrated and formed numerous local pastoral cultural groups throughout the region identified as Final Bronze cultures 1300–800 BCE (Chercascul, Sargary-Alekseevo, Begazy-Dandybai, etc.) [10-12, etc.].

In addition to copper artifacts, the main evidence of ancient metallurgical activity consists in discoveries of ingots, moulds and metallurgical slag fragments in cultural layers [13]. Metallurgical slags, which mark the environment and techniques of copper production, are among the most informative artifacts for clarifying production technologies. They are used to identify raw material sources used for copper smelting, fluxes and alloying additions [14]. Slags contain numerous relicts and neogenic inclusions, which can indicate the copper ore sources used for melting. In Uralian metallurgical slags, the main indicator minerals are Cr-rich spinels and sulphides [15]. In previous research, Cr-rich spinels in copper slags were used as indicators for copper ore sources in the Urals [16]. X-Ray spectra and SEM-EDS analyses of sulphide inclusions failed to yield any significant results until they were replaced by high-precision mass-spectrometric methods. Laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) has found wide application in the study of sulphides in geological samples [17,18, etc]. Recently, LA-ICP-MS analysis has also become widespread in the archaeological studies for determining trace elements in small samples [19,20, etc].

Relict sulphides and sulphide droplets have been found in numerous ancient Eurasian slags. Rich bornite-chalcocite-covellite droplets were identified in several copper slag types in the LBA Trentino archaeological site in North Italy [21,22]. Relict fragments of chalcopyrite and secondary copper sulphides have also been examined in North Italy [23]. Pyrrhotite, sphalerite, galena and Cu-(Fe)-S minerals have been examined in medieval slags from the Czech Republic [24]. Early Bronze Age (EBA) relict bornite, chalcocite and chalcopyrite fragments from slags of Seriphos [25] and Kea [26] islands in Greece. Chalcopyrite, bornite, digenite and chalcocite have been the subject of a study, while covellite droplets are widespread in the EBA copper slags of Austrian Tirol [27]. Cu-(Fe)-S minerals are widely represented in Bronze Age slags from the South Caucasus [28]. The mineralogical compositions of both LBA copper metallurgical slags and bronzes are known in Iberia (Portugal) [29]. Cu-sulphide microinclusions have been widely studied in ancient copper and bronzes [30-36]. Fe-sulphides (troilite, pyrrhotite) are known in non-metallurgical mortuary slags of Taksay 1 kurgan (Kazakhstan) [37].

In Bronze Age slags of the South Urals, we found relict inclusions and neogenic Cu-(Fe)-sulphides [5], represented by covellite, chalcocite and bornite. We surmised that slags of Cu-(Fe)-sulphide composition can be used to indicate the type of copper deposits and clarify the raw material sources. The secondary copper sulphides often tracing geochemical markers of deposits where they had been formed. As previously shown, the genetic types of copper deposits can be distinguished with reasonable certainty according to trace element contents in secondary Cu-sulphides [38]. In the supergenic zone, several elements can be moved from primary chalcopyrite having its own trace elements into secondary chalcocite and covellite [39]. It has been shown that covellite is enriched with numerous trace elements of primary chalcopyrite during weathering processes [40]. Then, as a

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consequence of ore melting during metal production, marker trace elements are moved into sulphide and copper droplets and enriched with alloying additions and fluxes. Thus, unlike the finished product metal, which may be refined or derived during the fusion of several sources, the composition of inclusions in slags is more informative than in the composition of copper artifacts because it demonstrates the primary geochemical ore markers.

The paper is aimed at providing indicator trace elements in Cu-(Fe)-sulphide droplets and relic fragments contained in Bronze Age metallurgical slags at South Urals and Kazakhstan. As far as we are aware, no similar investigation aimed at determining indicator trace elements in slag sulphides has yet been carried out.

2. Materials and methods

The slags from archaeological sites were collected by S.V. Bogdanov and V.V. Tkachev from the Institute of the Steppe UB RAS (Orenburg, Russia), L.N. Koryakova and S.V. Sharapova from the Institute of History and Archaeology UB RAS (Ekaterinburg, Russia), N.B. Vinogradov, I.P. Alaeva, P.S. Medvedeva from the Laboratory of archaeological researches of the South-Urals State Humanities-Pedagogical University (Chelyabinsk, Russia), N.L. Morgunova and I.A. Faizullin from the Orenburg State Pedagogical University (Orenburg, Russia), I.V. Chechushkov from Pittsburg University (Pittsburg, USA), A.S. Ermolaeva from the Institute of Archaeology named after A. Kh. Margulan (Almaty, Kazakhstan).

Two hundred polished sections were petrographically examined under reflected light using Axiolab Carl Zeiss and Olympus BX51 optical microscopes. Numerous slag types from the Urals and Kazakhstan were investigated. The main morphological and mineralogical types of sulphide inclusions were identified.

The trace elements in sulphides were studied using a New Wave Research UP-213 laser ablation system coupled with an Agilent 7700x (Agilent Technologies, USA) plasma mass spectrometer (operator D.A. Artemyev). The measurements were carried out with an Nd: YAG UV source, frequency quadrupled (wavelength 213 nm) with fluence settings of 2.5–4.5 J/cm^2, helium cell carrier gas and a flow rate of 0.6–0.7 L/min. Mass spectrometer settings were as follows: RF Power – 1550 W; carrier gas – Ar; flow rate – 0.95–1.05 L/min; plasma gas flow (Ar) – 15 L/min; auxiliary gas flow (Ar) – 0.9 L/min. Each analysis was performed with a laser spot size of 30–100µm diameter at a frequency of 10 Hz. The analysis time for each sample was 75–90 s, comprising a 30 s measurement of the background and a 45–60 s analysis. A pre-ablation of 3–4 s was carried out prior to each analysis; a 20 s washout took place between analyses. Production of molecular oxide species (i.e.^{232}Th^{16}O/^{232} Th) and doubly-charged ion species (i.e. ^{140}Ce^{++}/^{140}Ce^{+}) was maintained at levels below 0.2 %. The element contents were calibrated against reference materials NIST SRM-612, USGS GSD-1g, USGS MASS-1 using ^{65}Cu, as the internal standard. All mass fractions for NIST SRM-612, USGS GSD-1g and USGS MASS-1 were taken from the GeoReM base preferred values. The calibration standard was analysed every 10–18 spots to account for the instrument drift. Data processing was carried out using the Iolite software package [41].

Elements were determined and calculated by USGS MASS-1 [42] for each spot: ^{32}S, ^{33}S, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{69}Ga, ^{72}Ge, ^{75}As, ^{77}Se, ^{95}Mo, ^{107}Ag, ^{111}Cd, ^{115}In, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{197}Au, ^{202}Hg, ^{205}Tl, ^{208}Pb, ^{209}Bi. The dwell time was 10 ms. Concentrations of ^{115}In, ^{125}Te, ^{197}Au, ^{205}Tl, ^{209}Bi are "informational" rather than as certified in USGS MASS-1. Due to polyatomic interferences with ^{40}Ar+^{32}S and ^{56}Fe+^{16}O, ^{72}Ge values are conditional. Quantification of ^{65}Cu was performed using conventional approaches [43], with normalisation to 100 % total of components as an internal reference. Additionally, measured values of ^{7}Li, ^{23}Na, ^{25}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{39}K, ^{43}Ca, ^{45}Sc, ^{49}Ti, ^{85}Rb, ^{88}Sr, ^{133}Cs, ^{137}Ba, ^{181}Ta, ^{182}W, ^{232}Th were used, while ^{238}U was calculated by USGS GSD-1g.

