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Shiny bronze in glassy matter: an inconspicuous piece of slag from the Bronze Age mining site of Muşiston (Tajikistan) and its significance for the development of tin metallurgy in Central Asia

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Abstract
This paper aims at contributing to a better understanding of the beginnings of tin and bronze metallurgy in Central Asia by investigating a hitherto unique piece of a bronze slag. The object was originally discovered as a stray find only 4 km away from the large copper-tin deposit of Muşiston in Tajikistan. It contains many prills of bronze and copper as well as small charcoal particles. Radiocarbon dating of the charcoal places the slag in a period between 1900 and 1400 BCE and thus in the Late Bronze Age of the region. This date coincides with radiocarbon dates of relics from underground galleries of the Muşiston deposit. Chemical and microscopic examination demonstrated the slag to be a relic of a co-smelting process, in which a natural assemblage of tin and copper minerals was smelted simultaneously. Both the chemical and the tin and copper isotope compositions clearly link the slag to the nearby polymetallic ores from Muşiston, of which an extensive dataset is presented. The artefact’s lead isotope ratios and increased iron concentration in turn indicate intentional fluxing of the original ore charge with iron-dominated ores. These results are the first tangible evidence of a smelting process of tin ores in the entire region and therefore add a new dimension to the findings from previous mining archaeological investigations. At the same time, the results give significant information about the smelting process of secondary polymetallic ores from Muşiston and help in assessing the scientific data of Bronze Age bronze artefacts from Central Asia.

Keywords Smelting slag · Co-smelting · Late Bronze Age · Central Asia · Muşiston · Tin and copper ores · Isotopic analysis · Process reconstruction · Bronze production

Introduction
The largest part of the Central Asian Republic of Tajikistan (> 90%) is covered by mountains (Fig. 1; Rahmonov et al. 2017). Especially the southeast of the Tajik territory has extensive mountainous areas, reaching altitudes of more than 5000 m above sea level. Although seemingly barren and hostile to life, a flourishing cultural tradition developed in the numerous high valleys and adjacent plains during the 3rd and 2nd millennia BCE covering the Bronze and Iron Age (Kohl et al. 1984; Eichmann and Parzinger 2001; Vinogradova 2004; Kaniuth 2006; Garner 2013; Doumani Dupuy 2016; Lyonnet and Dubova 2020). While the northern and western regions of Tajikistan and the neighbouring Uzbekistan were influenced by the Andronovo cultural phenomenon (complex of steppe cultures), the Bactria-Margiana archaeological complex (BMAC) or Oxus civilisation extended to the Tajik south and southwest (historically...
known as Bactria) (Fig. 1). Large settlements and burial sites such as those of the Sapalli, Vakhsh and Beshkent cultures bear witness to the rich cultural tradition in the Bactrian plains and surrounding hill lands. Metallurgical remains are widespread in the whole region, also in the northern Andronovo-influenced areas (e.g. Chernykh 1992; Kraus 2020). Most of them from the 3rd millennium BCE (Early Bronze Age) consist of unalloyed copper. However, towards the end of the millennium and during the first half of the 2nd bronze became gradually common during the Middle and Late Bronze Age, often associated with Andronovo influences (Kuz’mina 1966; Chernykh 1992; Ruzanov 1999; Parzinger 2003; Kaniuth 2006; 2007; Kraus 2020). Like the mechanisms of cultural interaction between the different regions, the origin of the tin for these bronzes remained elusive for a long time. However, extensive research since the mid-1990s provided increasing evidence that tin resources in the Zeravšan valley and the circumjacent mountains (Fig. 1) played an important role in the supply of tin throughout the region’s Bronze Age (Cierny 1995; Weisgerber and Cierny 1999; Cierny and Weisgerber 2003; Parzinger and Boroffka 2001; 2003; Garner 2013; 2015). There is even speculation as to whether Central Asian tin may have reached Iran, Mesopotamia, the Arabian Peninsula and Egypt (Cleuziou and Berthoud 1982; Parzinger and Boroffka 2001; 2003; Thornton et al. 2005). Especially the tin sources of Karnab, Lapas and Čangali in Uzbekistan are promising candidates, but also the large copper-tin deposit of Mušiston (also Mushiston) in Tajikistan. Both mining areas were the subject of a joint research project (Volkswagen-Stiftung) of the Deutsche Bergbau-Museum Bochum, the German Archaeological Institute Berlin, the Max Planck Institute for Nuclear Physics Heidelberg, Germany, the Technical University Bergakademie Freiberg, Germany, and the Uzbek and Tajik Academies of Sciences from 1997 to 1999 (Parzinger and Boroffka 2003; Garner 2013). Prior to that, geological-archaeological investigations between 1961 and 1975 by the Uzbek Ministry of Geology revealed first indications of an ancient exploitation of tin sources (Avanesova 2020).

