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Bronze Age metallurgical slags from the South Urals: types, mineralogy and copper sources

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ABSTRACT

In the paper, an investigation of copper metallurgical slags found in the South Urals and dating to the Bronze Age between 4,000 and 1,300 BCE is presented. Four main mineralogical types are distinguished according to their mineral composition: Cr-rich-spinel-containing olivine, sulphide-containing olivine, sulphide-containing glassy and pyroxene type. The first slag type is composed of zoned olivine, magnetite and glass having relicts of Cr-rich spinels and serpentinites that indicate the use of azurite-malachite ores from ultrabasic rocks. These finds, determined in sites of the Early Yamna period in the Cis-Urals, are widespread in Sintashta culture. The second type, composed of skeletal olivine crystals, magnetite and wüstite with copper sulphide droplets, belongs to the Alakul period. Its raw material sources consist of sulphide ores from a secondary enrichment zone of volcanogenic massive sulphide (VMS), skarn and Cu-porphyry deposits. The sulphide-containing glassy type, primarily composed of glass with copper and sulphide droplets, is obtained from slags recovered in Srubna cultural sites. Here, the raw material sources were rich sulphide ores of cupriferous sandstones. The pyroxene type is composed of augite, pigeonite and/or wollastonite with a small amount of glass and sulphide inclusions. According to the composition of glass, slags can be distinguished into the Cis-Uralian type, including cupriferous sandstones, and the Trans-Uralian type having various volcanogenic-hydrothermal deposits as raw materials. Essential Ca, P, Ba and REE impurities in slag glass demonstrate the use of barite, calcite and bone fluxes. The phase diagrams, crystallisation temperatures and experimental data revealed that slag melt temperatures ranged between 1150-1300 °C.

Keywords: slags; Bronze Age; South Ural; copper; olivine; ancient mine.

INTRODUCTION

During the period 4,000-1,300 BCE, the South Urals comprised an important mining and metallurgical region of Eurasia. Several dozen copper deposits discovered in this area have been long exploited from the Early Bronze Age to the Iron Age (Chernykh, 1970). The copper ore exploration, metallurgy and manufacture of copper and bronze items are related to major arenas of the life and activity of the ancient communities. On the basis of archaeological excavations of settlements and burials, the large number of artifacts related to the mining and metallurgical activity was recovered as follows: ore fragments, metallurgical slags, metallic ingots, scraps, moulds, crucibles, as well as finished copper and bronze items (Vinogradov, 2013; Koryakova and Epimahov, 2007; Epimakhov and Berseneva, 2016). The first fundamental researches dedicated to the Bronze Age metallurgy in the Urals using natural scientific methods are described in the papers of E.N. Chernykh (Chernykh, 1970; Chernykh and Kuzminykh, 1989). These studies were focused on analysing the chemical composition of metallic items by atomic emission spectroscopy to determine possible sources of ore material. This particular research direction evolved largely due to the work of S.V. Kuzminykh and A.D. Degtyareva, who identified several paleometal groups using atomic emission spectroscopy to examine metallic items produced by cultures associated with different time periods (Chernykh et al., 2002; Degtyareva, 2010). A key contribution to the study of the Bronze Age moulding and malleating operations carried out in the South Urals based on metallographic analysis was made by A.D. Degtyareva (2003, 2010). S.A. Grigoriev (Grigoriev, 1999; Grigoriev et al., 2005; Grigoriev, 2016) began the ongoing examination of the Bronze Age metallurgical slags of the Trans-Urals using analytical methods. These researchers focused on the presence of Cr-rich spinels from ultrabasic rocks in slags. The samples from the Cis-Urals sites were examined by S.V. Kuzminykh (Chernykh et al., 2004) on the example of the large Gorny 1 Bronze Age settlement located in the area of the Kargaly mines using scanning and electron microscopy, as well as X-ray fluorescence analysis. The indicator minerals in slags, metals and melt inclusion structures of copper and bronzes are described by the group of Institute of Mineralogy SU FRC MG UB RAS supervised by V.V. Zaykov (Zaykov et al., 2012; Zaykov et al., 2013a; Zaykov et al., 2018). In recent works, scanning electron microscopy and LA-ICP-MS methods have been effectively used for mineralogical and geochemical research into ancient slags from archaeological sites of the Urals and Kazakhstan (Ankushev et al., 2020; Artemyev et al., 2018). The ancient mines in the oxidation zones of Main Uralian Fault deposits were examined in detail by V.V. Zaykov and colleagues (Zaykov et al., 2012), while the Mugodzhary mining and metallurgical centre (MMC) was studied by A.M. Yuminov (Yuminov et al., 2013).

The slag finds are of key importance to studying the ancient development of metal manufacture since, in most cases, they are confined to the archaeological cultural layer in which context they were produced. Moreover, the mineral composition and geochemical peculiarities of such slags allows a compositional identification of the ore protolith to be carried out along with a determination of the technological parameters and conditions of metallurgical manufacturing including temperatures, applicable reagents and fluxes, as well as metals that were directly smelted by these means. The geochemical features of relic minerals in slags indicate the types of mineral deposits, as well as, in some cases, a specific location of the raw material source. The study of these artifacts using high-precision analytical methods allows the reliable identification of the ore deposit types mined in ancient times, as well as features of metallurgic and manufacturing processes (Hauptmann, 2007; Addis et al., 2016).

While various archaeological features of numerous sites from the South Urals have been examined in detail, studies of the mineralogical and geochemical compositions of metallurgical slags from many sites have either been studied sporadically or are absent. The focus of this research paper is therefore to consider the metallurgical and technological peculiarities of ancient metallurgy throughout the Bronze Age using slags obtained from the South Urals archaeological sites. To solve this problem, we studied and typified samples from 11 settlements and ancient mines of the Bronze Age using various analytical methods. The tasks consisted of recording similarities and differences between mineralogical and geochemical peculiarities of metallurgical slags, as well as determining the conditions of formation and identifying the sources of raw material using ore relics reagents and fluxes used in Bronze Age metallurgy in the South Urals.

MATERIALS AND METHODS

The slag samples were collected by L.N. Koryakova from the Institute of History and Archaeology UB RAS (Ekaterinburg, Russia), N.B. Vinogradov, I.P. Alaeva, P.S. Medvedeva from Laboratory of archaeological researches of South-Urals State Humanities-Pedagogical University (Chelyabinsk, Russia), F.N. Petrov from State Historical and Cultural Arkaim Reserve Museum (Chelyabinsk, Russia), S.V. Bogdanov from Institute of Steppe UB RAS (Orenburg, Russia), N.L. Morgunova from Orenburg State Pedagogical University (Orenburg, Russia), and I.V. Chechushkov from Pittsburgh University (USA).

X-ray fluorescence analysis was used to identify significant impurities in slags, including Cu, As, Zn, Sn, Pb, Au, Ag, etc., as well as to divide them into geochemical groups for further studies. The analysis was performed by means of a portable INNOV-X α-4000 XRF Analyzer (operators M.N. Ankushev and I.A. Blinov; Soil and Process Analytical mode; exposure 30 s) The bulk X-ray phase analysis of powdered metallurgical slags was performed with a SHIMADZU XRD-6000 diffractometer equipped with Cu-anode and graphite monochromator; impurity contents were calculated using the Rietveld method in SIROQUANTV4 software (operator P.V. Khvorov).

Electron microscopy was used to examine the chemical compositions of the main minerals in slags, glasses, mineral and melt inclusions. The chemical composition of olivines, glasses and Cr-rich spinels was determined using a TescanVega 3 SBU scanning electron microscope equipped with EDA Oxford Instruments X-act (accelerating voltage-20 kV; absorbed current at the Co reference-260 pA; counting time for a peak -120 s; dead time-10-15%; operator I.A. Blinov). In addition, the chemical composition of Cr-rich spinels was identified using a JEOL-733 electron microscope (chromite standard - 79/62; accelerating voltage - 20 kV; probe current-30 pA; operator-E.I. Churin). For the quantitative analysis, we used the following standards: Micro-Analysis Consultants LT, Ltd.; X-ray microprobe standards (S/N 1362); Astimex Scientific Ltd.; MINM25-53; Mineral Mount (S/N 01-044). The structural formulae were calculated using stoichiometric quantities of oxygen and sulphur in the corresponding minerals. The glass component ratios were calculated according to the average compositions with an error of 61 formula units owing to the variety of component ratios during melting.

The chemical compositions of slags were obtained using the standard complexonometric titration method with EDTA (operators-M.N. Malyarenok, T.V. Semenova) in the South Urals Centre of Collective Usage for Mineral Material Study (Miass). The trace element compositions were determined using ICP-MS (operator K.A. Filippova). The slag samples were decomposed in an acidic environment with a SpeedWave microwave dissociation system (Berghoff, Germany) during two-stage 40 min heating up to 180 °C in an HF-HCl-HNO_3 mixture. The prepared solutions were examined with an Agilent 7700x inductively coupled plasma mass spectrometer calibrated using the standard multi-element solutions for a full mass scale of analysed elements. The BCR-2 international basalt standard was used to control the quality of the chemical analysis.

The trace elements in olivines 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 a frequency-quadrupled (wavelength 213 nm) Nd:YAG UV source, having fluence settings of 10-12 J/cm^2 for olivines. The cell carrier gas (He) had 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 of 1.0 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 of 40-110μm diameter and frequency of 10 Hz. The element contents were calibrated against reference material NIST SRM-612, USGS BCR-2g, USGS GSD-1g using ^{25}Mg and ^{29}Si as the internal standard for olivines.

ARCHAEOLOGICAL SITE

In the settlements of the South Urals and Kazakhstan, finds of copper slags have been the subject of extensive research (Chernykh and Kuzminykh, 1989; Koryakova and Epimakhov, 2007, etc). Three large Bronze Age mining and metallurgical centres are distinguished in the South Urals (Chernykh, 1970; Zaykov et al., 2013a) (Figure 1):

The Cis-Urals MMC contains numerous cupriferous sandstone deposits exploited by the mobile pastoralists of the Early Yamna culture during the Early Bronze Age (4000-3000 BCE) (Bogdanov, 2004; Morgunova, 2014; Bogdanov, 2017; Bogdanov et al., 2018). During the Late Bronze Age, members of the pastoralist Srubna and Alakul cultures exploited the southern cupriferous sandstone deposits (Chernykh et al., 2002; Kuptsova et al., 2018) (Figure 2).