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3. Archaeological sites

A brief overview of metallurgical cultures in the South Urals, where slags and their types were discovered, is presented in [5]. Among the wide range of metallurgical copper slag samples at South Urals and Kazakhstan, we distinguished 4 types occurring in South Urals [5]. However, copper sulphides in slags are identified in just two of these: sulphide-containing olivine and sulphide-containing glassy types. In other types, sulphides are rare submicron allocations. The only exceptions are Cr-rich spinel containing olivine slags from the Turganik and Kuzminkovskoe 2 settlements and pyroxene types from Rodnikovoe settlement, which contained copper sulphides with sizes up to 500 µm.

The objects are 14 Bronze Age settlements of South Urals and Kazakhstan (Figure 1, Table 1). Here we will briefly examine the main archaeological site with sulphide-containing slags.

The Kamenny Ambar settlement is situated in the Kartaly area (Chelyabinsk region) on the Karagayly-Ayat River left bank. The researches were carried out in 2005–2013 [44]. During the excavations, the majority of metallurgical slag fragments, copper ores, metallic ingots and copper artifacts were discovered. The history of this object includes two chronological periods – Sintashta-Petrovka and Alakul. Fragments of ores represented by malachite, malachite-azurite, tourmaline-malachite and magnetite-malachite with secondary sulphide types were found at the settlement.

The Konoplyanka settlement was discovered by I.M. Batanina in the course of aerial photo-interpretation. The site is situated on the Karagayly-Ayat River (Chelyabinsk region). During excavation, it turned out that the cultural layer had been damaged over the course of a long period of ploughing. Konoplyanka is the multi-layer archaeological site with carbon-dating (1920–1745 BCE) and dated (to ceramics) by Sintashta-Petrovka period. On the site, the fragments of metallurgical slags and copper splashes are detected [45].

The Ustye settlement is situated 30 km north from the town of Kartaly (Chelyabinsk region), in the northern part of the steppe zone. The site was discovered by N.B. Vinogradov in 1983. The site was constantly occupied from around the end of the Middle and beginning of the Late Bronze Age (LBA onwards). The majority of artifacts found here are related to metallurgy and copper manufacturing; fragments of metallurgical furnaces, copper ores, slags, copper droplets, ingots and various artifacts [46].

The Katzbach 6 settlement is located in the valley of the Zingeyka River, a left tributary of the Ural River (Chelyabinsk region). The site was opened by A.I. Gutkov in 1989. In 2014–2015, an archaeological excavation headed by I.V. Chechushkov and I.P. Alaeva was carried out using pits to examine the site's cultural layers. Metallurgical slags were exposed at the layers contained ceramic vessel fragments of Alakul cultures and dated to the LBA.

The Ordynsky Ovrag archaeological site formed a group of numerous historical pits with rock dumps. These are located 3 km south-east from Maksimovsky farm (Orenburg region) at the centre of Kargaly group of mines. In 2016, S.V. Bogdanov recovered the metallurgical slag fragments near the sunken mine of the Bronze Age. The dating of samples is difficult in the absence of linking to the cultural layer. We are assumed found samples have Srubna age.

The Turganik settlement is situated at the confluence of the Turganik and Tok Rivers. The site was recovered by N.L. Morgunova in 1982 and 2014–2015 [4]. The object has several cultural layers of the Palaeolithic, Eneolithic and Early Bronze Ages. The basic cultural layer, which is dated to 4000 BCE, is represented by ancient ceramics, ore fragments, metallurgical slags, copper ingots, melting pots, as well as traces of metallurgical furnaces and hammers [4]. Additional traces of the late, short-term occupation of the Srubna culture are recorded in ceramics finds.

The Tokskoe settlement is situated 6 km south of the village of Ivanovka (Orenburg region) on the right bank of the Tok River. Excavations were led by N.L. Morgunova in 1979 and by O.I.

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Porokhova in 1990. Between them, these processes uncovered more than 80 square metres of the site. The ceramic artifacts, which are dated to the Srubna culture, also features rare Alakul cultural peculiarities. A large metallurgical 4×5.4 m construction, constructed with limestone blocks and contained numerous copper slags, was also recovered [47].

The Ivanovskoe settlement is located 5 km south of Ivanovka village along the Tok River terrace (Orenburg region). The site was excavated by the Orenburg archaeological expedition supervised by N.L. Morgunova and O.I. Porokhova between 1978 and 1982. In the Ivanovka area, Neolithic, Eneolithic and LBA cultural layers were revealed. Evidence of metallurgical processes was recorded in the most recent layers, i.e. slags and casting moulds of the Srubna culture [47].

The Bulanoskoye 2 settlement is situated near Bulanovo village (Orenburg region) and confined to the inundated terrace on the right bank of the Salmysh River. About 650 square metres of the site have been excavated since 1998 led by N.L. Morgunova and M.V. Khalyapin. Here, were ceramics were recovered and dated to the cultural layers of the Abashevo and Srubna cultures along with numerous metallurgical slag fragments [48].

The Kuzminkovskoe 2 settlement is situated on the right bank of the Irtek River 2.5 km SE from the village of Kuzminka (Orenburg region). In 1986 it was investigated by the Orenburg archaeological expedition led by O.I. Porokhova [49]. The monument is dated by the LBA due to a Srubna culture ceramics. Here, the numerous copper slag fragments have been discovered.

The Pokrovskoe settlement is situated on the Samara River left side terrace in 3 km NW from the village of Pokrovka. During the excavation led by O.I. Porokhova in 1984 [47], a large number of Srubna ceramics and metallurgical slag fragments were discovered.

The Rodnikovoe settlement is located 5 km west from Chesnokovka village (Orenburg region) on a low-lying inundated terrace on the right bank of the Ural River. The site was examined from 1982 to 1983 by the Orenburg archaeological expedition supervised by N.L. Morgunova and O.I. Porokhova [47]. Among the evidence of metallurgical processes recovered from the site was the following: copper slags, copper ore fragments, and burnt ceramics fragments with slags. It seems that special places were used to manufacture the metallic items found at the site [50]. Two chronological layers – early with Srubna type ceramics and later – Final Bronze cultures (Sargary-Alekseevo and Chercaskul) can be distinguished.

The Sarlybay 3 settlement, which is situated 34 km SE from the village of Berchogur on the banks of the Sarlybay River (Mugodzhary, North Kazakhstan), was discovered in 2013 by V.V. Tkachev during archaeological prospecting and excavated by A.V. Fomichev in 2014–2015. During archaeological excavations, ceramic fragments pertaining the Alakul culture were discovered. Artifacts of the monuments include fragments of copper metallurgical slags and ironstones with thin malachite veins and crusts [51].

The Taldysay settlement, which is situated in the eponymous tract at the confluence of the Ulken Zhezdy and Bala Zhezdy Rivers (Ulytau, Central Kazakhstan), was discovered in 1990. The first excavations were provided by Zh. Kurmankulov in 1994. From 1998 to 2018, the excavation of the settlement was led by A.S. Ermolaeva. Here, housing and production complexes with furnace fragments were found out. Copper smelting workshops are dated by the LBA from Early Alakul up to the Final Bronze cultures (Begazy-Dandybai). Fragments of carbonate, oxidised and sulphide ores of cupriferous sandstones from the Jezkazgan area were also found at the site [52].

