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Trace Elements of Cu-(Fe)-Sulfide 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 sulfides from 14 archaeological Bronze Age settlements of the Cis-Urals, Trans-Urals, and North and Central Kazakhstan are presented. The study used Cu-(Fe)-sulfides 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 sulfides 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 sulfides, the main indicator elements, Fe, Co, Ni, As, Se, Te, Sb, Ag, Pb, and Bi, are important markers of copper deposit types. Sulfides from olivine Cr-rich spinel containing slags of Ustye, Turganik are characterized by As-Co-Ni high contents and confined to copper deposits in ultramafic rocks. Olivine sulfide-containing slags from Kamenny Ambar, Konoplyanka and Sarlybay 3 are characterized by Co-Se-Te assemblage and confined to mafic rocks. Glassy sulfide-containing slags from Katzbakh 6, Turganik, Ordynsky Ovrag, Ivanovskoe, Tokskoe, Bulanovskoe 2, Kuzminkovskoe 2, Pokrovskoe, Rodnikovoe, and Taldysay are characterized 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 sulfide 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; sulfide; 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 region of Central Eurasia [1]. This region, which comprises over 1 million square kilometers containing numerous copper deposits, is characterized 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 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 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 had 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 was slowly disintegrated and formed numerous local pastoral cultural groups throughout the region, identified as Final Bronze Age cultures 1300–800 BCE (Chercascul, Sargary-Alekseevo, Begazy-Dandybai, etc.) [10–12].

In addition to copper artifacts, the main evidence of ancient metallurgical activity consists in discoveries of ingots, molds, 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 sulfides [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 sulfide 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 sulfides in geological samples [17,18]. Recently, LA-ICP-MS analysis has also become widespread in archaeological studies for determining trace elements in small samples [19,20].

Relict sulfides and sulfide droplets have been found in numerous ancient Eurasian slags. Rich bornite-chalcocite-covellite droplets were identified in several copper slag types in the Late Bronze Age (LBA onwards) Trentino archaeological site in North Italy [21,22]. Relict fragments of chalcopyrite and secondary copper sulfides 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 onwards) relict bornite, chalcocite, and chalcopyrite fragments from slags of the Seriphos [25] and Kea [26] islands in Greece were found. Chalcopyrite, bornite, covellite, digenite, and chalcocite droplets and clasts were determined 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-sulfide microinclusions have been widely studied in ancient copper and bronzes [30–36]. Fe-sulfides (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)-sulfides [5], represented by covellite, chalcocite, and bornite. We surmised that slags of Cu-(Fe)-sulfide composition can be used to indicate the type of copper deposits and clarify the raw material sources. The secondary copper sulfides are often tracing geochemical markers of deposits where they have 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-sulfides [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 consequence of ore melting during metal production, marker trace elements are moved into sulfide and copper droplets and enriched with alloying additions and fluxes. Thus, unlike the finished item copper, 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)-sulfide droplets and relic fragments contained in Bronze Age metallurgical slags in South Urals and Kazakhstan. As far as we are aware, no similar investigation aimed at determining indicator trace elements in slag sulfides has yet been carried out. This knowledge will help to research the mineral resource base of the ancient metallurgical communities in North Central Eurasia.

2. 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 in South Urals and Kazakhstan, we distinguished four types occurring in South Urals [5]. However, copper sulfides in slags are identified in just two of these: sulfide-containing olivine and sulfide-containing glassy types. In other types, sulfides are rare submicron allocations. The only exceptions are Cr-rich spinel containing olivine slags from the Turganik settlement and pyroxene types from Rodnikovoe settlement, which contained copper sulfides 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 sulfide-containing slags.

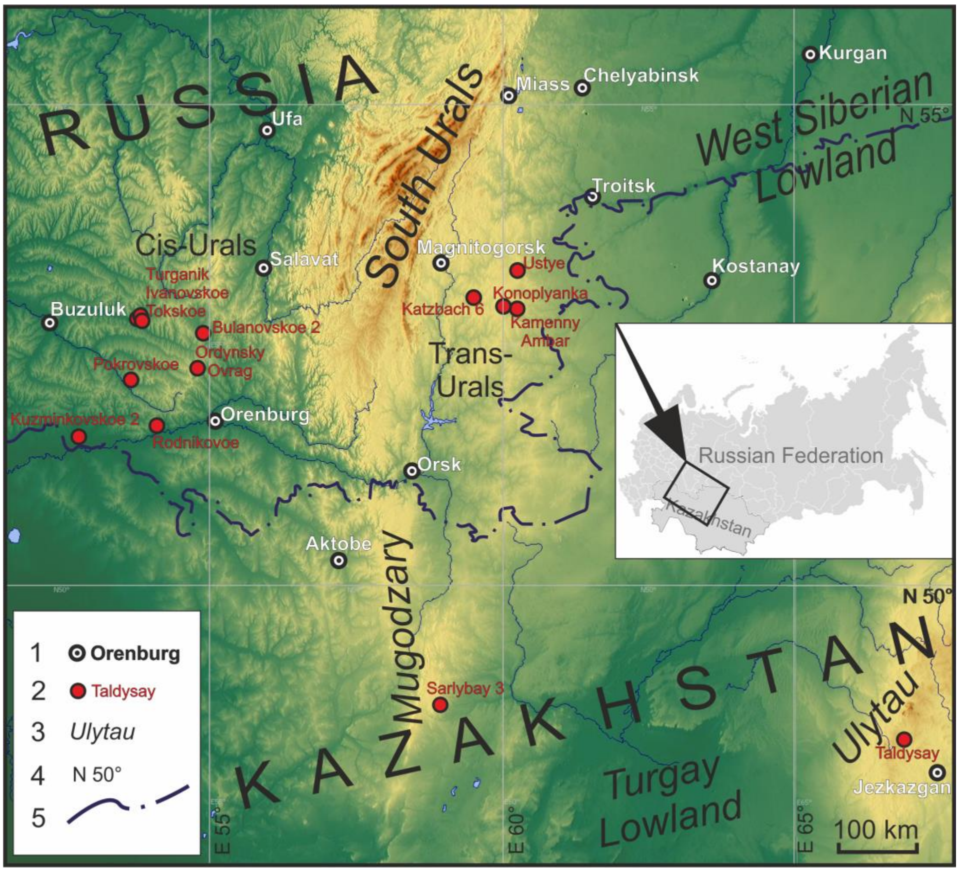

Figure 1. Map of Bronze Age settlements of the South Urals and Kazakhstan with Cu-(Fe)-sulfides of slags: 1—modern cities; 2—archaeological settlements; 3—mountain ranges; 4—geographical coordinates; 5—state border of Russian Federation and Kazakhstan.