Fig. 1 Topographical map of Central Asia showing the location of tin sources mentioned in the text. The red and green shaded fields correspond to the inhabited areas of the Andronovo cultural community (red) and the Bactrian-Margiana Archaeological Complex (green) during the 2nd millennium BCE with a zone of cultural overlap (map: D Berger, C Frank)
Karnab, Lapas and Čangali are located at moderate altitudes (450–700 m) in the steppe and uplands south of the Zeravšan River and were thus relatively easy to access. On contrast, Mušiston is situated at about 3000 m above sea level in the Zeravšan-Gissar mountain range and posed considerable challenges in terms of accessibility (Fig. 1). The valley of the Kaznok River, which opens out into the Zeravšan valley via the Negnot and Kshtut Rivers to the north, is the only natural gateway to the Mušiston deposit (Fig. 2). Despite adverse conditions, the ore body was exploited as early as the Bronze Age. During modern prospections by Soviet archaeologists and geologists, surface workings and underground galleries were discovered at several locations, which could later be dated to the 3rd and the 2nd millennia BCE by radiocarbon dating and potsherds (Garner 2013). The observations on site indicate that the oxidised ores in the deposit’s large oxidation zone were the focus of human attention. In contrast, the primary ore mineral stannite was apparently not sought (Alimov et al. 1998; Parzinger and Boroffka 2003; Cierney and Weisgerber 2003). In fact, the striking green and yellow colours of the secondary ores may have attracted the ancient miners more than the bronze to dull grey shade of stannite. The economic potential of the deposit itself and the rare paragenesis of copper and tin could have formed the basis for its exploitation despite the inhospitable environment: smelting of the ores produces a ‘natural’ bronze (Cierney 1995; Rovira and Montero 2003), which was probably the main motivation for extracting the resources. Archaeological prospection and excavation in the surroundings of Mušiston unveiled small finds and architectural structures (probably a sanctuary) of the Andronovo culture (2000–900 BCE). This suggests a temporary or seasonal inhabitation of the place during the Bronze Age (Alimov et al. 1998; Parzinger and Boroffka 2001; 2003), presumably for mining and ore processing.

During field inspections in 1997, some slag pieces were found near the Mušiston outcrops (Boroffka et al. 2003, 234–236). Since most of these were stray finds collected from the surface, none of them received much attention at this time. However, during reassessment of the material within the framework of the interdisciplinary ‘BronzeAgeTin’ project (PI: E Pernicka) at the Curt-Engelhorn-Zentrum Archäometrie Mannheim (CEZA), one of the slags, found only 4 km downstream at ca. 2500 m above sea level (Fig. 2b–c), proved to be of particular interest. On the one hand, enclosed prills of reddish and golden material were visible to the naked eye; on the other, tiny charcoal relics offered the possibility for radiocarbon dating (Fig. 3).