4. Results

4.1.Mineralogy of slag Cu-(Fe)-sulphides

Copper sulphides in investigated Uralian and Kazakhstan slags are presented by the mixture of covellite (CuS) – chalcocite (Cu_2S) (Table 2). At the present time, this series includes 8 IMA registered mineral species: covellite (66.5 % Cu) – yarrowite (69 % Cu) – spionkopite (73.4 % Cu) –

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geerite (76 % Cu) – anilite (77.6 % Cu) – digenite (78.1 % Cu) – djurleite (79.3 % Cu) – chalcocite (79.9 % Cu). However, it was not possible to diagnose any mineral in the mixture on the basis of chemical composition. Hereinafter, when referring to extreme mineral members, we assume the presence of intermediate species.

On several archaeological settlements, bornite and products of its alteration are identified (Cu_5FeS_4, 63.3 % Cu). A significant quantity of sulphides is presented by neogenic non-stoichiometric species with varying Fe contents. Sulphide droplets and grain sizes range from between several microns to inclusions measured in millimetres. Chalcopyrite ($CuFeS_2$ 34.6 % Cu) and other copper sulphides are completely absent from the slags. An isolated grain of altered chalcopyrite is found in a slag from Taldysay.

According to morphological peculiarities, sulphide inclusions are divided into relict clast and melt droplets. Copper sulphide relicts formed isolated angular clasts and grains 3–4 mm up size (Figure 2a). Relict clasts are found in slags from Kamenny Ambar, Konoplyanka, Katzbakh 6, Turganik, Tokskoe, Ivanovskoe and Taldysay settlements. Melt inclusions are subdivided into primary-melt, which melted without major chemical and mineral composition transformation (Figure 2b), and neogenic inclusions (Figure 2c) which were separated from sulphide-silicate melt with new components absorption.

Covellite was observed to form relict fragments of several millimetres in size and melted grains or rare neogenic droplets (Figure 2d). The colour of covellite in fragments and smelted grains is bright blue up to dark-blue, while neogenic droplets are often light-blue colour in reflected light. As copper sulphide it prevails in slags from Trans-Urals settlements (Kamenny Ambar, Konoplyanka, Katzbakh 6 and Rodnikovoe). In relict and melted grains covellite is often fractured, with copper oxide and carbonate and other supergenic copper mineral formations in the fractures. Neogenic aggregates formed rounded droplets with massive structures (Figure 2e).

Chalcocite prevails among the neogenic droplets and is widespread in the Cis-Urals where it is strongly dominated on several settlements (Turganik, Ivanovskoe, Pokrovskoe, Rodnikovoe, Kuzminkovskoe 2). Chalcocite formed in neogenic droplets is yellow-grey coloured, sometimes with a blue tinge in reflected light. Chalcocite formed small 1 μm inclusions and large 3–5 mm droplets. Rounded, crescent and ring-shaped droplets are dominated and rarely amoeba-like aggregates. Ring-shaped and crescent shapes were often seen to frame metallic copper droplets (Figure 2d). A wide range of covellite-chalcocite mixtures occurs in the Cis-Urals (Tokskoe, Bulanovskoe 2) and Kazakhstan (Sarlybay and Taldysay) settlements (Figure 2f).

The rarely-found bornite, which has a light pink colour in reflected light (Figure 2g), can serve as an indicator mineral. Bornite typically forms melt relic grains size up 1 mm. It found out only in Katzbakh 6, Ivanovskoe, Tokskoe, Turganik and Taldysay settlements. Chalcopyrite occurs only in isolated cases. The only chalcopyrite grain is found out in samples from Taldysay (Figure 2h). It is formed rounded melted fragments which are secondary altered up to covellite. Additionally, many isolated droplets of metallic copper and bronzes were found in samples having sizes ranging from several microns up to 5 mm. However, the present paper does not deal with composition of metal droplets.

4.2.Trace elements of slag Cu-(Fe)-sulphides

Copper sulphides vary widely in trace element contents. They contain a wide range of chalcophile, siderophile and noble metal elements. In this paper, we determine the distribution of numerous elements, focusing on the marker elements that indicate ore source genesis, fluxes and technological features of copper melting.

Fe is a widespread minor element in copper sulphide. Moreover, in addition to copper and iron minerals (bornite and chalcopyrite) and their pyrogenic transformed species, it comprises a mixture

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in the covellite-chalcocite mineral group. Higher Fe contents are determined in Tran-Urals sulphides (Figure 3, Table 3). Here, the average Fe contents reached 1–3 wt. % (up to 22 wt. % in some cases) in sulphides of samples in the Kamenny Ambar, Konoplyanka and Katzbakh 6 settlements and slags from Kazakhstan (Sarlybay 3, Taldysay). In Cis-Urals slags, Fe contents are lower, comprising 0.1–0.5 wt. % on average.

As is an important element used to alloy copper in Eurasia [1]. **As** in natural objects is confined to sulphide ores of different genesis located in ultramafic rocks. According to As contents in sulphides (Figure 3, Table 3), 4 slag groups are divided. The first low-arsenic type with As contents less than 30 ppm is typical for the Alakul culture slags from Trans-Urals settlements (Kamenny Ambar, Konoplyanka and Katzbakh 6) for which the ore source is not determined. Such contents are usual for several Cis-Urals settlements (Tokskoe, Rodnikovoe) for which the local raw material of cupriferous sandstones is supposed. The bulk of slag sulphides from Cis-Urals settlements is confined to the second group and contain As up to 20–200 ppm. Sarlybay 3 slag sulphides can also be added for which the ore source is Sarlybay VMS deposit in basalts.

According to As contents of 300–5000 ppm, the third sulphide group relates to the objects connected confined to ultramafic rocks. Due to ores application from these deposits, arsenic-copper alloys were obtained naturally. But As is not enough for arsenic bronzes production. These include the Early Yamna culture samples from Turganik settlements and Srubna slags from Pokrovskoe and Rodnikovoe settlements. The fourth group with contents more than 0.5 % is special alloying addition arsenic in copper. Typical for LBA slags. Copper arsenides occur in a view of inclusions in copper droplets often. These include samples from the Ustye and Taldysay.

Se replaces sulphur in minerals. In natural objects, Se is confined to the oxidised zone of VMS deposits in basalt-rhyolite and ultramafic complexes. 3 main groups are subdivided according to their Se content. Low-selenium sulphides having less than 100 ppm of Se are typical for the Ustye and Katzbakh 6 sites, as well as for the Srubna culture slags from the Pokrovskoe, Turganik and Ordynsky Ovrag sites (Figure 3, Table 3). An Se content of 100–1000 ppm is typical for glassy slags from cupriferous sandstones of Tokskoe, Ivanovskoe, Bulanovskoe 2, Kuzminkovskoe 2, Rodnikovoe and Taldysay. Slags with high Se content (more than 1000 up to 7000 ppm) are found at the Kamenny Ambar, Konoplyanka and Sarlybay 3 sites.

Sulphur can also be replaced by **Sb** in sulphides, where it can occur as microinclusions. Two main typological subdivisions can be distinguished according to Sb content: low-antimony (<10 ppm) and high-antimony with Sb contents up to 650 ppm. High Sb contents are typical for doped slags and reflect the input of alloying additions that is confirmed by correlation with As, Co and Ni. These include samples from Ustye, Rodnikovoe and Taldysay (Figure 3, Table 3).