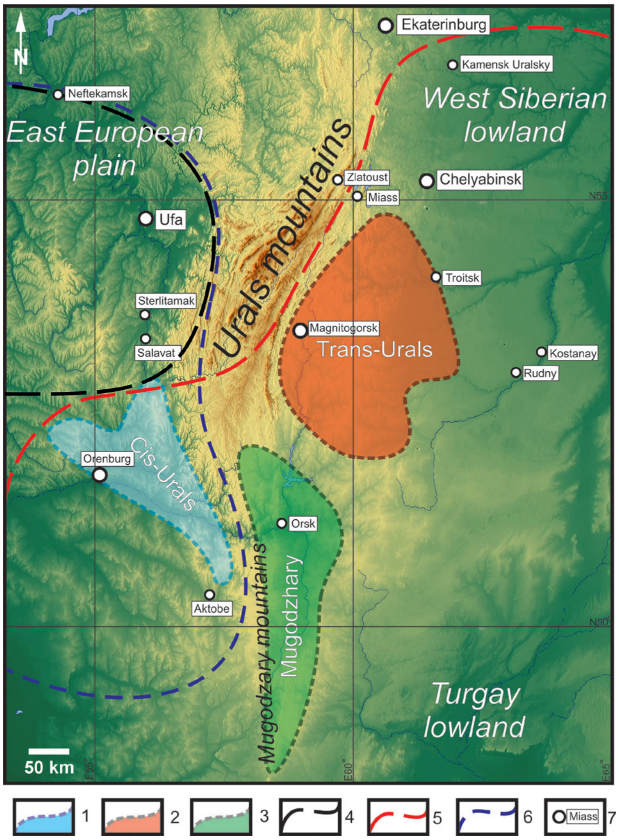

Figure 1. The basic cultures and metallurgical centers spread scheme in the Middle and Late Bronze Age of South Urals and Mugodzhary: 1 - Cis-Urals Mining Metallurgical Center (Bogdanov et al., 2018); 2 - Trans-Urals Mining Metallurgical Center and the spread of Sintashta culture (Zaykov et al., 2013; Koryakova and Epimahov, 2007); 3 - Mugodzary Mining Metallurgical Center (Yuminov et al., 2016); 4 - spread of Urals Abashevo culture (Gorbunov et al., 1986); 5 - spread of Alakul culture and to the east (Zdanovich, 1988); 6 - spread of Srubna culture and to the west (Chernykh et al., 2002); 7 - modern cities.

The Trans-Urals MMC is associated with oxidation zones of volcanogenic massive sulphide (VMS), skarn and Cu-porphyry deposits in volcanic and ultrabasic rocks. Researchers have distinguished several stages of deposit exploration as follows: Sintashta (2000-1700 BCE) (Koryakova and Epimahov, 2007), Alakul (1700-1200 BCE) (Hanks et al., 2005) and final Bronze Age cultures (Koryakova and Epimahov, 2007) (Figure 2).

The Mugodzhary MMC is the most recently investigated region. Although the northern group of mines has most likely been exploited since the Early Bronze Age by the bearers of Yamna culture, the most extensive mining of the ophiolite ore mineralisation of oxidation zone of numerous VMS, skarn and Cu-porphyry deposits (Yuminov et al., 2013) was carried out during the Late Bronze Age by bearers of the Alakul culture (Tkachev, 2017).

Further brief archaeological background is given to understand the geographical, cultural and historical context of the studied slags.

The Early Yamna culture of the Early Bronze Age (4000-3300 BCE) is the earliest important metal-producing pastoral archaeological culture of the Eastern

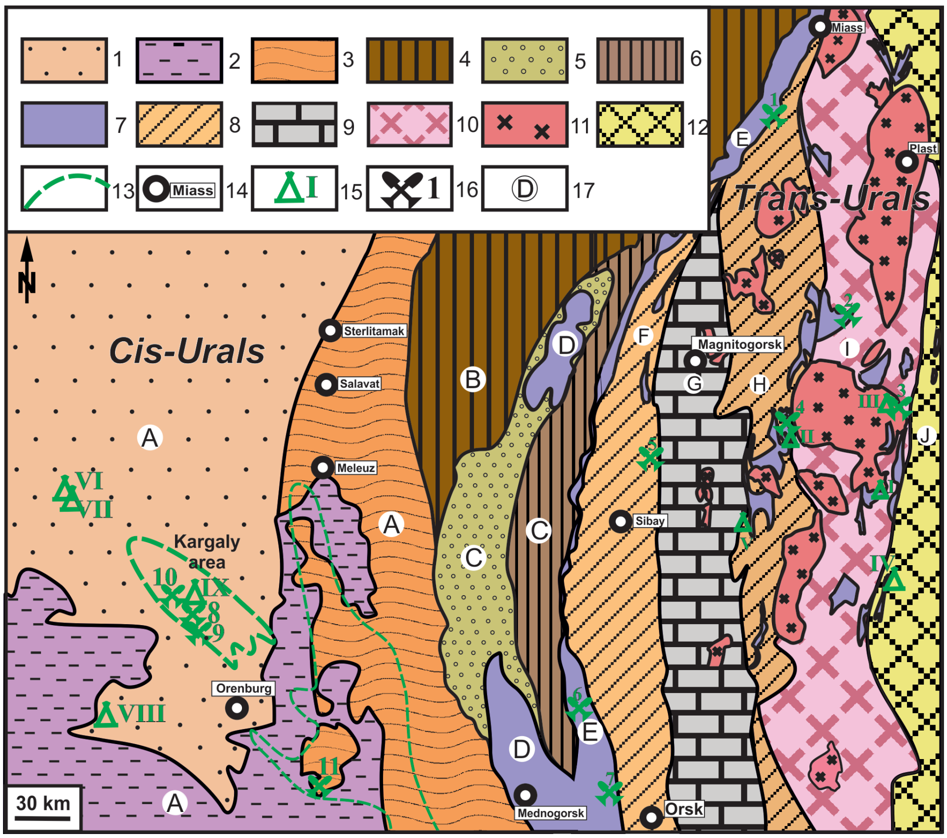

Figure 2. The Souths Urals geological structures and archaeological sites (Lurye, 1988; Ulanov, 2000; Kozlov et al., 2002; Zaykov, 2006): 1 - Permian shallow sea sediments 2 - Mesozoic sand, silt and pelitic sediments; 3 - Permian molasse sediments; 4 - precambrian metamorphic shales with a Paleozoic sediments; 5 - Devon-carbonian batial, shelf and flisch sediments; 6 - precambrian-paleozoic metamorphic complexes; 7 - ultrabasic-basic complexes of Paleozoic ophiolites; 8 - Devon-Carbonian volcanogenic-sedimentary complexes; 9 - Carbon limestones and volcanogenic sediments; 10 - Proterozoic volcanogenic and granite-gneisses; 11 - Carbon granitic batholiths; 12 - Proterozoic-Paleozoic volcanogenic-sedimentary complexes with a Mesozoic sediments; 13 - copper sandstone ore fields; 14 - modern cities; 15 - studied archaeological settlements; 16 - Bronze Age mines, 17 - structural and formation zones of Urals.
Basic structures of the Urals: A - Pre-Ural marginal deflection and East European platform; B - West Urals megazone; C - Central Urals megazone; D - Kraka and Sakmara allochthones; E -Main Ural Fault; F - West Magnitogorsk island arc; G - Sibay inter-basin zone; H - East Magnitogorsk island arc; I - East Ural microcontinent; J - Trans Urals megazone.
Archaeological settlements: I - Kamenniy Ambar; II - Sarym-Sakly, Katzbakh 1, Katzbakh 6; III - Ustye; IV - Levoberezhnoe; V - Arkaim. VI- Turganik; VII - Ivanovskoe; VIII - Rodnikovoe; IX - Gorny 1.
Bronze Age Mines: 1 - Nikolskoe and Tash-Kazgan; 2 - Novotemirsky; 3 - Novonikolaevsky; 4 - Vorovskaya Yama; 5 - Bakr-Uzyak; 6 - Dergamysh; 7 - Ishkinino; 8 - Ordynsky Ovrag; 9 - Belousovka; 10 - Mikhaylovka; 11 - Kzyloba.

Europe steppe. The extensive mining and metallurgical development of deposits confined to the Donetsk Basin, Cis-Urals and other regions of the Northern Europe is dated to 4000-3000 BCE. Early Yamna culture sites in the Urals included kurgan burials with metallic items, moulds and copper ore fragments (Bogdanov, 2004; Morgunova, 2014). The earliest observed site featuring 'slag metallurgy' in the Cis-Urals is the ***Turganik*** Early Yamna culture site, which is situated at the confluence of the Turganik and Tok Rivers (Orenburg region). It contains ore fragments and copper items, copper ingots and slags fragments, melting pot, metallurgical furnace decaying and hammers dated to 4000 BCE (Morgunova et al., 2017; Bogdanov, 2017).

The Sintashta culture of the Late Bronze Age (2000-1700 BCE), extended in the Western Trans-Urals from the eastern slope of the Urals to the border between the Trans-Urals peneplain and Western-Siberian lowland (Gening et al., 1992). Currently, 23 fortified settlements and over 15 necropolises located on the Ural and Tobol River bank basins are known to archaeologists (Logvin, 2002; Koryakova and Epimahov, 2007; Tkachev, 2007). N.B. Vinogradov, who is one of the leading researchers of Sintashta culture, considers that mining and metallurgical activity played a particularly significant role in the formation of cultural identities, regularising other areas of life of this culture (Vinogradov, 2013).

The ***Kamenny Ambar*** settlement is situated in the Kartaly District of the Chelyabinsk Region on the left bank of the Karagayly-Ayat River. This settlement, having a rounded rectangular shape, is surrounded by a defensive rampart. The majority of metallurgical slag fragments, copper ores, metallic ingots and finished tools were discovered during the excavations (Krause and Koryakova, 2013, Zaykov et al., 2013b). The history of this settlement comprises two chronological periods, determined as follows: Sintashta-Petrovka (2030-1870 cal. BCE) and Srubna-Alakul (1980-1780 cal. BCE) (Epimakhov and Krause, 2013). The ***Levoberezhnoe*** settlement is located on the left bank of the Sintashta River near Komsomolsky village of the Chelyabinsk Region. The researchers determined that this settlement was characterised during Sintashta period by a linear design with two housing complexes situated along a central street and surrounded by a rampart and trench. At this settlement, abundant evidence of metallurgical manufacture has been observed, including slags, ingots, metal globules, as well as copper and arsenical bronze artifacts (Petrov et al., 2018). The ***Sarym-Sakly*** is situated on the right bank of the Zingeyka river between the Katzbakh and Zarya villages of the Chelyabinsk Region. This circular settlement was surrounded by a defensive wall, an external ditch and an outer rampart. Here, Sintashta-type ceramic vessel fragments and metallurgical slags were discovered (Makurova and Petrov, 2017). The ***Ustye*** settlement is situated in 6 km south-west from Solntse village of Chelyabinsk region. The history of the settlement, which was occupied continuously from the end of the Middle and into the beginning of the Late Bronze Age, can be divided into two periods: Sintashta and Petrovka. The majority of artifacts found here are related to metallurgy and copper manufacturing: relics of metallurgical furnaces, copper ores, slags, metal globules and ingots, casting patterns and metallic items (Vinogradov, 2013).

The Alakul culture of the Late Bronze Age (1700-1300 BCE), which formed at the Trans-Urals forest-steppe regions, is based on Sintashta culture. It is synchronic to the Srubna archaeological sites of the Volga, middle Don and Cis-Urals regions. The Alakul cultural and chronological horizons are identified in several burial and settlement sites of Sintashta culture (Epimakhov, 2009). Evidence of metallurgy in Alakul settlements is rare in contrast to Sintashta sites.

The ***Kamenny Ambar*** multilayer settlement is the primary site at which the metallurgy of the Alakul culture has been examined. In addition, slags from the ***Zingeyka archaeological site*** (Zingeyka river valley, Chelyabinsk region) have been examined to characterise the metallurgy of this culture in the Trans-Urals. The cultural layering of the Zingeyka sites has been examined by means of test pits, with metallurgical slags exposed at six sites. The ***Vorovskaya Yama*** ancient mine is located near Zingeyka village (Chelyabinsk region). The cultural layer contains ash, bones of pets, metallurgical slags and Alakul type vessel fragments. The copper ores consist of malachite with traces of azurite and cuprite.

The Srubna culture of the Late Bronze Age (1700-1300 BCE) was widespread in the steppe and forest-steppe ecoregions of Eastern Europe, occupying an area from the Dnieper in the west to the Ural Mountains in the east, and from the Upper Volga and Bashkir Cis-Urals to the North Caucasus. Evidence of metallurgical processes has been described in all settlements, where the majority of finds consist in tools, casting moulds, cups, slags and etc.