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

No	Settlement Site	Localization	Culture (Age Sites)	Slag Type	Reference
1	Kamenny Ambar	Trans-Urals	Sintashta–Alakul (2030–1730 cal. BC)	Cr-rich spinel-containing olivine slags, sulfide-containing olivine slags	[41]
2	Konoplyanka	Trans-Urals	Sintashta–Alakul (1920–1745 cal. BC)	Cr-rich spinel-containing olivine slags, sulfide-containing olivine slags	[42]
3	Ustye	Trans-Urals	Sintashta (2030–1740 cal. BC)	Cr-rich spinel-containing olivine slags	[43]
4	Katzbach 6	Trans-Urals	Alakul (by ceramic dating)	Sulfide-containing glassy slags	-
5	Ordynsky Ovrag (Kargaly)	Cis-Urals	Srubna (1690–1390 cal. BC)	Sulfide-containing glassy slags	[2]
6	Turganik	Cis-Urals	Early Yamna (3940–3480 cal. BC)–Srubna (by ceramic dating)	Cr-rich spinel-containing olivine slags, sulfide-containing glassy slags	[4]
7	Tokskoe	Cis-Urals	Srubna (by ceramic dating)	Sulfide-containing glassy slags	[44]
8	Ivanovskoe	Cis-Urals	Srubna (by ceramic dating)	Sulfide-containing glassy slags	[44]
9	Bulanovskoe 2	Cis-Urals	Abashevo–Srubna (by ceramic dating)	Sulfide-containing glassy slags	[45]
10	Kuzminkovskoe 2	Cis-Urals	Srubna (by ceramic dating)	Sulfide-containing glassy slags	[44]
11	Pokrovskoe	Cis-Urals	Srubna (by ceramic dating)	Sulfide-containing glassy slags	[44]
12	Rodnikovoe	Cis-Urals	Abashevo–Srubna–Sargary-Alekseevo (by ceramic dating)	Sulfide-containing glassy slags, pyroxene slags	[46]
13	Sarlybay 3	Mugodzary	Alakul (by ceramic dating)	Sulfide-containing glassy slags	[47]
14	Taldysay	Ulytau	Alakul–Begazy-Dandybai (by ceramic dating)	Sulfide-containing glassy slags	[48]

Note: Abashevo (2200–1650 cal. BC), Sintashta (2050–1700 cal. BC), Alakul (1900–1500 cal. BC), Srubna (1700–1450 cal. BC), Sargary-Alekseevo (1450–800 cal. BC), Begazy-Dandybai (1200–800 cal. BC) [49].

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 [41]. 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 and Alakul. Fragments of ores represented by malachite, malachite-azurite, tourmaline-malachite, and magnetite-malachite with secondary sulfide 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 cal. BC) and dated (to ceramics) by Sintashta and Alakul periods. On the site, the fragments of metallurgical slags and copper splashes are detected [42].

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 LBA. 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 [43].

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 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 center of the 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 assume 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 EBA. The basic cultural layer, which is dated to 4000 BCE, is represented by ancient ceramics, ore fragments, metallurgical slags, copper ingots, and crucibles, 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. Porokhova in 1990. Between them, these processes uncovered more than 80 square meters of the site. The ceramic artifacts, which are dated to the Srubna culture, also feature rare Alakul cultural peculiarities. A large metallurgical 4 × 5.4 m construction, constructed with limestone blocks and containing numerous copper slags, was also recovered [44].

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 molds of the Srubna culture [44].

The Bulanoskoye 2 settlement is situated near the Bulanovo village (Orenburg region) and is confined to the inundated terrace on the right bank of the Salmysh River. The expedition led by N.L. Morgunova and M.V. Khalyapin has excavated about 650 square meters since 1998. Here, ceramics were recovered and dated to the cultural layers of the Abashevo and Srubna cultures, along with numerous metallurgical slag fragments [45].

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 [44]. The monument is dated by the LBA due to a Srubna culture ceramics. Here, numerous copper slag fragments have been discovered.

The Pokrovskoe settlement is situated on the Samara River left side terrace 3 km NW from the village of Pokrovka. During the excavation led by O.I. Porokhova in 1984 [44], 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. 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 [46]. Two chronological layers—early with Srubna type ceramics and later Final Bronze Age 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 [47].

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 Age cultures (Begazy-Dandybai). Fragments of carbonate, oxidized and sulfide ores of cupriferous sandstones from the Jezkazgan area were also found at the site [48].

3. Materials and Methods

Two hundred polished sections (p.s. onwards) 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 sulfide inclusions were identified. In these samples, the most sulfide-rich fragments were selected: Kamenny Ambar—4 p.s., Konoplyanka—2 p.s., Katzbach 6—2 p.s., Ustye—1 p.s., Ordynsky Ovrag—2 p.s., Turganik—4 p.s., Tokskoe—2 p.s., Ivanovskoe—3 p.s., Bulanovskoe 2—2 p.s., Kuzminkovskoe 2—1 p.s., Pokrovskoe—2 p.s., Rodnikovoe—3 p.s., Sarlybay 3—2 p.s., and Taldysay—2 p.s (Table 2).

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

Settlement Site	P.S.	Slag Type	Morphology	Size Sulfides	Copper Sulfides
Kamenny Ambar	4	Sulfide-containing olivine slags	Rounded droplets, crescent droplets, clasts	Up to 5 mm	covellite
Konoplyanka	2	Sulfide-containing olivine slags	Rounded droplets, clasts, crescent droplets	Up to 1 mm	covellite
Ustye	1	Cr-spinel-containing olivine slags	Rounded droplets	Up to 0.05 mm	Copper sulfoarsenides
Katzbach 6	2	Sulfide-containing olivine slags	Clasts, xenomorphic droplets	Up to 0.25 mm	covellite, bornite
Ordynsky Ovrag (Kargaly)	2	Sulfide-containing olivine slags	Rounded droplets, crescent droplets	Up to 3 mm	Chalcocite-covellite
Turganik	2	Cr-spinel-containing olivine slags	Crescent droplets, clasts	Up to 2 mm	Chalcocite, bornite
	2	Sulfide-containing olivine slags	Crescent droplets, clasts, rounded droplets	Up to 2 mm	Chalcocite-covellite
Tokskoe	2	Sulfide-containing olivine slags	Crescent droplets, clasts, rounded droplets	Up to 1 mm	Chalcocite, bornite, covellite
Ivanovskoe	3	Sulfide-containing olivine slags	Rounded droplets, crescent droplets, clasts	Up to 2 mm	Chalcocite-covellite, bornite
Bulanovskoe 2	2	Sulfide-containing olivine slags	Rounded droplets	Up to 1 mm	Chalcocite-covellite
Kuzminkovskoe 2	1	Sulfide-containing olivine slags	Rounded droplets	Up to 0.5 mm	Chalcocite-covellite
Pokrovskoe	2	Sulfide-containing olivine slags	Crescent droplets, rounded droplets	Up to 2 mm	Chalcocite-covellite
Rodnikovoe	2	Sulfide-containing olivine slags	Crescent droplets, rounded droplets	Up to 0.5 mm	Chalcocite-covellite
	1	Pyroxene slags	Rounded droplets, Crescent droplets	Up to 0.1 mm	covellite
Sarlybay 3	2	Sulfide-containing olivine slags	Crescent droplets, rounded droplets	Up to 0.4 mm	Chalcocite-covellite
Taldysay	2	Sulfide-containing olivine slags	Clasts, rounded droplets	Up to 1 mm	covellite, chalcocite, bornite, chalcopyrite