Co and **Ni** are widespread in sulphides of slags and subdivided into 3 groups. According to geochemical peculiarities these elements are both similar, e.g. in ultramafic rocks with high Co and Ni contents, and differ significantly, e.g. high Co and absent Ni in VMS deposits hosted in basalts. The majority of sulphides in slags from Cis-Urals settlements (Ordynsky Ovrag, glassy slags from Turganik, Tokskoe, Ivanovskoe, Bulanovskoe 2 and Rodnikovoe with possible sources from cupriferous sandstones, as well as Katzbakh 6) are related to low cobalt and low nickel group with less than 20 ppm content (Figure 3, Table 3). Sulphides from Kamenny Ambar, Konoplyanka and Sarlybay are related to high-cobalt (more than 20 ppm) and low-nickel groups. Natural slags from Ustye, Rodnikovoe, Taldysay, as well as those artificially-doped by As are related to high-cobalt and high-nickel sulphide groups; this also applies to Cr-rich spinel-containing olivine Turganik slags.

Despite ranging a widely in terms of its contribution to the contents of sulphides, **Ag** can also serve as an indicator mineral. The studied slags are subdivided into 2 main types in terms of their Ag content. Low-silver sulphides having an Ag content of less than 30 ppm are typical for the Kamenny Ambar, Konoplyanka and Sarlybay 3 sites. High-silver type slags with 50–500 ppm Ag content are

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typical for all Cis-Urals objects, as well as occurring at the Ustye, Katzbakh 6 and Taldysay settlements. In several samples, e.g. Kuzminkovskoe 2 and Rodnikovoe, the Ag content can exceed the second type to reach 0.4 % (Figure 3, Table 3).

Ba can form neogenic sulphides and barite inclusions. A low Ba content (<50 ppm) is typical for sulphides of slags from the Cis-Urals and Kazakhstan (Figure 3, Table 3). Slags having a high Ba content ranging from 50 up to 1500 ppm are typical for Cis-Urals sites. Katzbakh 6 (Trans-Urals) and Rodnikovoe (Cis-Urals) settlements are characterised slags with a Ba content exceeding 0.5 %, which probably indicates the addition of barite fluxes in charges.

The lowest values of **Pb** not exceeding 10 ppm, are typical for Kamenny Ambar, Konoplyanka, Sarlybay 3 slags, as well as the Cr-rich spinel containing olivine slags at the Turganik site. A slightly higher Pb (10–100 ppm) content is found in sulphides from Ustye, Katzbakh 6, glassy Turganik slags, Ivanovskoe, Bulanovskoe 2, Kuzminkovskoe 2, Pokrovskoe, and Rodnikovoe settlements. High Pb amounts (100–1000 ppm) are in slags from Ordynsky Ovrag, Tokskoe and pyroxene slags of Rodnikovoe. Extremely high values (more than 0.1 % Pb) are found in samples from the Taldysay settlement where numerous findings of galena and metallic Pb ingots were also discovered. A similar pattern is expressed in terms of **Bi** although its contents are far smaller.

Zn is present in small amounts in slag sulphides ranging between 4 and 40 ppm. However, the contents are widely varied within the same object to reach 0.1–0.2 % at Kamenny Ambar, Ordynsky Ovrag, Pokrovskoe and Taldysay settlements. Due to the heterogeneity of content, Zn distribution cannot serve as an indicator of raw material sources.

Sn in sulphides of slags is significant except for Taldysay samples. The majority of Sn contents in Cu-(Fe)-S ranges from a few tens of degree ppm up to the first ppm. Only a few values reach hundreds of ppm at Kamenny Ambar, Ustye, Sarlybay 3 and Taldysay settlements. At Taldysay, Sn rarely contributes as much as 0.45 %.

Mo contents in slags are not suitable as indicators, since varying widely up to hundreds of ppm. The lowest values of a few ppm are typical for samples from Kazakhstan and olivine slags from Turganik. The highest concentrations contained in slag sulphides from the Tokskoe and Rodnikovoe settlements reached up to 600 ppm.

Although **Cr** generally appears in slag sulphides at values much smaller than the limit of detection, significant amounts are found in the Turganik olivine type. A few values within the a few tens of ppm are obtained in sulphides from Cis-Urals slags.

U is also undetected in any significant amounts or regularities. The elevated contents are in slags of the second type from the Rodnikovoe and Ivanovskoe settlements.

Other siderophile (**Mn, V)** and chalcophile **(Ga, Ge, Kd, In, Au,** and **Hg)** contents, as well as the majority of lithophile elements, are minor and consequently cannot serve as indicators.

5. Discussion

The mineralogical and geochemical criteria of sulphide inclusions in Bronze Age slags from the Urals and Kazakhstan are quite diverse. The mineral composition of inclusions can only partially function as an indicator of raw material sources for Bronze Age metallurgists. It has long been believed that in the Bronze Age the main ore sources were oxidised azurite-malachite ore for the Urals [53]. This apparent fact was confirmed by numerous experimental smelting using carbonate ores from the Trans-Urals and Cis-Urals [54, 55]. However, the significant quantity of sulphide inclusions found in several slag types of the Urals and Kazakhstan indicates that the usage of sulphide ores was common in some cases. It is likely that, at the end of the LBA, due to poor quality of the raw malachite ore materials, ancient metallurgists were testing a new ore type. Due to the use of secondary Cu-(Fe)-S minerals, the copper content for the unit of ore volume higher than for carbonate ores increased the number of value-added products. This fact greatly extended the raw-material base for the local

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population. This is associated with a shift in the proximity of raw material sources and the increased sizes of melted ingots [56].

According to our data, covellite-chalcocite ores with rare bornite inclusions were predominantly used in Urals. Secondary copper sulphides are widespread in the supergene enrichment zone of many copper deposits of the Urals and Kazakhstan – VMS, skarn and quarts-sulphide types [57]. In Cis-Urals, sulphides were used particularly intensive where covellite-chalcocite concretions occur in cupriferous sandstone layers [58]. The diameter of concretions reaches 5–8 cm size. Probably, due to the creation of a smelting technology, concretion ores of cupriferous sandstones become the main ore sources of the Srubna culture. As a result, the majority of the LBA in Cis-Urals slags contains sulphide inclusions. In Trans-Urals, the usage of sulphides was not so common because of the deepest ore level and absence of large sulphide mineralisation in a near-surface environment. Accordingly, only a few settlements contain large fragments or sulphide droplets typical for the Alakul and Final Bronze Age cultures

If covellite-chalcocite ores contain bornite, this mineral appears in slags. However, no special application of bornite ores was recorded. Although bornite content in slags is a relic, for the most part its grains have been melted. Due to the rare distribution, large bornite aggregates can be used as an indicator of the raw material source. We recorded bornite in the Srubna slags of the Turganik, Ivanovskoe and Tokskoe settlements, i.e. confined to the same archaeological microregion within 2 km. This indicates that the common raw material source has not been identified to date. The nearby mine of Kargaly is situated 100 km SE up the Tok river where bornite has not been described. In the Trans-Urals, bornite is detected in slags from Katzbakh 6 settlement; however, sulphide deposits are not in evidence. The ancient mine of Vorovskaya Yama which hosts ultramafic ores having a different geochemical speciality is located 10 km away. Another example of bornite-containing ores is found in the Taldysay settlement slags located 20 km from the Jezkazgan cupriferous sandstones.