The ***Ivanovskoe*** settlement is located 5 km south from Ivanovskoe village and 500 m north from Turganik in Tok River terrace (Orenburg region). At the area of Ivanovskoe, Neolithic, Eneolithic and Late Bronze Age cultural layers were revealed. The evidence of metallurgical process was recorded in the most recent layers, consisting of slags and casting moulds with slag material (Morgunova and Porokhova, 1989). The ***Rodnikovoe*** settlement is located 5 km west of the village of Chesnokovka (Orenburg region) in the right bank of the Ural River. Amongst others, evidence of metallurgical process was recovered as follows: copper slags, copper ore fragments, ceramic vessel fragments with slag walls. From this evidence, it appears that special places for the manufacture of metallic items existed at the settlement (Morgunova and Porokhova, 1989; Kuptsova and Fayzullin, 2012). The ***Ordynsky Ovrag*** ancient mines comprise numerous ancient pits with 'empty' rock dumps. These are located 3 km of Maksimovsky farm (Orenburg region) at the centre of the Kargaly group of mine workings. Metallurgical slag fragments were recovered by S.V. Bogdanov near a sunken Bronze Age mine. However, the dating of these samples is problematic due to the absence of links to the associated cultural layer. The ancient mine of ***Kzyloba*** is located at the confluence of the Ural and Ilek rivers, 25 km west of the village of Belyaevka (Orenburg region). Here again, S.V. Bogdanov recovered metallurgical slag fragments without obtaining time references in the ore field. However, it is generally supposed that these artifacts are related to Srubna culture.

RESULTS

Slags dating to the Early Bronze Age were recovered at the Turganik settlement, which is the only known archaeological site in the Urals featuring a clearly-identified metallurgical process. Late Bronze Age Cis-Urals slags were examined on the example of materials from excavations of Rodnikovoe and Ivanovskoe Srubna settlements, as well as exceptional artifacts from the ancient mines at Ordynsky Ovrag and Kzyloba. We used samples from Sintashta period settlements at Levoberezhnoe, Sarym-Sakly, Ustye and Kamenny Ambar to describe slags from the Trans-Urals. The Late Bronze Age slags were explored on the samples confined to the Alakul horizon of Kamenny Ambar and Katzbakh 1, Katzbakh 6 and Vorovskaya Yama ancient mines. Across the full range of Bronze Age metallurgical slags at South Urals, we distinguished four main types according to their mineral, chemical and structural peculiarities (Table 1):

1) *Cr-rich spinel-containing olivine slags* were found on the Sintashta fortified settlements, e.g. Sarym-Sakly, as well as at the Sintashta horizons of the multilayer archaeological sites, e.g. Kamenny Ambar, Ustye and Levoberezhnoe. This group was recovered at the Turganik settlement and Kzyloba ancient mine in the Cis-Urals. These slags are composed of olivine (60-80%; hereinafter the proportion of bulk slag sample volume), magnetite (10-30%), glass (10-20%) and relic Cr-rich spinels (rarely more than 1%). In addition, pyroxenes (up to 30%), singular relic quartz, as well as serpentinite fragments and sulphide microinclusions were detected at Turganik.

2) *Sulphide-containing olivine slags* were identified on the Alakul horizon of the Kamenny Ambar multilayer archaeological site (Krause and Koryakova, 2013). Earlier, similar samples were recovered at the Konoplyanka settlement (Sharapova et al., 2014). Here, the mineral composition is as follows: olivine (40-60%), magnetite (20-30%), wüstite (15-30%), glass (5-10%) and sulphides (<1%).

3) *Sulphide-containing glassy slags* were detected at the Katzbakh 6 settlement of the Trans-Urals, the Vorovskaya Yama ancient mine, as well as at the Srubna culture horizons of the Ivanovskoe settlement and at Ordynsky Ovrag. This group is mainly comprised of glass (50-80%), relic quartz (20-40%) and plagioclase (1-5%), sulphides (1-5%), as well as single barite and apatite grains.

4) *Pyroxene slags* are found at the Katzbakh 1 and Vorovskaya Yama ancient mines relating to the Alakul period. At the Cis-Urals, similar samples were identified at the Rodnikovoe Srubna settlement. Previously, identical slags have been described at the Gorny 1 settlement during the Srubna cultural period where these samples are widespread throughout the cultural layer (Chernykh, 2004). The slag bulk is composed of pyroxenes (50-80%), glass (20-40%) and magnetite (5-10%). The secondary copper minerals are cuprite, atacamite, chrysocolla, brochantite and malachite formed in all of four groups and gradually replaced by melt sulphide inclusions and copper globules.

Cr-rich spinel-containing olivine type

Although the largest fragments of this group are up to 5-7 cm, they are typically 2-3 cm in diameter having a flat shape and characteristic edges (Figure 3). Slags vary in colour from a dark-brown or dark-grey to black colours with a matte glass-like surface. The porosity is low-to-medium, while textures are porphyritic. There were no significant differences in terms of morphological, textural or mineral-geochemical peculiarities between Cr-rich spinel-containing slags from different Bronze Age archaeological sites of the South Urals.

The bulk of the analyses of the main and trace elements were performed for metallurgical slags from the best-studied Kamenny Ambar settlement. According to chemical analysis, the composition of Cr-rich spinel-containing olivine slags from Kamenny Ambar is as follows (wt%): SiO_2 31-40, Al_2O_3 2.3-5.8, Fe_2O_3 4-25, TiO_2 0.1-0.2, FeO 32-46, MnO 0.1-0.7, MgO 4-11, CaO 1.4-3.7, Na_2O 0.05-0.65, K_2O 0.3-1.1, P_2O_5 0.2-0.5, CuO 0.6-2.9. According to bulk ICP-MS analysis, the contents of several trace elements in Cr-rich spinel-containing group is (ppm): Cr 600-1200, V 55-210, Ni 170-860, As 50-910, Co 95-200, Mo 3-26, Se 1-20.

Olivine formed prismatic euhedral grains having well-expressed zonality and rare skeletal crystals are presented in Figure 4. In reflected light, a light rim can be observed on the periphery of grains having elevated Fe contents as compared with the central parts of the grains. Olivine

Table 1. Main minerals of Bronze Age metallurgical slags from South Urals.

Mineral	Amount in sample, %	Morphology	Grains size	Compositions	Geochemical features
Cr-spinel containing olivine slags					
Olivine	60-80	Prismatic zoned crystals, chain-like and skeletal crystals	Zoned crystals up to 0.4-0.6 mm skeletal crystals - first µm	Zoned large forsterite-fayalite composition crystals, skeletal fayalite composition crystals	High concentrations of Cu, P, REE
Magnetite	10-30	Idiomorphic grains, skeletal crystals and small symplectic insets in olivine	Up to 0.2 mm	Stoichiometric	
Glass	10-20	Matrix	-	Basic, normal petrochemical series	High concentrations of P, REE
Cr-spinels	1-2	Idiomorphic grains, sometimes with corroded borders	0.1-0.5 mm	Cr-rich spinel	With Cr-magnetite rim on the periphery
Sulphide-containing olivine slags					
Olivine	40-60	‘Chain’-like and skeletal crystals	0.1-0.3 mm	Fayalite	High concentrations of Cu, P, REE
Magnetite	20-30	‘Amoeba’-like aggregates, skeletal crystals and small symplectic insets in olivine	0.1-0.2 mm	Stoichiometric	
Wüstite	15-30	‘Amoeba’-like aggregates, skeletal crystals	0.1-0.2 mm	Stoichiometric	
Glass	<10	Matrix	-	Low-silica, ferrous, normal petrochemical series	
Sulphides	<1	Round melted regulus, xenoklasts	0.1-0.8 mm	Chalcocite, covellite	
Sulphide-containing glassy slags					
Glass	50-80	Matrix	-	Intermediate, normal petrochemical series	High concentrations of Ba
Quartz	20-40	Fragments, often fractured	Up to 0.2 mm	Stoichiometric	
Plagioclase	1-5	Melted relics, with newly-formed phases halo	Up to 0.2 mm	Labradorite	
Sulphides	1-5	Round regulus with disintegration strusture	0.1-0.2 mm sporadic to 3 mm	Chalcocite, covellite, anilite	
Barite	Sporadic	Unmelted fragments in glass	10-20 µm	Stoichiometric	Admixture of Sr
Apatite	Sporadic	Grains in quartz fragments	10 µm	Stoichiometric	
Pyroxene slags					
Pyroxene	50-80	Skeletal, pinnated crystals	Up to 0.3 mm	Augite, pigeonite	
Glass	20-40	Matrix	-	Various: ultrabasic, normal petrochemical series; intermediate alkaline	High concentrations of Ba in Cis-Urals objects
Wollastonite	0-50	‘Box’-like crystals	Up to 0.3 mm	Stoichiometric	Admixture of Fe
Magnetite	1-5	Skeletal crystals, lamellas	Up to 0.1 mm	Stoichiometric	

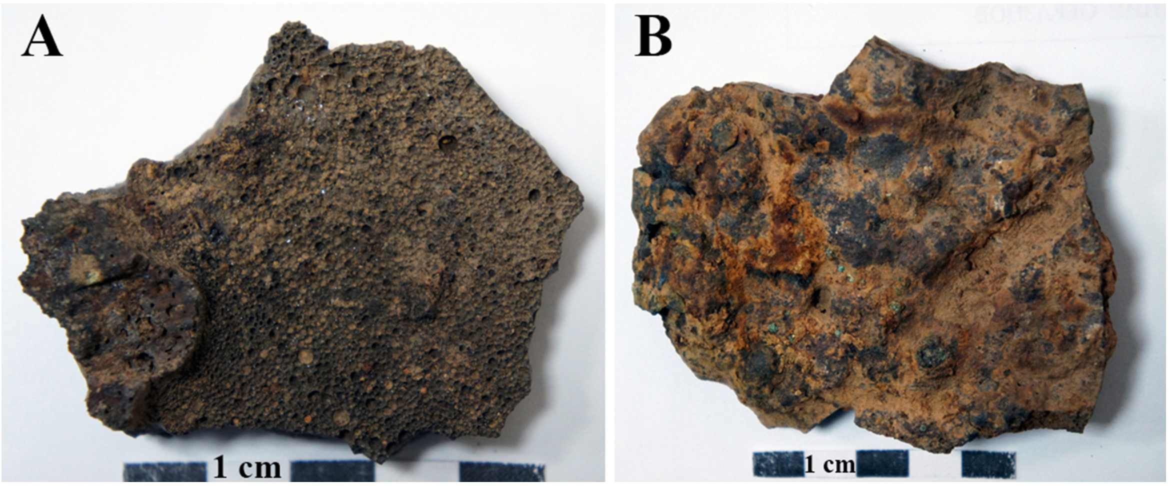

Figure 3. Olivine metallurgical slags: A - flat shape Cr-rich spinel-containing olivine slag; B - massive shape sulphide-containing olivine slag. Kamenny Ambar settlement.

appears in fayalite form, but in the central parts of the crystals, the forsterite component becomes prevalent (Table S1). The trace elements in olivines of slags from the Turganik, Kamenny Ambar, Ustye, and Sarym-Sakly settlements were determined using the LA-ICP-MS (Table S2). According to individual analyses and mapping, Ni, Co - and sometimes Cr and Mn - are related to the magnesia part of crystal. Although the fayalite rim is not enriched with any trace elements as compared to other phases, it contains a greater quantity of elements typical for a glass. Several spatially-distributed elements correlate with fayalite and forsterite phases. The most informative trace elements having a clear zonality are Ni and Co, which are distributed identically to Mg. Olivines from Ustye manifesting elevated Zn, As and Sb contents as compared with other settlements. The metallurgical slags from Turganik are divergent in terms of elevated Cu and As contents: here the high metal saturation of a melt is highlighted. The REE contents in olivines exceeded their natural analogues that were caused by olivine trapping of glass inclusions during crystallisation.