The trace elements in sulfides were studied using a New Wave Research UP-213 laser ablation system, coupled with an Agilent 7700x (Agilent Technologies, Santa Clara, CA, USA) plasma mass spectrometer in the Institute of Mineralogy SU FRC MG UB RAS (Miass, Russia). 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 30–100 μm 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, and 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 analyzed every 10–18 spots to account for the instrument drift. Data processing was carried out using the Iolite software package [50].

Elements were determined and calculated by USGS MASS-1 [51] 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, and ^{209}Bi. The dwell time was 10 ms. Concentrations of ^{115}In, ^{125}Te, ^{197}Au, ^{205}Tl, and ^{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 [52], with normalization 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, and ^{232}Th were used, while ^{238}U was calculated by USGS GSD-1g.

4. Results

4.1. Mineralogy of Slag Cu-(Fe)-Sulfides

Copper sulfides 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 eight IMA registered mineral species: covellite (66.5% Cu)–yarrowite (69% Cu)–spionkopite (73.4% Cu)–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 sites, bornite and products of its alteration are identified (Cu_5FeS_4, 63.3% Cu). A significant quantity of sulfides is presented by neogenic non-stoichiometric species with varying Fe contents. Sulfide droplets and grain sizes range from between several microns to inclusions measured in millimeters. Chalcopyrite ($CuFeS_2$ 34.6% Cu) and other copper sulfides are completely absent from the slags. An isolated grain of altered chalcopyrite is found in a slag from Taldysay.

According to morphological peculiarities, sulfide inclusions are divided into relict clast and melt droplets. Copper sulfide 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 sulfide-silicate melt with new components absorption.

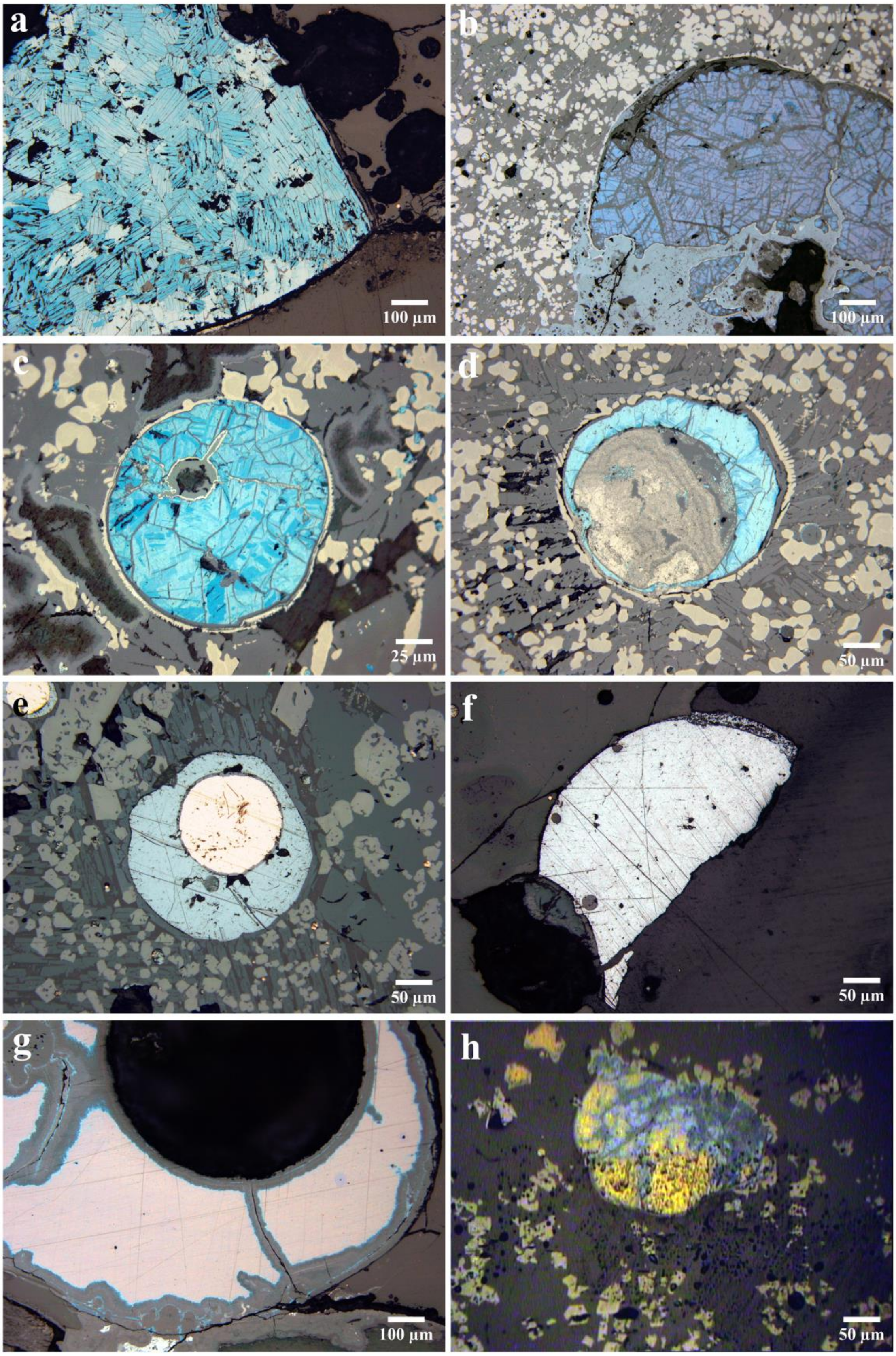

Figure 2. Relics and neogenic sulfides in metallurgical copper slags: (**a**) relic covellite clast, Kamenny Ambar; (**b**) partially melted covellite clast, Kamenny Ambar; (**c**) melted covellite fragment, Konoplyanka; (**d**) crescent covellite inclusion, Konoplyanka; (**e**) neogenic chalcocite-covellite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