It has not been possible to demonstrate that chalcopyrite ores were used in Bronze Age in Urals, despite their widespread use during the European LBA (according to S.G. Grygoriev [53]). It is supposed that chalcopyrite is weakly preserved during the pyrometallurgical processes. Chalcopyrite weathering during the supergenic processes in slags is also possible. However, if this were so, more relics should be found since the slag system is closed during sintering. In previous studies in the Urals, chalcopyrite was not found even when using SEM-EDS to study submicron inclusions in more than 500 slag fragments (our data). An altered chalcopyrite fragment found at the Taldysay (Kazakhstan) settlement is probably formed due to a random used from covellite-chalcocite ores of Jezkazgan cupriferous sandstones.

Due to their greater diversity, geochemical criteria of slag sulphides can accurately reflect the raw material sources and alloying additions with a full range of geochemical characteristics (Figure 4). In archaeometry, As is the main element-marker in Bronze Age copper industry [59,60]. There are debates about the boundaries of natural alloying or deliberated mixtures in As bronzes. Typically, their boundary is 0.5–1.0 % content in copper or bronze [61]. Moreover, there is a difference in As contents between those observed in deliberately alloyed slag and as a consequence of natural additions in slag sulphide inclusions [62]. In natural objects, arsenic is often confined to hydrothermal sulphide ores located in ultramafic rocks. Slag sulphides from these ores in Urals usually contain between 500 and 5000 ppm of As. This was caused by the random usage of small amounts of As minerals from the oxidation and secondary enrichment zones. These include sulphide-containing olivine slags from the Turganik, Pokrovskoe and Rodnikovoe settlements. The high contents indicate the deliberated adding of As minerals (realgar, orpiment erythrite, etc.) that is confirmed by elevated contents of Co, Ni, and Sb confined to arsenic mineralisation. These samples are typical for Ustye and Taldysay settlements.

The elevated As contents in slag sulphides testify that As alloying occurs immediately following the primary smelting of copper from ores. Zinc and tin comprise the components of brasses and Sn

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bronzes. Although their contents are low and uneven in slag sulphides that caused by the natural addition of these elements in covellite-chalcocite, elevated quantities of these elements are typical for the Taldysay Jezkazgan ores, where they appear in amounts up to 0.1 % Zn and 0.45 % Sn 0.45 %. In copper ore genesis, the elevated Zn and Sn are often related to VMS deposits in volcanogenic complexes and polymetallic ores in volcanogenic-sedimentary rocks.

In sulphides, the important indicators are Se and Te. These are typical for mafic VMS deposits and often concentrated in the oxidation zone [57,63]. Characteristically, the high amounts (hundreds and thousands of ppm) are confined to high-temperature VMS chalcopyrites [18]. Ultra-high Se contents (up to 0.5 %) are detected in sulphides from Cyprus-type VMS deposits [64]. However, the main enrichment with Se of secondary sulphides from the majority of deposits is caused by supergenesis [57]. In slag sulphides from Kamenny Ambar and Konoplyanka settlements contents and Se and Te high contents indicate the single source of raw ore material. However, such an ore mineralisation is yet to be discovered at the present time. The geochemical ore peculiarities imply an oxidation zone of Cyprus-type VMS or skarn deposits in mafic complexes (high Se and Co and low Ni and Ag). A similar situation is observed for the Sarlybay 3 settlement and ores of Sarlybay deposit.

Relatively high Se contents (1000–1500 ppm) are typical for olivine Cr-rich spinel containing slags from the Turganik and Kuzminkovskoe settlements. Ores from these sites were sourced from ultramafic complexes as confirmed by mineralogical and geochemical peculiarities of slags (serpentinite and Cr-rich spinel relics, mafic/ultramafic glass) and trace elements in sulphides (Co-Ni-As). The nearest known ancient mine with similar geochemical markers is Ishkinino, located in the ultramafic rocks of the Main Urals Fault. However, the distance between these two sites is more than 350 km. For slag sulphides from Turganik settlement, high Ag and Pb contents and the presence of quartz are observed. It is suggested that this fact may indicate a mixed raw-material source for copper production, as follows from the presence of minerals from ultramafic rocks and cupriferous sandstones and possibility of long-distance ore transportation during the Bronze Age (more than 300 km). Slag sulphides are clearly divided into several groups having different sources of copper according to the Se–As ratio (Figure 4c).

Cobalt, nickel and antimony often correlate with each other and As. In sulphides of non-alloying slags, the higher contents of these trace elements are related to sulphide-hydrothermal ores in ultramafic rocks (see above). Elevated Co and low Ni and As are markers of VMS and Cu skarn deposits in basalts. These include slag sulphides from Kamenny Ambar, Konoplyanka and Sarlybay 3 settlements. According to the Co-Ni ratio (Figure 4b), we can distinguish between groups of cupriferous sandstones (Ni<Co), mafic substrate (Co>Ni) and ultrabasic substrate (Co=Ni). The elevated Sb contents are confined to alloying copper by As and typical for Ustye and Taldysay settlements. On the Ni-Sb plot for copper, the elevated contents of these elements reflect the additional metal alloying [65]. A similar pattern is observed in sulphides. Elevated Sb levels mark the deliberate alloying of slag by As (Figure 4c).

The elevated contents and correlation of Ag, Pb and Ba in sulphides are typical for the majority slags of archaeological settlements confined to the Cis-Urals cupriferous sandstones. The typical mineralisation is confined to microinclusions in ores and concretions of native Ag, galena and barite. Pb, Ag, and Ba are typical for all glassy sulphide-containing slags from Ordynsky Ovrag, Turganik, Tokskoe, Ivanovskoe, Bulanovskoe 2, Pokrovskoe, and Rodnikovoe. Thus, during the Srubna period of the LBA, metallurgists from Cis-Urals settlements have predominantly used local raw materials. The melting technology included the utilisation of sulphide concretions from cupriferous sandstone ores.

Similar mineralisation with decreased Ag contents is typical for slags from Katzbakh 6. Ag in higher amounts (more than tens of ppm) is a widespread trace element in sulphides of cupriferous sandstones, where its presence can be found in slag sulphides and copper ingots. Pb is also a widespread element in numerous settlements – especially in Taldysay, where galena ores were examined. According to the Ag-Se content, a group of sources of copper raw materials is identified; these are associated with volcanogenic-hydrothermal sulphides (Figure 4d).

Ba can be an indicator of polymetallic ores or cupriferous sandstones with high Ba-containing mineral amounts. These include Cis-Urals cupriferous sandstones, as well as ultra-enriched sandstones from Nigeria [66]. Ultra-high Ba contents in Katzbakh 6 and Rodnikovoe settlements may testify to the deliberate use of Ba as a flux.

On the example of sulphide-containing slags, we highlighted several main markers of copper ore sources (Table 4). The table shows the examples of Bronze Age mines from the Urals and Kazakhstan. The different genetic types of deposits and geochemical specialisation are recorded in the composition of sulphides from the oxidation zone.

6. Conclusions

The sulphide-containing slags studied in the Urals and Kazakhstan can serve as markers of ore sources and copper alloying methods in the Bronze Age. The presence of sulphide significant amount in different types from the Early to Late Bronze Age indicates that ancient metallurgists from the Urals and Kazakhstan had been using sulphide ores since this time. It was previously believed that the main ore sources were azurite-malachite crusts and concretions from supergenic zones of copper deposits.