The glass, which has undergone devitrification to varying degrees, comprises a majority of small chain- and pinnate-shaped olivine crystals. According to SEM, the glass composition can be varied across different settlements and samples, particularly in terms of its Si, Al, Fe, and Ca contents (Table S3, Figure 5). In general, the glass composition corresponds to basic-ultrabasic; more rarely, according to the TAS diagram, it consists of intermediate and felsic rocks; in petrochemical terms, it is normal or, more rarely, moderately alkali. The glass from Turganik is marked by its high Fe content, which - along with a high proportion of magnetite - indicates the high Fe content of ore protoliths. Furthermore, the glass from Turganik is low-aluminous (Table S3). According to LA-ICP-MS analysis, the glass of Cr-rich spinel-containing slags contain lithophile elements such as Li, Ca, Al, Na, K, Sc, Ti, Ga, Nb, P, Pb, Rb, Sr, Ba, Zr, U and REE (Ankushev et al., 2020). The elevated contents of Ca, P, Ba, S and REE in glass can be explained by usage of calciferous and barite fluxes and bone relics. Many burnt and crushed bone relics were found during archaeological excavations of Ustye metallurgical complexes (Vinogradov, 2013). The glass of slags from Turganik and Kzyloba has been partially devitrified up to the formation of skeletal and rare euhedral pyroxene grains related to pigeonite and augite (Table S4).

Magnetite forms 0.05-0.2 mm euhedral crystals, skeletal and small symplectitic intergrowths in olivine. With the exception of the Turganik settlement, where magnetite content reaches 10%, the proportion of magnetite does not exceed 5%. Microinclusions of neogenic magnetite contain the trace elements Cr, V and Ti.

The relict mineral inclusions are composed of 0.1-0.5 mm euhedral and anhedral Cr-rich spinel grains with corroded borders. Here, porous and partially-crushed aggregates are typically observed. On the periphery, a thin (3-5 μm) solid or dotted chrome-magnetite rim is observed. The compositions of Cr-rich spinels are varied in the main components, but typically formed the only field on the classification plot (Figure 6).

A few serpentinised ultrabasic and quartz fragments with dimensions of 0.1-2 mm, often with fritted rims, are observed in samples from Turganik.

In this group, we observed monophase and multiphase inclusions of copper, bronzes, sulphides and arsenides, having round, crescent and elongated shapes with dimensions of 1-2 to 3-5 μm (Figure 4). In Turganik, we

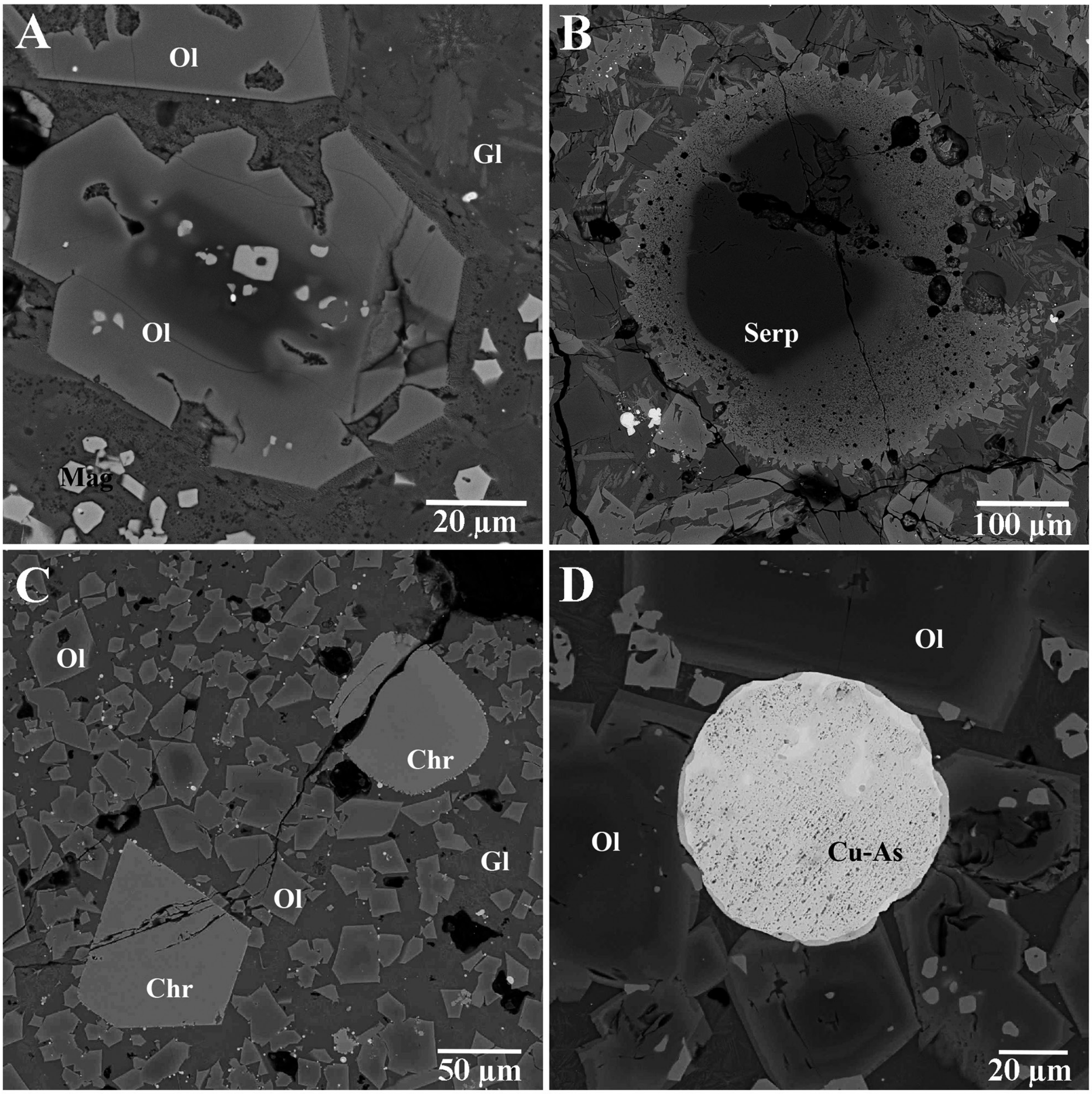

Figure 4. Mineralogy of Cr-rich spinel-containing olivine slags: A - zoned crystal of olivine (Ol) and fine grains of magnetite (Mag) in glass (Gl), Turganik settlement; B - unmelted relic of serpentinite (Serp) in the slag, Turganik settlement; C - grains of Cr-rich spinels (Chr) and zoned olivines in glass (Gl), Sarym-Sakly settlement; D - two-phase arsenic bronze melt inclusion and zoned olivine crystals (Ol) in glass (Gl), Ustye settlement. BSE images.

identified As-Fe bronzes and copper arsenides having Fe and Al impurities (Table S5). The Cr-rich spinel-containing slags from Ustye contain a wide variety of melt inclusions with As-Cu-Fe-Ni alloy and ferriferous copper-sulphide phases: tinny bronzes with high Sb; Ni-As, Cu-As, and Fe-As-Cu phases; monophase copper inclusions with Fe impurities; sulphide beads with As and Se (Table S5). Native Ag microinclusions are observed in weathered beads. However, the diversity of melt-inclusion chemical compositions at Sarym-Sakly is not quite so wide. The inclusions contain sulphides of Au, Ag and Fe with As, Ni and Se admixtures. The beads in slags from Levoberezhnoe are presented by monophase sulphide inclusions and arsenic bronzes; here, two- and three-phase sulphide intergrowths with Cu-As-Ni phases can also be observed. The melt globules in samples from the ancient mine of Kzyloba are composed of monophase copper inclusions with Fe and Ni impurities and intergrowths with sulphides. The chemical composition of melt inclusions from Kamenny Ambar is pure copper with Fe (up to 1.5%) and a hundredth of a percent of Sn, As, Ag, Zn, Ni and Co (Table S5).

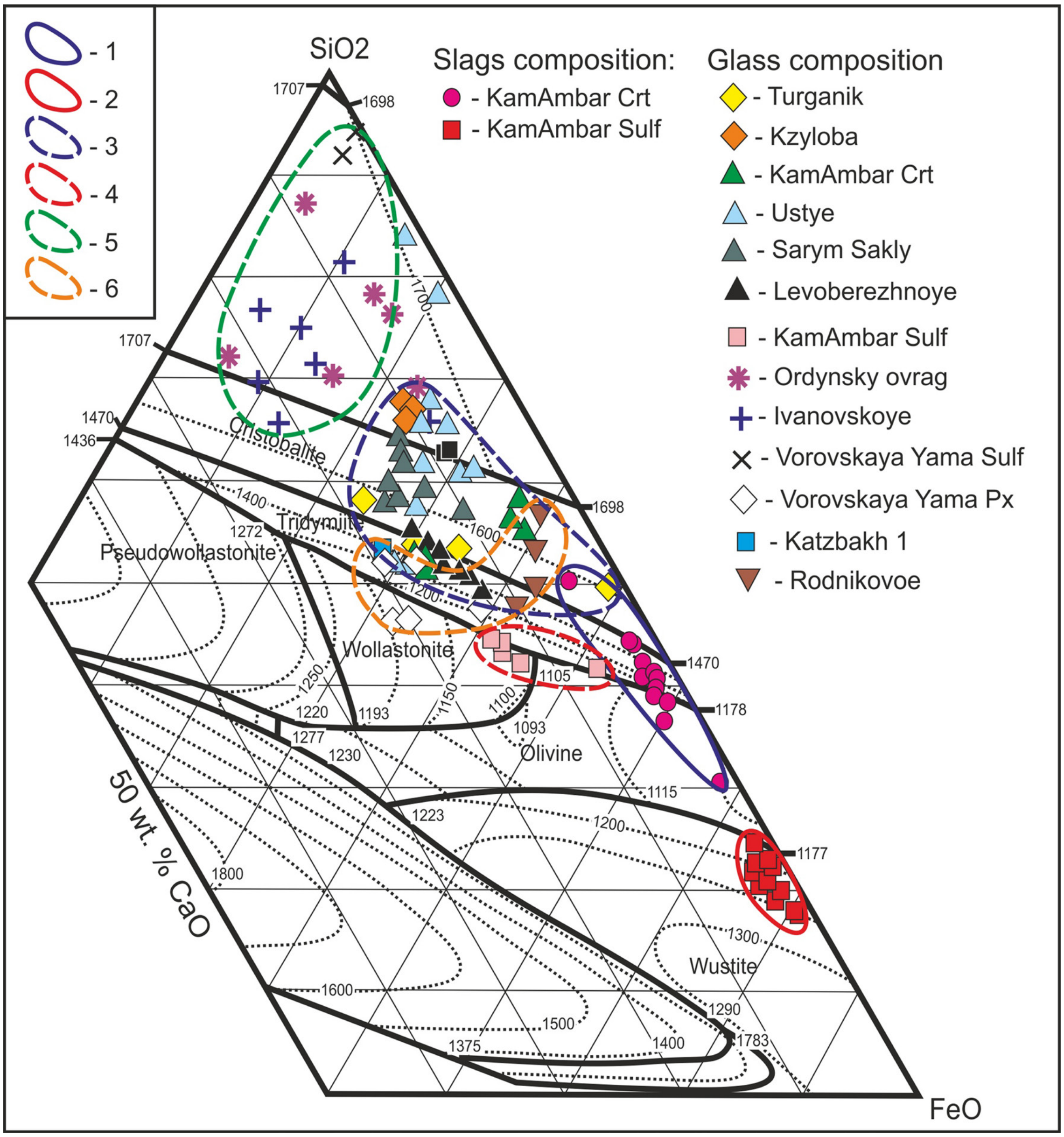

Figure 5. Fragment of CaO-SiO_2-FeO phase diagram by (Slag Atlas, 1995). Plotted are glass (dotted lines by SEM analysis) and slags (solid lines by ICP-MS analysis) composition of copper slags South Urals: 1 - total composition of olivine Cr-rich spinel-contained slags; 2 - total composition of olivine-sulphide-contained slags; 3 - glass composition of olivine Cr-rich spinel- contained slags; 4 - glass composition of olivine-sulphide-contained slags; 5 - glass composition of glassy sulphide-contained slags; 6 - glass composition of pyroxene slags.