Covellite was observed to form relict fragments of several millimeters in size and melted grains or rare neogenic droplets (Figure 2d). The color of covellite in fragments and smelted grains is bright blue up to dark-blue, while neogenic droplets are often light-blue color in reflected light. As copper sulfide, 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 colored, 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 color in reflected light (Figure 2g), can serve as an indicator mineral. Bornite typically forms melt relic grains size up 1 mm. It was found only in Katzbakh 6, Ivanovskoe, Tokskoe, Turganik, and Taldysay settlements. Chalcopyrite occurs only in isolated cases. The only chalcopyrite grain was found out in samples from Taldysay (Figure 2h). It was formed by round melted fragments which were 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)-Sulfides*

Copper sulfides 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 smelting.

Fe is a widespread minor element in copper sulfide. Moreover, in addition to copper and iron minerals (bornite and chalcopyrite) and their pyrogenic transformed species, it comprises a mixture in the covellite-chalcocite mineral group. Higher Fe contents are determined in Tran-Urals sulfides (Table 3). Here, the average Fe contents reached 1–3 wt. % (up to 22 wt. % in some cases) in sulfides of samples in the Kamenny Ambar, Konoplyanka, and Katzbakh 6 settlements and slags from Kazakhstan (Sarlybay 3, Taldysay). In copper sulfides of Cis-Urals slags, Fe contents are lower, comprising 0.1–0.5 wt. % on average.

Arsenic (As) is an important element used to alloy copper in Eurasia [1]. Arsenic in natural objects is confined to sulfide ores of different genesis located in ultramafic rocks. According to arsenic contents in sulfides (Figure 3, Table 3), four 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 sulfides from Cis-Urals settlements is confined to the second group and contains arsenic up to 30–200 ppm. Sarlybay 3 slag sulfides can also be added for which the ore source is Sarlybay volcanogenic massive sulfide (VMS) deposit in basalts.