Trace elements typical for sulphides obtained from the various settlements show different ore mineralisation in volcanogenic (VMS, Cu-porphyry, skarn and quartz-veined), ultramafic (VMS, skarn and quartz-veined), and sedimentary complexes (cupriferous sandstones). Both sulphide assemblages and their trace elements can potentially be used as markers for ancient slags.

Sulphides from the oxidation zones of deposits confined to ultramafic rocks contain Co-Ni-As mineralisation. These mines were the sources of raw materials for Cr-rich spinel containing olivine slags of Sintashta settlements [5] and sulphide-containing olivine slags from the Ustye, Turganik, Kuzminkovskoe 2 and Rodnikovoe sites we reviewed. Ultra-high contents of these elements together with Sb indicate the special copper alloying by As that was typical for the Ustye and Taldysay settlements.

The oxidation zones of skarn, Cu-porphyry and VMS deposits in basalts were also marked by high contents of Co (and low Ni), Se and Te. These include sulphide-containing olivine slags from Kamenny Ambar, Konoplyanka and Sarlybay 3 settlements. The additional marking trace elements are Fe, Zn, Ba, Mo and Ag.

Trace elements in sulphides from sedimentary complexes of cupriferous sandstones are Ag and Pb accompanied by relatively low amounts of other elements. These include slag sulphides from the Cis-Ural Srubny sites, including Turganik, Ordynsky Ovrag, Tokskoe, Ivanovskoe, Bulanovskoe 2, Pokrovskoe and Rodnikovoe. These cupriferous sandstones additionally contain high concentrations of Ba and Bi. The alloyed slags from Taldysay settlement related to ores from another cupriferous sandstone type. Sulphides from Taldysay samples contain elevated Pb and Ag, along with the As-Co-Ni-Sb alloying complex.

On the basis of the new obtained data, we have concluded that the presence of sulphide assemblages, along with their trace elements, are versatile markers of the ore type, raw material source and additional alloying processes used as evidenced from Bronze Age metallurgical slags.

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References

1. Chernykh, E.N. *Ancient metallurgy of the Urals and Volga region*; Nauka: Moscow, Russia, 1970; 181 p. (In Russian)
2. Chernykh, E.N.; Lebedeva, E. Yu.; Kuzminykh, S.V.; Lunkov, V. Yu; Gorozhanin, V.M.; Gorozhanina, E.N.; Ovchinnikov, V.V.; Puchkov V.N. *Kargaly: Geological and geographical characteristics. History of discovery, operation and research. Archaeological sites, V. 1*; Yazyki slavyanskoy kultury: Moscow, Russia, 2002; 112 p. (In Russian)
3. Bogdanov, S.V. *The Copper Era of the Steppe Ural*; UrO RAN: Yekaterinburg, Russia, 2004; 286 p. (In Russian)
4. Morgunova, N.L.; Vasilyeva, I.N.; Kulkova, M.A.; Roslyakova, N.V.; Salugina, N.P.; Turetskiy, M.A.; Fayzullin, A.A.; Khokhlova, O.S. *Turganik settlement in the Orenburg region*; OGPU: Orenburg, Russia, 2017; 300 p. (In Russian)
5. Ankushev M.N.; Artemyev D.A.; Blinov I.A.; Bogdanov S.V. Bronze Age metallurgical slags from the South Urals: types, mineralogy and copper sources, **2019**. *(in press) ???????*
6. Matyushin, G.N. *Eneolithic of the South Urals*; Nauka: Moscow, Russia, 1982; 328 p. (In Russian)
7. Epimakhov, A.V.; Chuev, N.I. Abashevo and Sintashta sites: preliminary results of spatial analysis. *Bulletin of archaeology, anthropology and ethnography* **2011**, *2 (15)*, 47–56. (In Russian)
8. Zdanovich, G.B. *The Bronze Age of the Ural-Kazakhstan steppes*; UrU: Sverdlovsk, 1988; 184 p. (In Russian)
9. Margulan, A. Kh. Mining in Central Kazakhstan in the Ancient and Middle Ages. In *Searches and excavations in Kazakhstan*. Nauka: Alma-Ata, Kazakhstan, 1972; 3–30. (In Russian)
10. Zdanovich, S.Ya. Sargary culture – the Bronze Age final stage of North Kazakhstan. PhD thesis, MSU: Moscow, Russia, 1979. (In Russian)
11. Margulan A.Kh. *Begazy-Dandybai culture of Central Kazakhstan*; Nauka: Alma-Ata, Kazakhstan, 1979; 336 p. (In Russian)
12. Degtyareva, A.D. Metal production in Kazakhstan and Kyrgyzstan in the Late Bronze Age. PhD thesis, MSU: Moscow, Russia, 1985. (In Russian)
13. Bachmann, H.G. *The identification of slags from archaeological sites;* Occasional Publications no 6; Institute of Archaeology: London, Great Britain, 1982; 37 p.
14. Tylecote, R.F. *The early history of metallurgy in Europe*; Longman: London, Great Britain, 1987; 424 p.
15. Zaykov, V.V.; Yuminov, A.M.; Ankushev, M.N.; Tkachev, V.V.; Noskevich, V.V.; Epimakhov, A.V. Mining and metallurgical centers of the Bronze Age in the Trans-Urals and Mugodzhary. *Bulletin Irkutsk state university. Geoarkhaeology. Etnology. Antropology* **2013**, *1*, 174–195. (In Russian)
16. Grigoriev, S.A.; Dunaev, A.Yu.; Zaykov, V.V. Chromites: an indicator of copper ore source for ancient metallurgy. *Dokl. Earth Sci.* **2005**, *400(1)*, 95–98.
17. Danyushevsky, L.V.; Robinson, R.; Gilbert, S.; Norman, M.; Large, R.; McGoldrick, P.; Shelley, J.M.G. Routine quantitative multielement analysis of sulfide minerals by laser ablation ICP-

Peer-reviewed version available at *Minerals* **2019**, *9*, 746; doi:10.3390/min9120746

MS: Standard development and consideration of matrix effects. *Geochem. Explor. Environ. Anal.* **2011**, *11*, 51–60. doi:10.1144/1467-7873/09-244

18. Maslennikov, V. V.; Maslennikova, S. P.; Large, R. R.; Danyushevsky, L. V.; Herrington, R. J.; Ayupova, N. R.; Zaykov, V.V.; Lein, A.Yu.; Tseluyko, A.S.; Melekestseva, I.Yu; Tessalina, S. G. Chimneys in Paleozoic massive sulfide mounds of the Urals VMS deposits: mineral and trace element comparison with modern black, grey, white and clear smokers. *Ore Geol. Rev.*, **2017**, *85*, 64–106. doi:10.1016/j.oregeorev.2016.09.012
19. **Dussubieux**, L.; **Golitko**, M.; **Gratuze**, B. *Recent advances in laser ablation ICP-MS for archaeology*; Springer-Verlag: Berlin Heidelberg, Germany, 2016. 358 p. doi:10.1007/978-3-662-49894-1
20. Glascock, M.D.; Speakman, R.J.; Popelka-Filcoff, R.S. *Archaeological chemistry analytical techniques and archaeological interpretation*, v. 968; American Chemical Society, 2007, 571 p.
21. Addis, A.; Angelini, I.; Nimis, P.; Artioli, G. Late Bronze Age copper smelting slags from Luserna (Trentino, Italy): Interpretation of the Metallurgical Process. *Archaeometry* **2015**, *58(1)*, 96–14. doi:10.1111/arcm.12160
22. Artioli, G.; Angelini, I.; Tecchiati, U.; Pedrotti, A. Eneolithic copper smelting slags in the Eastern Alps: Local patterns of metallurgical exploitation in the Copper Age. *J. Archaeol. Sci.* **2015**, *63*, 78–83. doi:10.1016/j.jas.2015.08.013
23. Chiarantini, L.; Benvenuti, M.; Costagliola, P.; Fedi, M. E.; Guideri, S.; Romualdi, A. Copper production at Baratti (Populonia, Southern Tuscany) in the early Etruscan period (9th–8th centuries BC). *J. Archaeol. Sci.* 2009, *36(7)*, 1626–1636. doi:10.1016/j.jas.2009.03.026