Sulphide-containing olivine type

This group was examined using the materials from the Alakul horizon of the Kamenny Ambar settlement. The fragments are 2-4 cm in diameter and have a massive shape (Figure 3). In terms of visual appearance, the samples are black or dark-brown in colour, exhibiting oxidised copper beads and a matte surface. The slags have low- to medium porosity. Their textures are porphyritic or - rarely - aphyric (Figure 7).

The mineral composition is as follows: neogenic olivine (40-60%), magnetite (20-30%), wüstite (15-30%), glass (5-10%), as well as relic and neogenic sulphides (<1%). Cr-rich spinel grains are not detected. According to bulk chemical analysis, the composition of sulphide-containing olivine slags is as follows (wt%): SiO_2 15-21, Al_2O_3 1-2.2, Fe_2O_3 16-33, TiO_2 0.05-0.1, FeO 37-57,

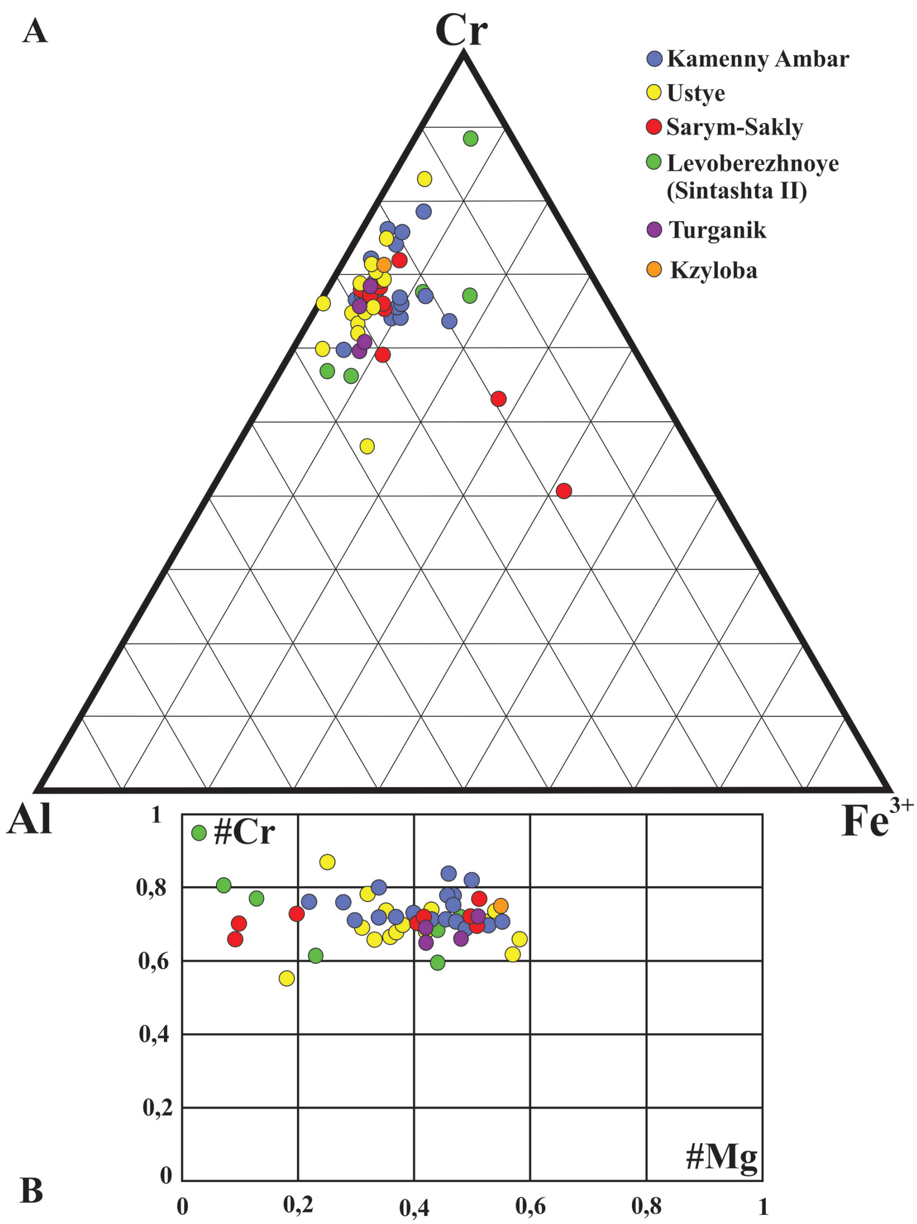

Figure 6. South Urals Bronze Age metallurgical slags Cr-rich spinels composition diagrams: A - plot of Cr-Al-Fe^{3+}; B - plot of Cr/(Cr+Al) - Mg/(Mg+Fe^{2+}).

MnO 0.04-0.09, MgO 0.8-1.8, CaO 1.2-2.9, Na_2O 0-0.6, K_2O 0.04-0.11, P_2O_5 0.3-0.5, CuO 2.6-8.7.

According to bulk ICP-MS analysis, the olivine sulphide-containing group from Kamenny Ambar settlement (as compared with Cr-rich spinel-containing slags) contains significantly lower contents of Cr (7-23 ppm), V (13-28 ppm), Ni (3-52 ppm) and As (0-18 ppm). Meanwhile, sulphide-containing slags are characterised by elevated amounts of Co (300-550 ppm), Mo (40-68 ppm) and Se (18-90 ppm).

The chained olivine 0.1-0.3 mm crystals exhibit a skeletal morphology. Olivine, which is stoichiometric, corresponds to fayalite with minor impurities of Mg, Ca Mn. The zonality of these crystals is considerably weaker than that exhibited in prismatic Cr-containing crystals. The elongated fayalite crystals can be grown together forming a parquet-like texture (Figure 7). According to X-ray phase analysis, the slags contain a significant amount of neogenic magnetite (19-28%) and wüstite (15-27%) of 'teardrop'-shaped and amebiform and 0.1-0.2 mm size.

The glass, which is quite pure and does not manifest any

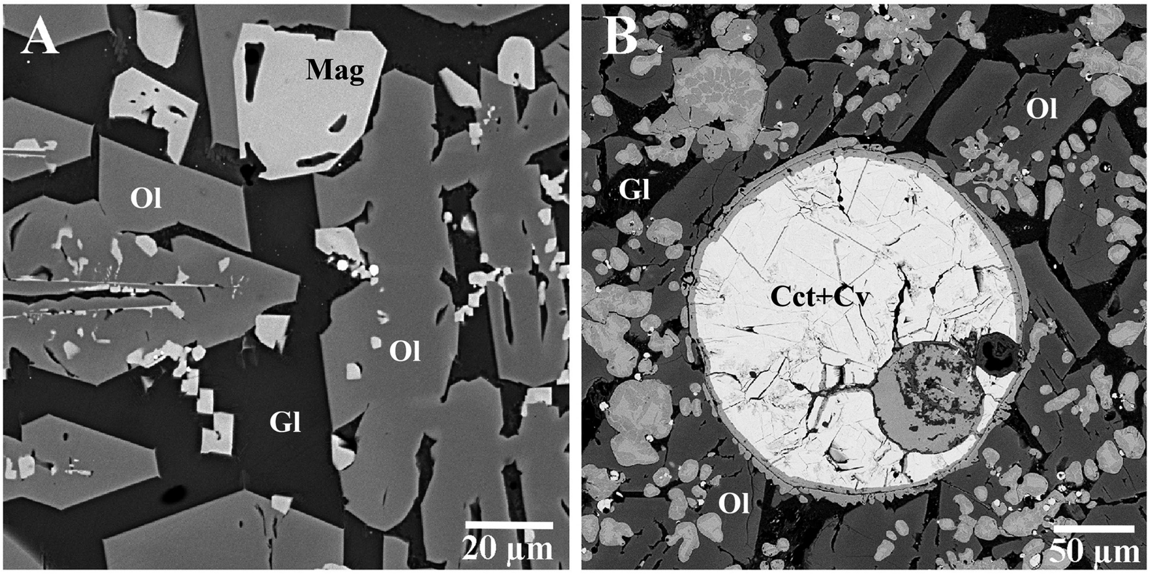

Figure 7. Mineralogy of sulphide-containing olivine slags: A - skeletal crystals of olivine (Ol) and magnetite (Mag) in glass (Gl), Kamenny Ambar settlement; B - chalcocite-covellite droplets (Cct + Cv) and olivine crystals (Ol) in glass (Gl), Kamenny Ambar settlement. BSE images.

small olivine crystallites, occurs in the interstices between olivines, magnetite and wüstite. The glass is low-siliceous and high-ferriferous low-alkali with elevated P_2O_5 content (5-6%) and BaO impurity (0-0.45%) (Table S3).

The most important inclusions comprise elongated and angular 1 mm relic sulphide ore fragments composed of chalcocite and covellite. The melt inclusions consist of partially-remelted sulphide beads (chalcocite and covellite) and minor copper inclusions (Figure 7). These are 0.1-0.8 mm in diameter, having rounded and elongated shapes. Submicron chalcocite veinlets are also observed in the slags. Chalcocite and covellite have a typical mineral composition with minor Fe impurities. The chemical formula of chalcocite is $Cu_{1.92-2.1}Fe_{0-0.08}S$; while that of covellite is $Cu_{1.07-1.27}Fe_{0.02-0.1}S$. The content of other trace elements is considered in the paper of D.A. Artemyev and M.N. Ankushev (2019).

In sulphide-containing slags from Kamenny Ambar, we observed two- and three-phase melt inclusions. Two-phase inclusions contain copper + chalcocite; arsenic bronze with Se sulphides globules, copper + cuprite; and Sn bronze + copper. Tin bronze inclusions consist of aggregates with dendritic-, parquet-, and "leopard" structures (Zaykov et al., 2013a). The three-phase inclusions consist of Ni-As bronze + Cu sulphide + Cu-Ni-As alloy in interstices; As bronze + Cu sulphide + Fe-Cu-As alloy in interstices. In a few cases, we observed 10-15 µm cupriferous gold beads with following chemical composition (wt%): Au 54.7-55.9, Ag 1.4-1.8, Cu 40.1-41.4, and As 1.4-1.8.