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

Concentration, wt. %			**Concentration, ppm**													
Cu	**Fe**	**S**	**Co**	**Ni**	**As**	**Zn**	**Mo**	**Se**	**Ag**	**Sn**	**Sb**	**Te**	**Ba**	**Pb**	**Bi**	**U**
			0.1 †	0.15 †	0.50 †	5.0 †	0.15 †	8.0 †	0.10 †	1.0 †	0.2 †	3.0 †	0.3 †	0.4 †	0.15 †	0.1 †
Kamenny Ambar (63 analyses)																
49.4–73.7 62.8 (62.9)	0.30–22.6 3.4 (1.5)	24.3–39.7 33.5 (34.1)	3.73–319 88.0 (47.5)	<0.09–16.8 3.2 (2.1)	<1.5–19.6 4.1 (1.9)	<2.9–1720 102 (17.3)	<0.36–133 15.5 (6.7)	1003–9200 2818 (2686)	0.85–78.7 9.3 (5.6)	<1.5–229 7.9 (1.1)	<0.40–1.13 0.2 (0.2)	3.10–39.0 12.5 (10.0)	<0.14–841 29.2 (1.6)	<0.45–4.80 0.6 (0.4)	<0.20–5.51 1.0 (0.6)	<0.12–17.3 1.5 (0.2)
Konoplyanka (32 analyses)																
62.0–73.0 65.5 (65.4)	0.29–4.57 1.1 (1.0)	25.3–36.5 32.6 (33.2)	1.18–144 33.6 (36.4)	0.23–8.81 3.3 (3.0)	<0.32–82.1 8.8 (1.3)	<1.1–55.0 7.7 (5.7)	0.30–55.0 5.8 (1.1)	1745–7100 5064 (5145)	3.57–33.5 12.4 (10.9)	<0.46–44.4 2.9 (0.4)	<0.2	6.90–49.8 29.7 (29.1)	<0.12–110 13.6 (1.9)	<0.42–1.67 0.7 (0.5)	<0.08–1.38 0.4 (0.3)	<0.03–14.8 2.0 (0.4)
Ustye (7 analyses)																
33.7–86.2 66.3 (73.1)	0.03–49.8 12.9 (0.4)	1.18–19.0 8.0 (7.8)	2.30–732 224 (88.6)	52.9–2400 701 (480)	0.64–35.7% * 12.7% (12.8%) *	<1.0–370 64.6 (10.0)	<1.6–38.7 12.9 (1.7)	40.0–186 110 (124)	26.0–168 74.3 (51.0)	<1.0–109 37.9 (23.2)	10.0–678 327 (382)	<2.6–102 32.7 (20.0)	0.49–49.0 20.0 (9.9)	1.41–57.0 21.4 (9.0)	0.19–53.1 24.6 (22.7)	<0.22–5.63 3.0 (3.2)
Katzbakh 6 (30 analyses)																
44.5–78.0 61.1 (59.3)	0.03–21.9 3.8 (2.9)	20.8–41.6 35.0 (35.8)	0.48–63.9 8.2 (6.0)	0.28–31.8 2.9 (1.5)	<3.2–122 20.7 (3.0)	<0.8–234 28.8 (11.6)	<0.26–168 39.3 (27.6)	<4.0–46.9 19.5 (17.0)	24.1–1396 330 (224)	<1.17	0.57–1.80 1.2 (1.1)	<1.6	12.5–28,100 3393 (590)	<0.58–6010 250 (8.1)	<0.12–2.01 0.4 (0.3)	<0.10–11.0 1.8 (0.6)
Ordynsky Ovrag (47 analyses)																
49.8–84.1 71.3 (70.9)	0.00–3.50 0.8 (0.4)	15.0–49.0 27.7(28.0)	0.48–25.4 6.95 (6.55)	<0.3–124 10.3 (5.30)	3.00–610 76.8 (50.0)	<5.0–1590 117 (27.0)	0.21–74.0 13.3 (4.4)	12.0–107 51.2 (50.0)	8.30–840 167 (133)	<1.5	0.40–42.5 6.2 (4.7)	<10.0	0.31–790 75.9 (37.0)	9.50–683 172 (163)	<1.4–3.20 1.0 (0.8)	<0.08–17.3 1.1 (0.1)
Turganik type 1 (9 analyses)																
54.8–76.3 64.2 (56.7)	0.23–13.86 7.1 (11.1)	23.1–32.6 28.4 (30.8)	9.00–61.4 31.0 (38.4)	3.80–213 76.0 (88.7)	872–4150 1946 (1963)	<1.0–106 36.9 (30.0)	0.38–11.8 3.2 (2.1)	969–1681 1279 (1392)	102–232 155 (126)	<1.14–3.38 1.5 (1.3)	0.91–9.00 3.3 (2.6)	15.3–68.8 26.2 (20.3)	<0.26–5.60 1.6 (1.4)	2.08–10.8 6.5 (8.3)	0.31–4.62 1.3 (0.9)	<0.37–2.43 0.8 (0.5)
Turganik type 2 (17 analyses)																
71.4–80.8 77.1 (78.2)	0.01–5.60 0.7 (0.2)	19.1–28.1 22.2 (21.2)	<0.1–8.50 1.9 (1.2)	0.21–28.3 4.9 (1.6)	12.0–207 91.6 (88.2)	<1.3–99.0 23.9 (7.1)	1.94–125 17.4 (7.2)	21.8–157 58.5 (43.0)	82.6–757 234 (163)	<0.6–8.10 1.2 (0.6)	<0.12–8.40 1.6 (1.2)	<2.2	1.58–6600 527 (9.5)	0.54–210 44.3 (19.9)	<0.16–7.10 0.8 (0.2)	<0.16–9.40 1.8 (0.1)
Tokskoe (24 analyses)																
50.6–83.6 68.5 (71.0)	0.00–10.5 3.6 (1.5)	16.1–40.0 27.7 (27.4)	0.20–34.4 7.8 (5.6)	0.30–117 8.7 (1.9)	6.35–136 30.1 (22.1)	<1.0–557 72.2 (9.8)	1.72–598 121 (63.9)	34.6–936 332 (143)	35.5–2380 509 (296)	<0.87–1.90 0.5 (0.4)	<0.44–14.4 1.9 (0.9)	<2.8	9.40–6600 534 (106)	1.90–624 182 (165)	<0.12–3.80 0.5 (0.2)	<0.15–39.0 4.1 (0.2)
Ivanovskoe (75 analyses)																
52.6–83.9 74.5 (76.9)	0.00–13.4 1.2 (0.1)	15.8–35.2 24.2 (22.8)	<0.15–68.7 6.2 (0.5)	0.28–60.7 7.1 (2.8)	4.70–247 54.6 (41.7)	<1.4–263 25.1 (4.1)	0.26–265 25.1 (11.1)	8.00–1026 206 (82.5)	24.5–994 288 (228)	<0.4–2.42 0.5 (0.4)	<0.26–8.60 1.6 (1.1)	<3.2	<0.15–48,500 1285 (15.3)	0.78–452 35.4 (10.4)	<0.12–1.60 0.2 (0.2)	<0.08–146 8.0 (0.3)
Bulanovskoe 2 (19 analyses)																
67.2–76.8 71.3 (70.0)	0.01–2.89 0.5 (0.1)	23.1–32.2 28.1 (28.2)	<0.05–4.89 1.2 (0.4)	0.57–38.3 5.9 (3.4)	5.70–94.1 45.2 (47.6)	<3.3–36.0 10.3 (5.3)	1.92–101 17.1 (9.6)	<4.4–201 123 (133)	111–492 261 (225)	<0.59–2.04 0.7 (0.7)	<0.1–3.20 0.8 (0.7)	<2.4	<0.23–1286 190 (2.6)	1.70–114.4 29.9 (22.1)	<0.16–1.60 0.2 (0.1)	0.16–9.00 1.1 (0.5)
Kuzminkovskoe 2 (4 analyses)																
75.7–83.9 78.8-77.9	0.11–0.60 0.3 (0.2)	14.9–23.7 20.5 (21.8)	0.49–5.69 2.2 (1.4)	14.0–75.0 38.0 (31.5)	274–778 562 (598)	<8.0–30.0 12.2 (9.4)	2.37–55.3 25.7 (22.5)	371–1328 867 (884)	53.1–4680 2109 (1852)	<1.0	5.60–14.7 8.0 (5.9)	<3.2	1.63–1850 631 (337)	7.50–19.0 14.2 (15.2)	<0.22–0.79 0.3 (0.2)	4.20–9.90 6.6 (5.8)