24. Ettler, V.; Cervinka, R.; Johan, Z. Mineralogy of medieval slags from lead and silver smelting (Bohutin, Pribram district, Czech Republic): towards estimation of historical smelting conditions. *Archaeometry* **2009**, *51(6)*, 987–1007.
25. Georgakopoulou, M.; Bassiakos, Y.; Philaniotou, O. Seriphos surfaces: a study of copper slag heaps and copper sources in the context of Early Bronze Age Aegean metal production. *Archaeometry* **2011**, *53(1)*, 123–145. doi:10.1111/j.1475-4754.2010.00529.x
26. Pelton, A.; Stamatakis, M. G.; Kelepertzis, E.; Panagou, T. The origin and archaeometallurgy of a mixed sulphide ore for copper production on the Island of Kea, Aegean Sea, Greece. *Archaeometry* **2014**, *57(2)*, 318–343. doi:10.1111/arcm.12080
27. Krismer, M.; Töchterle, U.; Goldenberg, G.; Tropper, P.; Vavtar, F. Mineralogical and petrological investigations of Early Bronze Age copper-smelting remains from the Kiechlberg (Tyrol, Austria). *Archaeometry* **2012**, *55(5)*, 923–945. doi:10.1111/j.1475-4754.2012.00709.x
28. Erb-Satullo, N.L.; Gilmour B.J.J.; Khakhutaishvili, N. Crucible technologies in the Late Bronze – Early Iron Age South Caucasus: copper processing, tin bronze production, and the possibility of local tin ores. *J. Archaeol. Sci.* **2015**, *61*, 260–276. doi.org/10.1016/j.jas.2015.05.010
29. Valério, P.; Monge Soares, A. M.; Silva, R. J. C.; Araújo, M. F.; Rebelo, P.; Neto, N.; Santos R.; Fontes, T. Bronze production in Southwestern Iberian Peninsula: The Late Bronze Age metallurgical workshop from Entre Águas 5 (Portugal). *J. Archaeol. Sci.* **2013**, *40(1)*, 439–451. doi:10.1016/j.jas.2012.07.020
30. Ryndina N.; Indenbaum G.; Kolosova V. Copper production from polymetallic sulphide ores in the Northeastern Balkan eneolithic culture. *J. Archaeol. Sci.* **1999**, *26(8)*, 1059–1068.
31. Chen, K.; Rehren, T.; Mei, J.; Zhao, C. Special alloys from remote frontiers of the Shang Kingdom: scientific study of the Hanzhong bronzes from southwest Shaanxi, China. *J. Archaeol. Sci.* **2009**, *36(10)*, 2108–2118. doi:10.1016/j.jas.2009.04.016
32. Frame, L. Metallurgical investigations at Godin Tepe, Iran, Part I: the metal finds. *J. Archaeol. Sci.* **2010**, *37(7)*, 1700–1715. doi:10.1016/j.jas.2010.01.030

33. Valério, P.; Silva, R. J. C.; Monge Soares, A. M.; Araújo, M. F.; Braz Fernandes, F. M.; Silva, A. C.; Berrocal-Rangel, L. Technological continuity in Early Iron Age bronze metallurgy at the South-Western Iberian Peninsula – a sight from Castro dos Ratinhos. *J. Archaeol. Sci.*, **2010**, 37(8), 1811–1819. doi:10.1016/j.jas.2010.01.038

34. Park, J.-S.; Honeychurch, W.; Chunag, A. Ancient bronze technology and nomadic communities of the Middle Gobi Desert, Mongolia. *J. Archaeol. Sci.* **2011**, *38(4)*, 805–817. doi:10.1016/j.jas.2010.11.003

35. EL Morr, Z.; Cattin, F.; Bourgarit, D.; Lefrais, Y.; Degryse, P. Copper quality and provenance in Middle Bronze Age I Byblos and Tell Arqa (Lebanon). *J. Archaeol. Sci.* **2013**, *40(12)*, 4291–4305. doi:10.1016/j.jas.2013.05.025

36. Park, J.-S.; Shinde, V. Characterization and comparison of the copper-base metallurgy of the Harappan sites at Farmana in Haryana and Kuntasi in Gujarat, India. *J. Archaeol. Sci.* **2014**, *50*, 126–138. doi:10.1016/j.jas.2014.07.005

37. Artemyev, D.A.; Ankushev, M.N.; Blinov, I.A.; Kotlyarov, V.A.; Lukpanova, Ya.A. Mineralogy and origin of slags from the 6th kurgan of the Taksay 1 burial complex, Western Kazakhstan. *Can. Mineral.* **2018**, *56*, 883–904. doi.org/10.3749/canmin.1800025

38. Cook, N.J.; Ciobanu, C.L.; Danyushevsky, L.V.; Gilbert, S. Minor elements in bornite and associated Cu-(Fe)-sulfides: A LA-ICPMS study. *Geochim. Cosmochim. Acta* **2011**, *73*, 4761–4791.

39. Wang,Y.; Han, X.; Petersen, S.; Frische, M.; Qiu, Z.; Cai, Y.; Zhou, P. Trace metal distribution in sulfide minerals from ultramafic-hosted hydrothermal systems: examples from the Kairei Vent Field, Central Indian Ridge. *Minerals*, 2018.

40. Melekestseva, I.Y.; Maslennikov, V.V.; Maslennikova, S.P.; Danyushevsky, L.; Large, R. Covellite from Semenov-2 hydrothermal field (13_31.130 N, Mid-Atlantic Ridge): Enrichment in trace elements according to LA-ICP-MS analysis. *Dokl. Earth Sci.* **2017**, *473*, 291–295.

41. Paton, C.; Hellstrom, J.; Paul, B.; Woodhead, J.; Hergt, J. Iolite: Freeware for the visualisation and processing of mass spectrometric data. *J. Anal. Atomic Spectrom.* **2011**, *26*, 2508–2518.

42. Wilson, S.A.; Ridley,W.I.; Koenig, A.E. Development of sulfide calibration standards for the laser ablation inductively-coupled plasma mass spectrometry technique. *J. Anal. At. Spectrom*. **2002**, *17*, 406–409.

43. Longerich, H.P.; Jackson, S.E.; Günther, D. Inter-laboratory note. Laser ablation inductively coupled plasma mass spectrometric transient signal data acquisition and analyte concentration calculation. *J. Anal. Atomic Spectrom.* **1996**, *11*, 899–904.