Sulphide-containing glassy types

This group is known in the Trans-Urals Alakul sites (Katzbakh 6, Vorovskaya Yama) and the Cis-Urals Srubna culture sites (Ivanovskoe and Ordynsky Ovrag). The fragments are coarse shaped and 2-3 cm in diameter. The samples, which are black, dark-brown and dark-grey in colour, have a porphyritic structure and a spotted texture. They exhibit a matte, glassy surface and are of low- to medium porosity. The primary glass component of the slags can account for up to 80% of their mass. The mineral composition includes relic quartz clasts (20-40%), relic melted plagioclase (1-5%) and sulphide inclusions (1-5%). In the Katzbakh 6 slags, the significant quantity of quartz fragments observed in the glass is associated with a high Ba content in the form of relic barite.

According to the TAS plot, the average glass composition from the Cis-Urals sites conforms to normal petrochemical sequence. The key feature is the high Ba content, which ranges between 2.6 and 14.2 wt% BaO (Table S3). In addition, we determined a significant Cl content (up to 1 wt%). A significant proportion of the glass content is made up of quartz grains approximately 0.2 mm in diameter (Figure 8); in many cases, these exhibited fracturing. In the fractures, secondary minerals (e.g. chrysocolla) are formed; in some cases, these included apatite inclusions. In slags from the Ivanovskoe site, a large quantity of barite fragments was recorded. In rare cases, skeletal wollastonite crystals are formed in the glass.

In the glass component of slags from Ordynsky Ovrag,

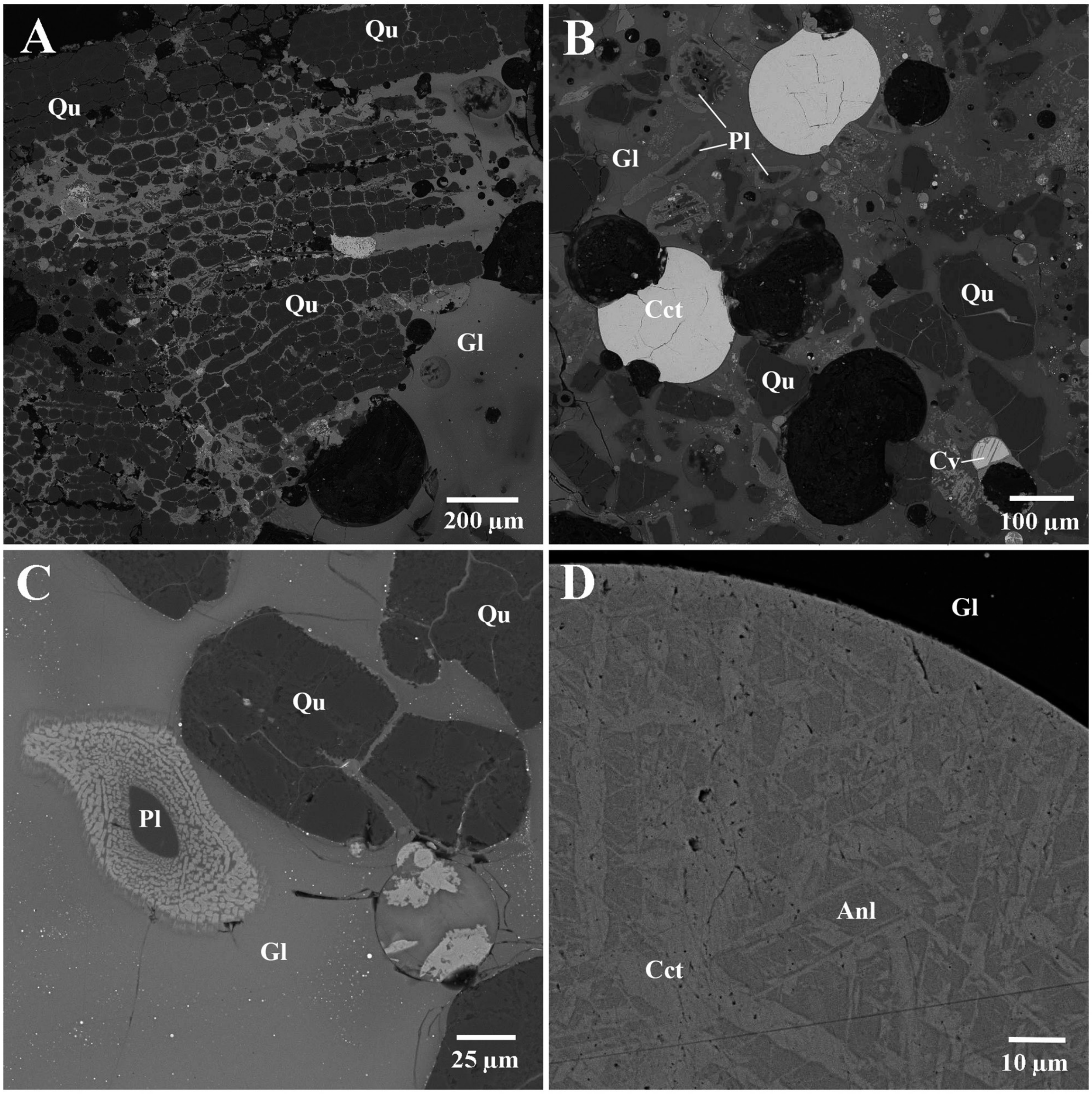

Figure 8. Mineralogy of glassy sulphide-containing slags: A - relics of silicified organic matter (Qu) in a glass of slag (Gl), Ordynsky ovrag ancient mine; B - relics of quartz grains (Qu), unmelted plagioclase relics (Pl), droplets of chalcocite and covellite (Cct, Cv) in slag glass (Gl), Ordynsky ovrag ancient mine; C - relics of quartz grains (Qu), unmelted plagioclase (Pl) relics with nonstoichiometric halos in the slag glass (Gl), Ordynsky ovrag ancient mine; D - chalcocite (Cct) - anilite (Anl) droplets in slag glass (Gl), Ordynsky ovrag ancient mine. BSE images.

partially-melted plagioclase relics of about 0.2 mm in diameter (Figure 8) were observed. The composition of plagioclase corresponds to labradorite (Table S6). The non-stoichiometric Ba-contained 'brain'-shaped growths occur around the plagioclase relics (Figure 8).

At the Vorovskaya Yama ancient mine at the Trans-Urals, we recorded a special group of glassy slags. These samples consist of glass (80%) including elongated euhedral anorthite 50 µm crystals. In the cuprite rim of copper melt inclusions, we identified submicron aggregates of Ag, S, Se and Te. However, it was not possible to quantify these inclusions due to their small size.

The melt inclusions in this group are presented by globules of metallic copper and sulphides of about 0.1 mm size. In addition, 50 µm sulphide fragments were occasionally observed. The metallic copper is pure with low Fe impurity (Table S5). The copper, which occupies the inner bead parts, is surrounded by a sulphide 'envelope' in which submicron Ag inclusions can also be identified. In large copper beads, we detected sulphide inclusions

5 μm in diameter. The typical feature of the Cis-Urals archaeological sites is the presence of submicron metallic Pb and Ag inclusions in a copper matrix. The secondary copper sulphides formed large (up to 3 mm) beads having a solid solution decomposition in slags from Ordynsky Ovrag (Figure 8). These minerals consist of intergrowths of chalcocite, covellite and anilite (Table S5). The content of other trace elements is considered in the paper of D.A. Artemyev and M.N. Ankushev (2019).

Pyroxene type

This group of slags was recovered in the Vorovskaya Yama ancient mine, Katzbakh 1 Alakul settlement of the Trans-Urals, as well as at the Rodnikovoe Srubna settlement of the Cis-Urals. The bulk of slag is composed of Fe-wollastonite (40-50%), wollastonite (10-15%) and small augite crystallites (20-35%) occurring in the glass bulk. In addition, we identified magnetite (5-10%) along with copper and sulphide melt inclusions. The relic minerals, detected only in samples from the Vorovskaya Yama ancient mine, are presented by rare Cr-rich spinels and quartz fragments.

The samples from the Vorovskaya Yama ancient mine consist of flat shape slags up to 1 cm thick and 2-3 cm long, dark-grey, brown and black in colour, having a porosity of 3-5%. The structure is porphyritic. Using X-ray fluorescence analysis, we determined the elevated Zn contents (Ankushev et al., 2018). The Fe-wollastonite formed elongated euhedral 0.3 mm crystals. In some cases, a crust quenching occurred on the surface of slag in the form of pyroxene feathery crystal intergrowths up to 0.2 mm size (Figure 9). Wollastonite is formed in long prismatic and ‘box’-like crystals about 0.2 mm size and radial fibrous aggregates. The mineral composition is close to stoichiometric (Table S4). The glass is characterised by extremely low quantities of FeO and CaO, but with elevated K_2O contents (up to 20 wt%) (Table S3). Magnetites form different-shaped aggregates: subhedral grains about 0.02 mm size, skeletal crystals, amebiform aggregates and small symplectic ingrowths in pyroxene crystals.

The relic minerals comprise elongated quartz fragments and Zn-containing Cr-rich spinel fragments about 0.1 mm in size. Here complicated porous grains and rounded relics with thick magnetite rim had formed. The melt inclusions are presented by isometric, rounded - as well as, in some cases, elongated - monophase copper inclusions of sizes ranging from submicron to 5 mm. The copper beads are oxidised on the periphery up to full replacement by cuprite. According to SEM data, the As impurity is detected in copper melt inclusions, while Se and Bi occur in the sulphide envelope.

The slags from Katzbakh 1 are similar to the samples from Vorovskaya Yama. The main components are pyroxene skeletal crystals, ‘box’-like and chained wollastonite crystals, as well as glass and skeletal magnetite crystals. The melt inclusions are comprised of small copper beads, sometimes containing Fe impurities. In oxidised inclusions, we observed large native Ag inclusions (up to 10 μm) (Table S5).

The primary mineral of metallurgic slags from Rodnikovoe is augite, which contributed up to 70%. The bulk mass is ultrabasic ferriferous glass containing high BaO contents (8-16 wt%), as well as Sr and Cl impurities (Table S3). In glass, neogenic magnetite lamellas had uncrystallised forms. The melt inclusions from Rodnikovoe are composed of small copper globules (5-10 μm) with Fe and Pb impurities, as well as partly oxidised large beads of copper and sulphides. Reaching 0.25 mm in diameter, their central and peripheral parts consist of sulphides with Ag impurity (Table S5).

DISCUSSION

The first information concerning the usage of copper in the Urals is dated to the Eneolithic or Copper Age. As of the present time, no known slags dating from this period bear witness to native copper usage (Pernicka and Anthony, 2010). The Early Yamna culture mainly used a copper from the Caucasus and Bakhmuth Basin, importing this material to the Cis-Urals (Bogdanov, 2004). The first reliable evidence of metal manufacturing, discovered at the Turganik settlement at the Cis-Urals and dating to 3900 BCE, is related to the Early Yamna culture (Morgunova et al., 2017). From this period until 2000 BCE there is only indirect evidence of metal usage and processing by the Yamna, Catacomb and Abashevo cultural groups. It was only in the Late Bronze Age that the development of metallurgy and arsenic bronzes led to the widespread appearance of this metal associated with the Sintashta culture in the Trans-Urals. The rapid expansion of the metal manufacturing area at all of mining and metallurgical centres (Cis-Uralian, Trans-Uralian and Mugodzhary) occurred during the Srubna-Alakul period. Along with arsenic, tin and lead bronzes dating from this time can also be observed.