Table 3. *Cont.*

Concentration, wt. %			Concentration, ppm													
Cu	**Fe**	**S**	**Co**	**Ni**	**As**	**Zn**	**Mo**	**Se**	**Ag**	**Sn**	**Sb**	**Te**	**Ba**	**Pb**	**Bi**	**U**
			0.1 [†]	0.15 [†]	0.50 [†]	5.0 [†]	0.15 [†]	8.0 [†]	0.10 [†]	1.0 [†]	0.2 [†]	3.0 [†]	0.3 [†]	0.4 [†]	0.15 [†]	0.1 [†]
Pokrovskoe (20 analyses)																
68.0–80.0 75.9 (76.4)	0.04–3.13 0.5 (0.2)	19.9–30.3 23.5 (23.2)	<0.05–26.8 3.0 (1.2)	0.47–164 25.4 (9.9)	1.00–163 28.9 (20.8)	<3.3–2180 194 (13.0)	0.27–38.0 7.5 (2.3)	<24.1–631 91.6 (45.4)	0.73–266 59.6 (49.2)	<1.2–4.10 1.7 (1.6)	<0.27–9.10 2.4 (1.5)	<1.6	<1.3–24,900 1864 (72.3)	0.37–638 54.2 (28.8)	<0.25–3.07 0.5 (0.1)	<0.10–53.2 5.4(0.6)
Rodnikovoe type 1 (23 analyses)																
63.0–77.9 72.9 (74.0)	0.01–0.13 0.04 (0.03)	22.0–36.9 27.0 (25.9)	<0.18–6.09 0.9 (0.4)	<0.11–64.0 11.1 (6.4)	5.90–114 29.7 (17.1)	<9.0–29.0 11.2 (9.6)	3.21–378 43.4 (15.7)	<3.6-467 142 (154)	19.9-818 287 (243)	<1.1–6.15 0.8 (0.5)	<0.8–4.30 1.3 (1.0)	<3.1	<0.56–1019 142 (17.8)	2.11–26.8 10.5 (10.9)	<0.33–2.20 0.5 (0.3)	<0.08–4.16 0.6 (0.4)
Rodnikovoe type 2 (4 analyses)																
31.4–82.2 63.4 (70.0)	0.46–32.0 8.4 (0.5)	17.0–36.6 28.0 (29.2)	0.59–56.0 14.9 (1.5)	0.46–124 44.6 (27.0)	548–3010 1467 (1155)	1.00–580 197 (11.2)	4.10–256 90.9 (51.8)	215–242 229 (229)	187–2779 1103 (722)	<1.4–22.5 6.9 (2.2)	12.9–196 71.9 (39.4)	<4.6	146–86,000 24,097 (5120)	130–810 453 (436)	<0.16–1.10 0.5 (0.1)	2.00–196 56.9 (14.8)
Sarlybay 3 (23 analyses)																
55.5–78.1 73.2 (75.2)	0.06–19.6 3.8 (1.3)	14.3–28.4 22.9 (22.7)	2.35–299 58.7 (27.1)	0.31–115 14.6 (2.9)	5.70–162 35.8 (15.6)	3.50–446 83.0 (38.6)	<1.1–11.8 1.5 (0.1)	360–2440 1640 (1920)	2.18–375 28.1 (7.7)	<3.3–131 10.8 (2.9)	<0.11–4.50 0.9 (0.3)	<2.0–49.0 11.1 (4.4)	1.00–2.10 1.6 (1.6)	<0.67–31.6 6.8 (2.1)	<0.35–8.20 2.7 (1.5)	<0.08–3.44 0.5 (0.2)
Taldysay (29 analyses)																
31.4–82.8 63.4 (64.2)	0.45–24.1 4.4 (2.6)	0.60–43.0 22.4 (22.1)	6.24–1626 247 (73.4)	1.06–1451 249 (40.0)	0.24–45.5% * 10.7% (2.53%) *	<4.7–1010 147 (38.5)	<0.7–7.00 2.77 (2.59)	45.0–2550 317 (233)	16.5–1981 256 (130)	0.79–4460 371 (27.6)	0.32–138 30.8 (17.6)	<2.0	<0.45–698 56.7 (14.6)	83.4–45,300 5292 (2060)	0.20–800 115 (22.2)	<0.05–17.2 4.4 (3.5)

Note: [†] values of limit of detection (LOD, ppm). The first underlined line is the limit of value; the second line is the average value (median values in brackets). “<”—values less than limit of detection. *—values by wt. %.

According to arsenic contents of 300–5000 ppm, the third sulfide 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 high contents arsenic more than 0.5% is represented by special alloying addition arsenic minerals in slags. Copper arsenides often occur in a view of inclusions in copper droplets. These include samples from the Ustye and Taldysay.

Se replaces sulfur in minerals. In natural objects, Se is confined to the oxidized zone of VMS deposits in basalt-rhyolite and ultramafic complexes. Three main groups are subdivided according to their Se content. Low-selenium sulfides 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 sulfides, 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 sulfides of slags and are subdivided into three 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 sulfides 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). Sulfides from Kamenny Ambar, Konoplyanka, and Sarlybay are related to high-cobalt (more than 20 ppm) and low-nickel groups. Natural slags from Ustye, Rodnikovoe, and Taldysay, as well as those artificially-doped by arsenic, are related to high-cobalt and high-nickel sulfide groups; this also applies to Cr-rich spinel-containing olivine Turganik slags.

Despite ranging widely in terms of its contribution to the contents of sulfides, Ag can also serve as an indicator mineral. The studied slags are subdivided into two main types in terms of their Ag content. Low-silver sulfides 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 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 sulfides and barite inclusions. A low Ba content (<50 ppm) is typical for sulfides 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 characterized slags with a Ba content exceeding 0.5%, which probably indicates the addition of barite fluxes in charges.