44. Krause, R.; Koryakova, L.N. *Multidisciplinary investigations of the Bronze Age settlements in the South Trans-Urals (Russia)*; Verlag Dr. Rudolf Habelt GmbH: Bonn, Germany, 2013, 352 p.

45. Sharapova, S.V., Krauze, R., Molchanov, I.V., Shtobbe, A., Soldatkin, N.V. Interdisciplinary studies of the Konoplyanka settlement in the South Trans-Urals: preliminary results; *Bulletin of Novosibirsk State University. Series: History, Philology* **2014**, *13(3)*, 101–109. (In Russian)

46. Vinogradov, N.B. (Eds.) *Ancient Ustye: a fortified Bronze Age settlement in the South Trans-Urals;* ABRIS: Chelyabinsk, Russia, 2013, 482 p. (In Russian)

47. Morgunova, N.L.; Porokhova, O.I. Settlements of Srubna culture in the Orenburg region. In *Settlements of Srubna community;* VGU: Voronezh, Russia, 1989, 160–172. (In Russian)

48. Morgunova, N.L.; Khalyapin, M.V. Research in the Orenburg steppe. In *Archaeological discoveries of 2000*; Nauka: Moscow, Russia, 2002 (In Russian)

49. Morgunova N.L.; Khalyapin M.V.; Khalyapina O.A. Kuzminkovskoe settlement of the Bronze Age. In *Archaeological sites of the Orenburg region*. *V.5*; OGPU: Orenburg, Russia, 2001, 99–125. (In Russian)

Peer-reviewed version available at *Minerals* **2019**, *9*, 746; doi:10.3390/min9120746

50. Kuptsova L.V.; Fayzullin I.A. Rodnikovoe settlement of the Late Bronze Age in the Western Orenburg region. In *Archaeological sites of the Orenburg region. V.10*; OGPU: Orenburg, Russia, 2012, 70–100. (In Russian)

51. Tkachev V.V.; Baytleu D.A.; Yuminov A.M.; Ankushev M.N.; Zhalmaganbetov Zh.M.; Kalieva Zh.S. Mountain archeology new studies of the South Mugalzhary sites. In *Paper of the Institute of Archeology named after A. Kh. Margulana. V. 2;* Astana, Kazakhstan, 2013, 264–288. (In Russian)

52. Yermolayeva, A.S.; Kuzminykh, S.V.; Park, J.-S.; Dubyagina, Ye.V. Late Bronze Age weapons from foundry workshops of Taldysay settlement, Central Kazakhstan. *Stratum plus* **2019**, *2*, 109–120. (In Russian)

53. Grigoriev, S. *Metallurgical production in Northern Eurasia in the Bronze Age*; Archaeopress Access Archaeology: Germany, 2016; 832 p.

54. Grigoryev S.A.; Rusanov I.A. Experimental reconstruction of ancient metallurgical production. In *Arkaim: Research. Search. Discoveries.* Kamenny Poyas: Chelyabinsk, Russia, 1995; 147–158. (In Russian)

55. Rovira S.; App J. Appendix 6. Experimental work on the smelting of copper in Kargaly archaic way. In *Archaeological sites of the Orenburg region. V. 1.* OGPU: Orenburg, Russia, 2004, 64–69. (In Russian)

56. Bogdanov S.V. Early Yamna site systematics of the East Ponto-Caspian steppes in the problem's context of mining and metallurgical traditions transfer to North Eurasia. *Stratum plus*, **2017**, *2*, 133–158. (In Russian)

57. Belogub, E.V.; Novoselov, K.A.; Yakovleva, V.A.; Spiro, B. Supergene sulphides and related minerals in the supergene profiles of VHMS deposits from the South Urals. *Ore Geol. Rev.*, **2008**, *33*, 239–254. doi.org/10.1016/j.oregeorev.2006.03.008

58. Lurye, A. M. *Genesis of cupriferous sandstones and cambric schists*. Nauka: Moscow, Russia, 1988; 188 p. (In Russian)

59. *Charles, J. A. Early arsenical bronzes – a metallurgical view. American Journal of Archaeology,* ***1967****, 71(1), 21–26.*

60. De Ryck, I.; Adriaens, A.; Adams, F. An overview of Mesopotamian bronze metallurgy during the 3rd millennium BC. *Journal of cultural heritage*, **2005**, *6(3)*, 261–268. doi:10.1016/j.culher.2005.04.002

61. Budd, P.; Ottoway, B. S. Eneolithic arsenical copper – chance or choice? In *Ancient mining and metallurgy in Southeast Europe*; Archaeological institute: Bor-Belgrade, Serbia, 1995, 95–102.

62. *Lechtman, H. Arsenic bronze: dirty copper or chosen alloy? A view from the Americas. Journal of Field Archaeology,* ***1996****, 23(4), 477–514.*

63. Bullock, L. A.; Perez, M.; Armstrong, J. G.; Parnell, J.; Still, J.; & Feldmann, J. Selenium and tellurium resources in Kisgruva Proterozoic volcanogenic massive sulphide deposit (Norway). *Ore Geol. Rev.*, **2018**, *99, 411–424.* doi:10.1016/j.oregeorev.2018.06.023

64. Martin, A. J.; McDonald, I.; MacLeod, C. J.; Prichard, H. M.; McFall, K. Extreme enrichment of selenium in the Apliki Cyprus-type VMS deposit, Troodos, Cyprus. *Mineralogical Magazine*, **2018** *82(03)*, 697–724. doi:10.1180/mgm.2018.81

65. Dussubieux, L.; Walder, H. Identifying American native and European smelted coppers with pXRF: a case study of artifacts from the Upper Great Lakes region. *J. Archaeol. Sci.*, **2015**, *59*, 169–178. doi:10.1016/j.jas.2015.04.011

66. El-Nafaty, J.M. Geology and trace element geochemistry of the barite-copper mineralization in Gulani Area, NE Nigeria. *IOSR Journal of applied geology and geophysics*, **2017**, *5(2)* doi:10.9790/0990-0502020116

Figure 1. Map of Bronze Age settlements of the South Urals and Kazakhstan with Cu-(Fe)-sulphides of slags

Figure 2. Relics and neogenic sulphides in metallurgical copper slags: a – relic covellite clast, Kamenny Ambar; b – partially melted covellite clast, Kamenny Ambar; c – melted covellite fragment, Konoplyanka; d – crescent covellite inclusion, Konoplyanka; e – neogenic chalcocite-covellite intergrowth around copper droplet, Sarlybay 3; f – neogenic chalcocite-covellite droplet Rodnikovoe; g – partly melted bornite fragment, Tokskoe; h – partly transformed chalcopyrite fragment, Taldysay.

Figure 3. Box-and-whiskers diagram showing the scatter of the values of some trace elements in Bronze Age slag sulphides of the South Urals and Kazakhstan.

Figure 4. Relation diagram of some trace elements in Bronze Age slag sulphides of the South Urals and Kazakhstan.

Table 1. South Urals and Kazakhstan archaeological sites, containing sulphide inclusions of the Bronze Age copper slags

Table 2. Cu-(Fe)-sulphides of South Urals and Kazakhstan Bronze Age metallurgical slags

Table 3. Major and trace elements of Bronze Age slags Cu-(Fe)-sulphides

Table 4. Some Bronze Age mines of copper deposits South Urals and Kazakhstan and their marker trace elements