Condition of formation

The Bronze Age South-Uralian slags are subdivided into four main mineralogical types. Each type is associated with a particular cultural group, reflecting the technology that enabled the development of the corresponding metallurgical technologies. According to mineralogical and geochemical indicators, slags are related to copper sources, alloying additions and fluxes. The olivine Cr-rich spinel-containing group is confined to the cultural layer of the Sintashta horizon at the Kamenny

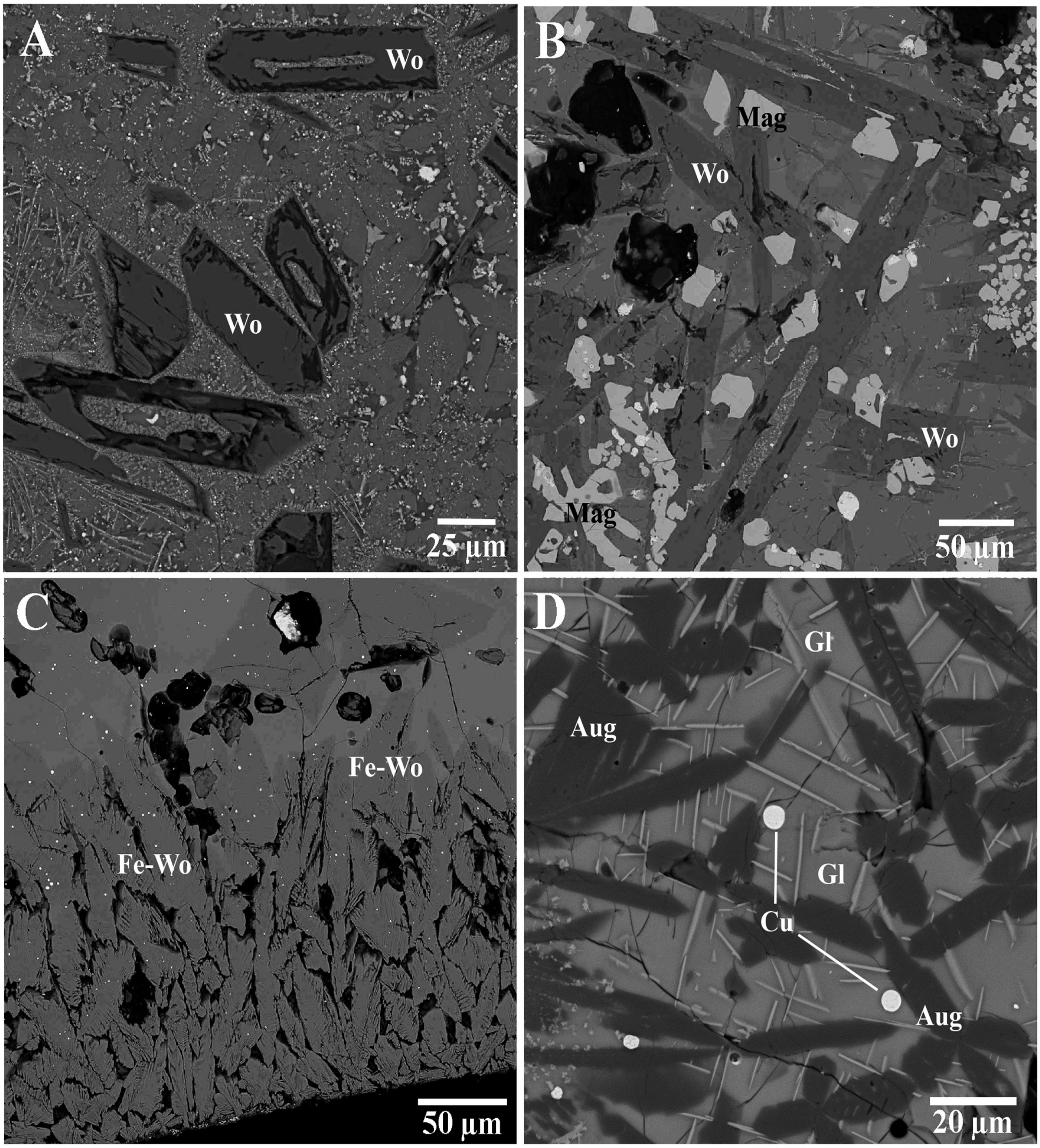

Figure 9. Mineralogy of pyroxene slags: A - wollastonite 'box'-like crystals (Wo) in the slag, Katzbakh 1 settlement; B - wollastonite 'box'-like crystals (Wo) and magnetite grain (Mag) in the slag, Vorovskaya Yama ancient mine; C - rapid quenching zone of slag, formed by crystals of ferrous wollastonite (Fe-Wo), Vorovskaya Yama ancient mine; D - augite skeletal crystals (Aug) and copper droplets (Cu) in a slag glass (Gl). BSE images.

Ambar, Levoberezhnoe and Sarym-Sakly settlements of the Trans-Urals. Rich sulphide ores were used for metallurgical processes at the Alakul settlements. The problem of interpreting ploughed up slags at the Ustye and Konoplyanka archaeological sites is somewhat more complicated. The Cis-Urals archaeological sites were not divided into similar types owing to insufficient study and the priority usage of cupriferous sandstones. In addition to the indicator minerals, an important sign of a specified ore protolith and associated technological characteristics is the glass composition. According to chemical composition analysis (Figure 5), we determined two main types of glass: high-siliceous glasses included the majority values of Ivanovskoe and Ordynsky Ovrag archaeological sites from the Cis-Urals as well as several values of Ustye and Vorovskaya Yama Trans-Urals settlements; meanwhile, ferriferous glasses included those obtained from the Trans-Urals settlements, as well as the Turganik, Rodnikovoe and Kzyloba sites of the Cis-Urals. The glasses can be further subdivided due to the usage of cupriferous sandstones at the Cis-Urals that provided high SiO_2 content. The differences between the glass compositions of Ustye and Vorovskaya Yama mines are caused by the application of the different mineralogical ore types and fluxes. Moreover, the samples produced during the manufacturing of the Cis-Urals cupriferous sandstones, contain Ba, Sr and Cl in glass that indicates the use of barite fluxes (Table S3). The glass of the olivine sulphide-containing type is low siliceous, high ferriferous and contains elevated P content. Here rich sulphide ores have been used with animal bone flux. A comparison of the total composition with the glass using two types slag from Kamenny Ambar showed that Fe in the sample is predominantly found in olivine, magnetite and wüstite. As can be seen in the diagram, the crystallisation temperature of olivine Cr-rich spinel-containing type is 1200-1400 °C, while that of the olivine sulphide-containing type is 1150-1270 °C.

The primary ore protolith for Cr-rich spinel-containing olivine slags of the Trans-Urals settlements relating to the Sintashta period consists of oxidised copper ores was derived from the oxidation zone upper horizons of deposits hosted by ultrabasic rocks. This fact is highlighted by the presence of relic Cr-rich spinels and serpentinite fragments, as well as the geochemical composition of slags having an elevated Ni, As, Cr, and V content. In addition, the copper melt inclusions, often including As impurities and Cu-As and Ni-As mineral intergrowths, support this interpretation. The oxidised copper ores in ultrabasic rocks comprised a geographically similar and easy exploited raw material for the Middle Bronze Age metallurgists from Kamenny Ambar, Ustye, Sarym-Sakly and Levoberezhnoe settlements, etc. The chemical composition of Cr-rich spinels demonstrates minor differences in the main component contents as shown in Figure 6. Such geochemical peculiarity is typical for Cr deposits and accessory Cr-rich spinels from ultrabasic rocks confined to the Main Uralian Fault and East-Urals Fault zones (Zaykov et al., 2009). However, the type of zonality and distribution of majority elements in Cr-rich spinels corresponds to their natural analogues. The LA-ICP-MS analysis observed high P and REE contents indicating the use of calciferous and bone fluxes (Ankushev et al., 2020). The particularly high Zn, As, Sb and REE contents are detected in samples from Ustye. These differences in mineral composition indicate the usage of another ore type in Ustye, as well as, probably, a different smelting technology to that used in Sarym-Sakly, Kamenny Ambar and Levoberezhnoe. Here the ores could have been related to an exploration of the polymetallic oxidation zone; moreover, fluxes and As alloying can be seen to have been used in Ustye.

The sulphide-containing olivine slags recovered in the Alakul horizon of the Kamenny Ambar site were formed during the manufacturing of sulphide- as well as both mixed-oxidised- and sulphide protoliths. This confirms the presence of relic secondary sulphide fragments, neogenic sulphide droplets and the special geochemical composition of slags expressed by the elevated Co, Mo and Se contents, along with correspondingly low amounts of Ni, As, Cr and V. The absence of quartz excludes the usage of sulphide ores confined to quartz veins. The absence of Cr-rich spinels and relic serpentinites, as well as the extremely low Si content in the slags, indicates that rich and massive copper ores confined to the secondary enrichment zone of VMS, skarn and Cu-porphyry deposits were used. The mineral composition of sulphide droplets and fragments consists of chalcocite and covellite growths with significant Fe impurities. The LA-ICP-MS data demonstrated significant Ag content, which is sufficiently typical for sulphides, as well as a Se impurity indicating that the sulphides were confined to ultrabasic-hosted deposits.

The glassy sulphide-containing group from the Srubna Cis-Urals archaeological sites, e.g. Ivanovskoe and Ordynsky Ovrag site, were formed during the metallurgical manufacturing of cupriferous sandstone ores, indicating that the archaeological sites are confined to the same ore formation. In addition, some characteristic peculiarities can be observed, namely, a large quantity of quartz and a slag bulk consisting of glass formed during plagioclase and feldspar melting with their relics. The presence of Ba-Pb assemblage is typical for cupriferous sandstones. The quantity of barite in the protolith, as indicated by the large relic barite fragments, is significant. Here, due to the mineral composition of ores being mixed, it is probable that both oxidised malachite and chalcocite-covellite ores were used. Sulphides demonstrate sustainable Ba-Pb-Ag geochemical assemblage. The genesis of the Trans-Urals glassy slags from the Katzbakh 6 Alakul settlements is still a matter for discussion. The close area of location of these objects from Vorovskaya Yama ancient mine exploited in Alakul period implies the usage of oxidised copper ores confined to ultrabasic rocks. Meanwhile, a large amount of quartz, sulphides and barite may have been used as flux. According to a mineral composition and structural features, the slags from Katzbakh 6 are similar to samples from the Srubna Cis-Ural archaeological sites. At the Vorovskaya Yama ancient mine, sporadic glassy slags contained a large amount of plagioclase; here inclusions with Ag, Se and Te also indirectly indicate the use of a sulphide substrate.

According to its mineralogical composition and structural peculiarities, the pyroxene type is highly heterogeneous. The relic indicator inclusions occurred only in samples of Vorovskaya Yama and those presented by Zn-Cr-rich spinels. The similar natural individuals are the result of primary accessory Cr-rich spinel transformation with a different composition due to hydrothermal-metasomatic and hydrogenous processes (Silaev et al., 2008). Further, in Cr-rich spinels from the ancient slags, no ZnO content higher than 0.5 wt% were identified. It is likely that Cr-rich spinels included significant amounts of Cu and Zn in the metal-rich melt. The high alkalinity of slags from Vorovskaya Yama ancient mine may indicate the use of carbonate fluxes.

Our research highlighted the textural features of olivine Cr-rich spinel-containing group, along with the morphology and zonality of olivine grains, according to the following crystallisation sequence. The first, fayalite is formed with a large amount of forsterite in the core. Later, due to the temperature decrease, a fayalite rim is formed around the grains followed by anhedral and skeletal magnetite aggregate growths filling the fractures and cavities. During the final stage, the glass was quenched and the metallic copper became solidified. The unaltered Cr-rich spinel grains and partially-melted serpentinite fragments comprise the primary ore protolith. According to experimental heating in a muffle furnace, the melting temperatures of Cr-rich spinel-containing slags from Kamenny Ambar are 1250-1285°C. Similar ancient copper slags were found in Valmalenco (Italy), where ultrabasic rocks comprised the raw source of copper ores and carbonate fluxes were used (Giacometti et al., 2014).