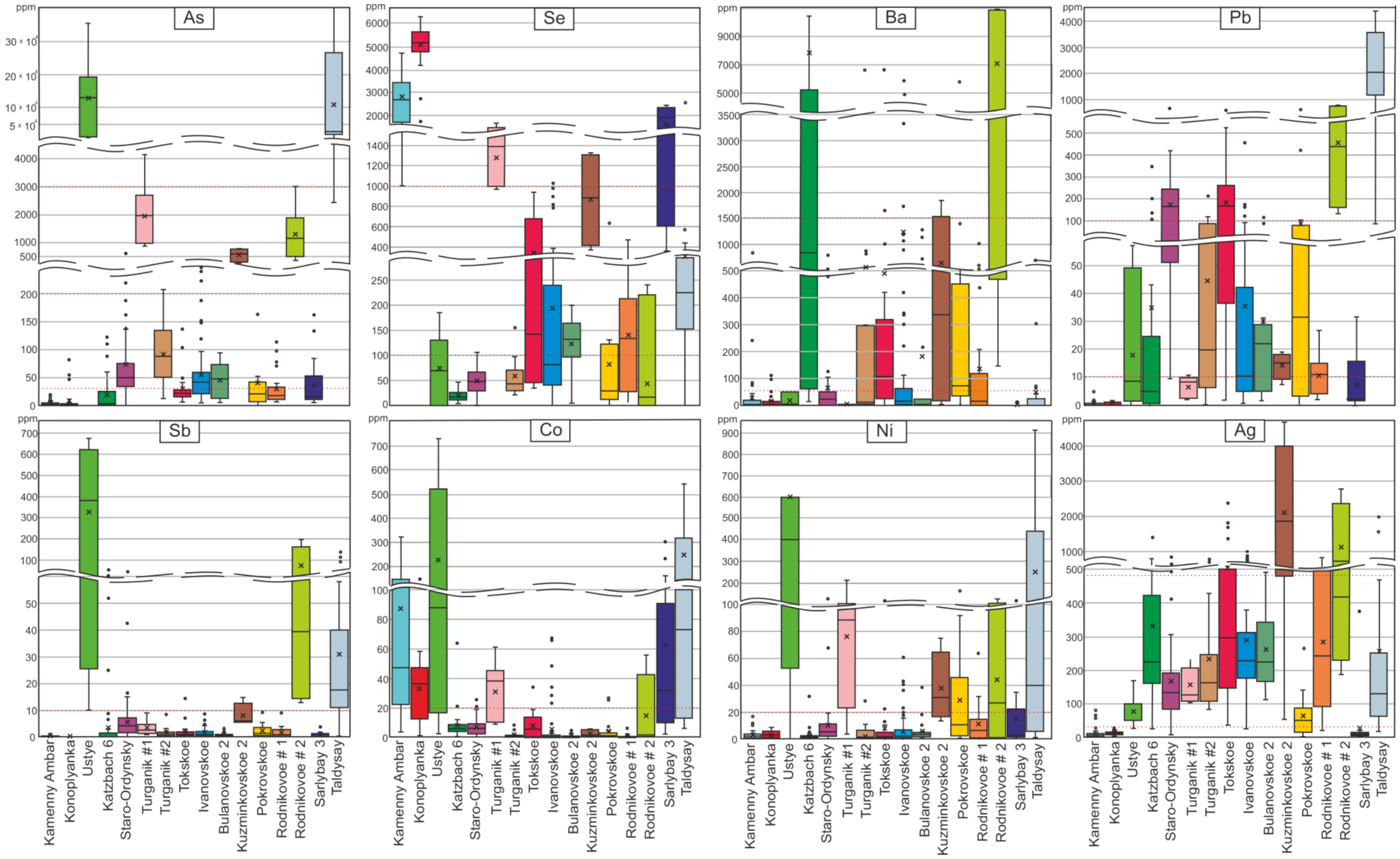

Figure 3. Box-and-whiskers diagram showing the scatter of the values of some trace elements in Bronze Age slag sulfides of the South Urals and Kazakhstan.

The lowest values of Pb not exceeding 10 ppm are typical for Kamenny Ambar, Konoplyanka, and 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 sulfides 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 sulfides 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 sulfides 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 sulfides from the Tokskoe and Rodnikovoe settlements reached up to 600 ppm.

Although Cr generally appears in slag sulfides 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 sulfides 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, Cd, In, Au, and Hg) contents, as well as the majority of lithophile elements, are minor and, consequently, cannot serve as indicators.

Thus, several archaeological site groups differ in the composition of copper sulfides in slags. The first group is represented by sulfides with high contents of Co, Ni, Sb, and As, including slags from Ustye, Kuzminkovskoe 2, Taldysay, Turganik type 1, and Rodnikovoe type 2 (Table 3). The second group is represented by high contents of Se and Co in copper sulfides, including slags from Kamenny Ambar, Konoplyanka, and Sarlybay 3 sites. The third group is represented by slag with high contents of Ag, Pb, and Ba, including Katzbach 6 and most of the Cis-Urals sites (Ordynsky Ovrag, Turganik, Tokskoe, Ivanovskoe, Bulanovskoe 2, Pokrovskoe, Rodnikovoe).

5. Discussion

5.1. Mineralogical Criteria

The mineralogical and geochemical criteria of sulfide 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 oxidized 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 sulfide inclusions found in several slag types of the Urals and Kazakhstan indicates that the usage of sulfide 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 population. This is associated with a shift in the proximity of raw material sources and the increased sizes of melted ingots [56]. The findings of Early Yamna slags are singular rare due to the nomadic lifestyle of the communities. Turganik slag is one isolated evidence of metallurgy of this time [4]. Cr-rich containing olivine slags with high arsenic content and an absence of sulfides also prevailed in Sintashta culture [5]. Sulfide ores were not used before Alakul time.

According to our data, covellite-chalcocite ores with rare bornite inclusions were predominantly used in Urals since Srubno-Alakul communities. Secondary copper sulfides are widespread in the supergene enrichment zone of many copper deposits of the Urals and Kazakhstan—VMS, skarn, and quarts-sulfide types [57]. In Cis-Urals, sulfides were used particularly intensively 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 sulfide smelting technology, concretion ores of cupriferous sandstones became the main ore sources of the Srubna culture. As a result, the majority of the Cis-Urals slags contains sulfide inclusions. In Trans-Urals, the usage of sulfides was not so common because of the deeper ore level and absence of large sulfide mineralization in a near-surface zone. Accordingly, only a few settlements contain fragments of sulfide droplets typical for the Alakul and Final Bronze Age cultures.

If covellite-chalcocite ores contain bornite, this mineral also appears in slags. However, no special application of bornite ores was recorded. Although bornite content in slags is a relict, 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. The common raw material source has not been identified to-date for these slags. 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, sulfide deposits are not in evidence. The ancient mine of Vorovskaya Yama, which hosts ultramafic ores, 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 the 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 was in the slag due to its rare inclusions in covellite-chalcocite ores of Jezkazgan cupriferous sandstones.

5.2. Geochemical Criteria

Due to their greater diversity, geochemical criteria of slag sulfides can accurately reflect the raw material sources and alloying additions with a full range of geochemical characteristics (Figure 4). In archaeometry, As in one of the main element-markers in the Bronze Age copper industry [59,60]. There are debates about the boundaries of natural alloying or deliberated mixtures in arsenic 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 sulfide inclusions [62]. In natural objects, arsenic is often confined to hydrothermal sulfide ores located in ultramafic rocks. Slag sulfides 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 sulfide-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 mineralization. These samples are typical for Ustye and Taldysay settlements.

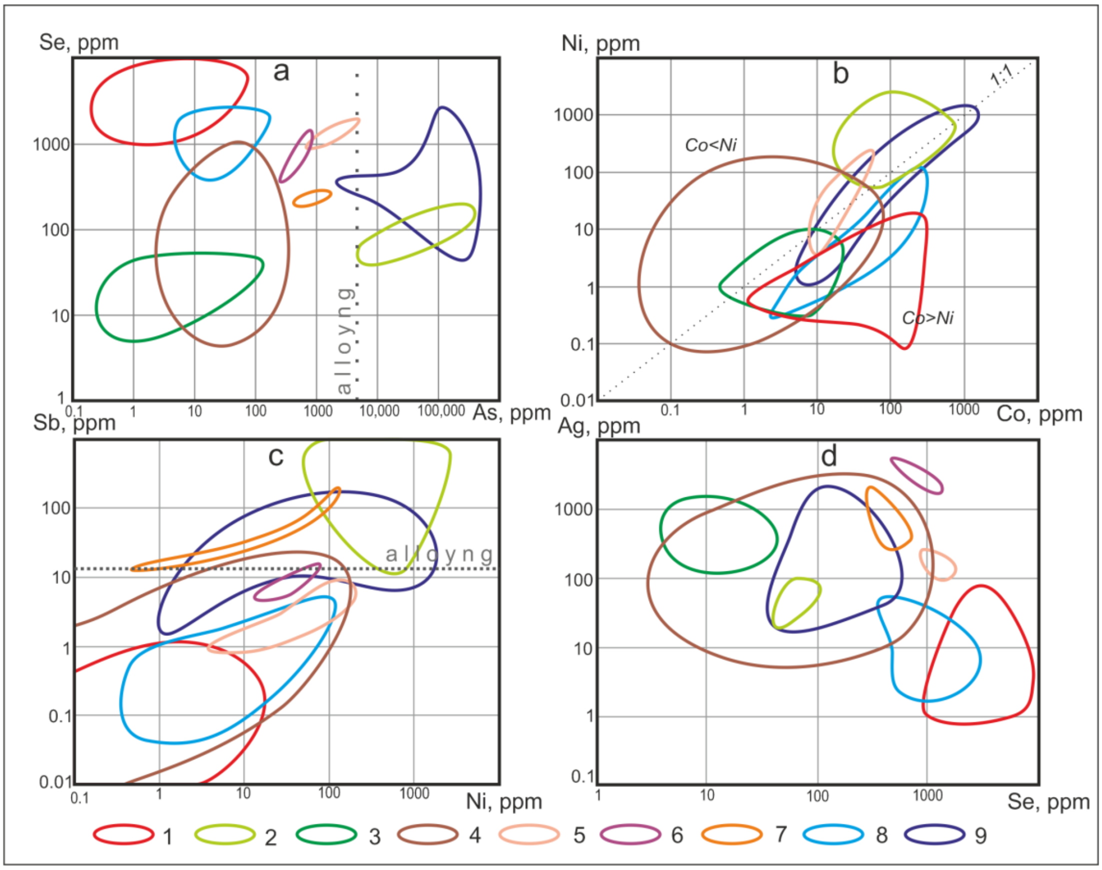

Figure 4. Relation diagram of some trace elements in Bronze Age slag sulfides of the South Urals and Kazakhstan: 1—Kamenny Ambar and Konoplyanka; 2—Ustye; 3—Katzbakh 6; 4—Ordynsky Ovrag, Tokskoe, Ivanovskoe, Bulanovskoe 2, Pokrovskoe, Turganik type 2 and Rodnikovoe type 1; 5—Turganik type 1; 6—Kuzminkovskoe 2; 7—Rodnikovoe type 2; 8—Sarlybay 3; 9—Taldysay. (**a**) As vs Se ratio; (**b**) Co vs Ni ratio; (**c**) Ni vs. Sb ratio; (**d**) Se vs Ag ratio.

The elevated arsenic contents in slag sulfides testify that the alloying occurs immediately, together with the primary smelting of copper from ores. Zinc and tin contents are low and uneven in slag sulfides that are caused by the natural addition of these elements in covellite-chalcocite, and 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. 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 sulfides, 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 sulfides from Cyprus-type VMS deposits [64]. However, the main enrichment with Se of secondary sulfides from the majority of deposits is caused by supergenesis [57]. In slag sulfides 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 mineralization 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 sulfide containing glassy slags from the Kuzminkovskoe 2. 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 sulfides (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 sulfides from the 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 sulfides are clearly divided into several groups having different sources of copper according to the Se–As ratio (Figure 4a).

Cobalt, nickel, and antimony often correlate with each other and As. In sulfides of non-alloying slags, the higher contents of these trace elements are related to sulfide-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 sulfides from the 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 sulfides. Elevated Sb levels mark the deliberate alloying of slag by As (Figure 4c).

The elevated contents and correlation of Ag, Pb, and Ba in sulfides are typical for the majority slags of archaeological settlements confined to the Cis-Urals. The typical mineralization is confined to microinclusions in ores and concretions of native Ag, galena, and barite. Pb, Ag, and Ba are typical for all glassy sulfide-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 utilization of sulfide concretions from cupriferous sandstone ores.

Similar mineralization 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 sulfides of cupriferous sandstones, where its presence can be found in slag sulfides and copper ingots. Pb is also a widespread element in slags from 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 sulfides (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 sulfide-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 specialization are recorded in the composition of sulfides from the oxidation zone.

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

Formation	**Basalt Volcanogenic Rocks**				**Ultrabasic Rocks**			**Sedimentary Rocks**
Deposits Type	**Volcanogenic Massive Sulfide (VMS)**	**Skarn Copper**	**Porphyry Copper**	**Quartz Vein**	**VMS**	**Skarn Copper**	**Quartz Vein**	**Copper Sandstone**
Marker elements	Co, Se, Te				As, Co, Ni			Ag, Pb
Additional elements	+Zn ±Ba	+Fe	±Mo ±B	+Ag ±Au	±Sb	+Fe	+Ag ±Au	±Ba ±Bi
Deposits	Bakr-Uzyak, Sarlybay, Shuuldak	Novonikolaevskoe, Mikheevskoe, Gumeshevskoe	Elenovskoe, Ush-Katta	Nikolskoe, Kichigino	Ishkinino, Dergamysh, Shanshar	Novotemirskoe, Vorovskaya Yama	Tash-Kazgan	Kargaly ore field (and Cis-Urals), Jezkazgan ore field
Ore sources for copper slags of archaeological sites	Sarlybay 3	Kamenny Ambar, Konoplyanka	-	Katzbach 6	Turganik	Ustye Kuzminkovskoe 2	-	Turganik, Ordynsky Ovrag, Tokskoe, Ivanovskoe, Bulanovskoe 2, Pokrovskoe, Rodnikovoe, Kuzminkovskoe 2, Taldysay

6. Conclusions

The sulfide-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 a significant amount of sulfide in different types from the Early to Late Bronze Age indicates that ancient metallurgists from the Urals and Kazakhstan had been using sulfide 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 sulfides obtained from the various settlements show different ore mineralization in volcanogenic (VMS, Cu-porphyry, skarn, and quartz-veined), ultramafic (VMS, skarn, and quartz-veined), and sedimentary complexes (cupriferous sandstones). Both sulfide assemblages and their trace elements can potentially be used as markers for ancient slags. Sulfides from the oxidation zones of deposits confined to ultramafic rocks contain Co-Ni-As minerals. These mines were the sources of raw materials for Cr-rich spinel containing olivine slags of Sintashta settlements and sulfide-containing 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 sulfide-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 sulfides from sedimentary complexes of cupriferous sandstones are Ag and Pb accompanied by relatively low amounts of other elements. These include slag sulfides 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 the Taldysay settlement related to ores from another cupriferous sandstone type. Sulfides 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 sulfide 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. In the future, we plan to study trace elements of slag copper inclusions and define the trace elements repartition from sulfides to copper droplets.

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