Since the olivine sulphide-containing group probably crystallised more quickly, the likely sequence is simple. Here, firstly, chained fayalite skeletal crystals were formed, followed by anhedral wüstite and magnetite aggregates; finally, the glass was quenched and metallic copper and bronze were solidified. Clasts and melted sulphide ore beads present the relic inclusions. During the glassy sulphide-containing slag melt cooling, sulphide melt droplets were formed with the decomposition of the solid solution, having non-stoichiometric alkaline phases around the partially melted plagioclase relics and Ba-containing glass. Quartz grains, melted plagioclase grain relics and rare apatite and barite present the non-melted relics.

We suppose that pyroxene was crystallised from the melt due to the pyroxene slag melt being more acid than in olivine groups. Whereas, since the crystallisation process was sufficiently slow in the Trans-Urals archaeological sites, the samples contain up to 80% pyroxene along with a correspondingly small quantity of glass.

Sources of copper ores

In the Southern Urals, especially in the Cis-Urals MMC, the presence of a large number of Bronze Age mines has already been established. The special features of these mines are the low level of exploration, their round shape, as well as the presence of heaps along the boundaries and concentrating platforms for manual ore selection. Very often, stone and copper tools, slags, ceramics and bones dated according to the cultural horizons are recovered on the deposits. According to the presence of Bronze Age mines, several genetic types with the oxidation zone exploited during 4000-1300 BCE are divided among the numerous Ural copper deposit types (Zaykov et al., 2012).

The important ore sources for the Cis-Urals MMC were the stratiform cupriferous sandstone deposits situated along the western margin of Uralian Ridge and Mugodzhary. The ore mineralisation is confined to Permian sedimentary sandstone stratum interbedded with marls and conglomerate lenses (Lurye, 1988). The ore bodies formed lenses with oxidised copper mineralisation; sulphide concretions consisted of chalcocite, covellite, cuprite, malachite, chrysocolla, azurite, rare chalcopyrite and native copper. The ancient mines occupied considerable areas of the Cis-Urals due to the near-surface ore body location, coupled with extensive reserves and the high copper content of the ores. During the Bronze Age, the area of exploration included the mountain-forest zone of Bashkortostan at the north (Bogdanov et al., 2018). The area most studied is Orenburg region where a few dozen Bronze Age mines have been discovered. These were exploited during the Early Yamna, Yamna and Srubna-Alakul cultures (Chernykh et al., 2002; Bogdanov et al., 2018). The majority of the Bronze Age mines were destroyed during excavations taking place during the 17-19th centuries AD (Chernykh et al., 2002). The largest and best-known area of copper extraction is the Kargaly ore area located to the north of Orenburg. The intensity of mining reached its peak during the Late Bronze Age (2000-1300 BCE) (Chernykh et al., 2002).

The mineralogical markers for recording the usage of cupriferous sandstone ores are the relics of quartz, plagioclase, barite grains and silicified organic material. The geochemical indicator recorded in copper and sulphide droplets of slags and copper items is the Ag+Pb(Bi)+Ba assemblage of trace elements. No usage of fluxes was determined on the basis of mineralogical and geochemical research.

The presence of olivine Cr-rich spinel-containing slags of Turganik settlement and Kzyloba ancient mine in the Cis-Urals, where the usage of copper ore having an ultrabasic substrate was determined, is harder to explain. The nearest copper mines with As mineralisation confined to the ultrabasic complexes are more 300 km away from

Turganik (Ivanovka in the Main Uralian Fault) and about 150 km away from Kzyloba (Ishkinino ancient mine).

The copper ores of the Trans-Urals and Mugodzhary mining and metallurgical centres are confined to the oxidation zone of VMS, skarn and Cu-porphyry deposits (Table 2). The individual mines of these deposits typically reached only small depths of the oxidation zones. The mines were situated relatively far from each other to enable the provision of raw material for the nearby corresponding settlements (Figure 2). It is mainly due to the small reserves of the associated deposits that these mines have been maintained in their original state.

The VMS type has been examined on the example of ancient mines with Co-As mineralisation located in ultrabasic rocks of the Main Uralian Fault zone (Ishkinino, Ivanovka and Dergamysh) as described by V.V. Zaykov and colleagues (Zaykov et al., 2009). E.N. Cherhykh investigates the ancient mines of Bakr-Uzyak deposit oxidation zone hosted by volcanogenic-sedimentary island-arc strata (Chernykh, 1970) and the Ushkattyn mine in Mugodzhary (Zaykov et al., 2012). Former ancient mines known to have existed at Dergamysh and Bakr-Usyak have been destroyed by modern quarrying activity.

The skarn type of deposits has been examined in a study of Vorovskaya Yama and Novotemirsky ancient mines situated in ultrabasic rocks, as well as the Novonikolaevsky mine hosted by volcanogenic-sedimentary rocks. The Vorovskaya Yama and Novotemirsky ancient mines are confined to the contact zone between small rodingite bodies and ultrabasic rocks. The oxidation zone composed of azurite-malachite ores with elevated quantities of magnetite. The Novonikolaevsky mine is also confined to the contact zone between granodiorites and Carboniferous volcanogenic-carbonate rocks. The ores are composed of malachite, azurite and Fe hydroxides, sometimes with magnetite. In separate parts of the heap ground, lenses of calcined soil are recovered and dated to 12-11 centuries BCE. The geochemical composition of ores is marked by Co+Ni+Cr+As assemblage.

An example of Cu-porphyry deposit exploration is given by the Elenovka mine. The ore mineralisation is confined to the contact zone between granodiorites and carboniferous volcanogenic rocks (Zaykov et al., 2012). The ores are molybdenite-chalcopyrite-tourmaline type with a malachite oxidation zone. Around the mine, the enrichment site including slag area, a burial and Kuduksay settlement are situated. According to Kuzmina, the exploitation of the Elenovka mine began at around 1700-1600 BCE; by the Alakul period, it had already

Table 2. Summary characteristic of South Urals deposits developed in the Bronze Age.

Ancient mine	Geodynamic position	Age	Genetic type	Host rocks	Oxidation zone ore mineralogy	Geochemical features
Ishkinino	Prearc zone of West Magnitogorsk island arc	D_1	VMS	Serpentinites	Malachite, azurite, Cr-spinels	Co, Ni, As
Dergamysh	Prearc zone of West Magnitogorsk island arc	D_1	VMS	Serpentinites	Malachite, azurite, Cr-spinels	Co, Ni
Bakr-Usyak	West Magnitogorsk island arc	D_{1-2}	VMS	Volcanic-sedimentary rocks	Malachite, azurite	Zn
Novonikolaevsky	Collision (East Magnitogorsk island arc)	C_1	Skarn	Granodiorites, volcanic-sedimentary rocks	Malachite, chalcocite, covellite	Fe
Vorovskaya Yama	Collision (East Magnitogorsk island arc)	C_{1-2}(?)	Skarn	Serpentinites, rodingites	Malachite	Zn
Novotemirsky	Collision (East Magnitogorsk island arc)	C_{1-2}(?)	Skarn	Serpentinites, rodingites	Malachite, azurite, chrysocolla, chalcopyrite, magnetite	As, Fe
Elenovsky	Forarc basin	C_{1-2}(?)	Copper porphyry	Rhyolites, basalts	Malachite, tourmaline	B
Nikolskoye ore field (Nikolsky, Tash-Kazgan, Kuraminsky)	Collision (East Magnitogorsk island arc)	C_{1-2}	Copper porphyry	Quartz veins in basalts, granites	Malachite, chalcocite, covellite, bornite, chalcopyrite	As, Ag
Kargaly ore field	Pre-Ural marginal deflection	P_3	Copper sandstones	Sandstones, siltstones	Malachite, azurite	Ba

reached its heyday. It then declined, ceasing altogether during the Late Alakul period (Kuzmina, 1963). The evidence for the exploitation of such deposits consists in the discoveries of copper-tourmaline ore fragments in the Bronze Age settlements and the elevated boron content of metallurgical slags from the Arkaim settlement (Bushmakin and Zaykov, 1997). The Cu-porphyry deposit Nikolsky ore field (Yuminov and Zaykov, 2009) included the Tash-Kazgan, Nikolsky and Kuramino ancient mines. The Nikolsky ore field is confined to the contact zone between carboniferous volcanogenic rocks and the ultrabasites of the Main Uralian Fault zone. The host rocks are interspersed with numerous quartz and carbonate-quartz veins enriched with Ag-sulphide mineralisation. The ores of these deposits contain elevated amounts of As and Ag (Chernykh, 1970).

CONCLUSIONS

The research has highlighted the most important markers of four main mineralogical types of metallurgical slags from the South Urals. The olivine Cr-rich spinel-containing group held large zoned fayalite grains transformed to forsterite in the core, as well as relic Cr-rich spinels and serpentinised ultrabasites; this resulted in elevated Cr and Ni contents, as well as high quantities of As in melt inclusions. The sulphide-containing olivine slags, which include chained fayalite crystals, relic sulphide globules and fragments, are marked by an elevated Co and Mo content, as well as a significant quantity of Se in sulphide form. The glassy sulphide-containing type, which provides the majority of quartz and barite fragments, represents the elevated Ba and Pb contents. The pyroxene slags are rather heterogeneous in composition; the main minerals are ferruginous wollastonite, augite and wollastonite having a specific ‘box-like’ morphology. The phase diagrams of neogenic minerals and experimental study indicate that the slags have crystallised very quickly, with maximum melt temperatures reaching 1150-1300 °C.

We observe that Cr-rich spinel-containing olivine slags are related to the Early Yamna period of the Cis-Urals (4000-3300 BCE) and Sintashta period of the Trans-Urals (2000-1700 BCE); the distribution of the olivine sulphide-containing type, as recovered in Alakul cultural layer of Kamenny Ambar settlement (1700-1300 BCE), is rather limited; glassy sulphide-containing and pyroxene slag groups are related to the Srubna culture of the Cis-Urals (1700-1300 BCE) and the Alakul culture of the Trans-Urals (1700-1300 BCE).

In the Trans-Urals mining and metallurgical centre, mostly oxidised and rare sulphide ores of oxidation zone upper horizons of skarn, VMS and Cu-porphyry deposits were used. The majority of explored deposits are confined to ultrabasic massifs of the Main Uralian and East-Urals Faults where the basic mineral of metallurgical slags is olivine, quartz is absent and where a high Fe content and low Si / Na+K content is typical. In the Cis-Urals MMC, both rich sulphide and mixed sulphide-oxidised ores of cupriferous sandstones were used. Here, a large quantity of quartz is contained in slags; however, olivine and magnetite are absent and the glass has a high Si and Na+K content.

The elevated Ca, P and REE in olivines indicate the usage of calciferous and bone flux to decrease the temperature of ore melting. In the glassy slags, the non-melted barite relics and high Ba content provides evidence that barite has been used as a flux. The presence of arsenic bronzes and high arsenic content in olivines from bulk analyses of several Bronze Age settlements (e.g. Ustye in the Trans-Urals and Rodnikovoe in the Cis-Urals) indicate that alloying components were artificially added during the ore charge stage.

The objectives of further research are the establishment of geochemical markers in sulphide- and metal inclusions, along with the further investigation of additional Bronze Age archaeological sites of the South Urals.

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