The prospect of a possible prehistoric smelting in the immediate vicinity of a tin deposit is particularly electrifying: while evidence of early tin mining is rare in archaeological records, proof of tin smelting is even rarer due to the lack of finds. Only two handfuls of metallurgical debris are known from the Eurasian Bronze Age, including tin and bronze slags as well as smelting crucibles (Miles 1975; Tylecote et al. 1989; Herdits et al. 1995; Yener and Vandiver 1993; Adriaens 1996; Mahé-Le Carlier et al. 2001; Rodríguez Díaz et al. 2001; Rovira and Montero 2003; Rovira 2005; Figueiredo et al. 2010; Stöllner et al. 2011; Le Carlier de Veslud et al. 2017; Li et al. 2019). The potential evidence of smelting of the Mušiston copper-tin ores provided by a multi-analytical approach will thus significantly enhance our knowledge on the processing of tin in the Bronze Age. The results could also help to better understand the development of the early tin and bronze industry in Central Asia and probably beyond. In this paper, we present the results of the comprehensive investigation on the Mušiston slag using microscopic, mineralogical, chemical, isotopic (Sn–Cu–Pb), and radiocarbon methods. Furthermore, we try to relate the find to the nearby deposit by comparing the analytical data of the slag with those of ore samples. The paper concludes with a discussion of the smelting process and of the importance of Mušiston as a tin source in the Bronze Age.

Analytical methods

The slag from Mušiston (MA-171261) is the only archaeological find analysed in the present study (Fig. 3a). Due to the heterogeneous nature of the slag, a variety of microscopic and analytical methods was applied in order to characterise and date the object as accurately as possible. In a first step, the object was investigated macroscopically and cut into pieces. One part was embedded in epoxy resin and materialographically prepared according to standard preparation methods (Scott and Schwab 2019). The cross-section was examined by optical microscopy (Axioskop 40, Zeiss, Jena, Germany) and scanning electron microscopy (SEM) (CEZA: EVO MA 25, Zeiss, Jena, Germany; H.-P. Meyer: LEO 440 Zeiss, Jena, Germany) after carbon coating. Semi-quantitative chemical analysis at the section occurred with energy dispersive X-ray spectrometers (EDX) (CEZA: Quantax 400, Bruker AXS, Karlsruhe, Germany; H.-P. Meyer: X-Max-150, Oxford Instruments, Abingdon, UK) coupled with the respective electron microscopes. Point and areal analyses as well as elemental mappings were performed; the values from these measurements are reported in % by mass throughout the paper.

Another part of the slag was crushed to expose metallic residues and other components such as organic material (Fig. 3b–c). Tiny pieces of charcoal were carefully collected from the interior and subjected to radiocarbon dating with the MICADAS accelerator mass spectrometer at the CEZA (Kromer et al. 2013). Sample preparation for this purpose was challenging because of the low amount of sample material (ca. 50 µg) and contamination by soil particles. Accordingly, conventional preparation was not
Fig. 2 View from the north on the Cu–Sn deposit of Mušiston with the location of prehistoric galleries (a) and perspective view (b) and top view (c) of the Kaznok valley and its surroundings including the fertile valley of the Zeravšan River (photo (a): J Lutz; maps: D Berger after Google Earth, with modifications)
possible so that preparation was carried out at the Institute of Environmental Physics (IUP), Heidelberg University, Germany. Two sub-samples (31106a, 31106b) were pre-cleaned with 0.2% HCl for 15 min to remove contaminations (carbonates). The remaining sample material was combusted to CO2 in a closed-tube combustion procedure. CO2 was cryogenically trapped and measured at CEZA by using the Gas Interface System (GIS) of the MICADAS accelerator to analyse small masses (< 100 µg C) of CO2 (Hoffmann 2016; Hoffmann et al. 2018). Radiocarbon calibration was achieved with the Oxcal software v4.4.2 of the Oxford University and the calibration dataset IntCal20 (Reimer et al. 2020).

Pieces of the slag matrix (MA-171261–14 and -15) were pulverised to analytical grade and analysed for their mineralogical composition with X-ray diffractometry (D8 Discover eco, Bruker AXS, Karlsruhe, Germany) at the Institute of Geosciences, Heidelberg University, Germany. SEM–EDX at the CEZA served to determine the bulk chemical composition of the slag. An energy dispersive X-ray fluorescence spectrometer (EDXRF) (ARL Quant’X, Thermo Fisher Scientific, Bremen, Germany) at the CEZA was used for the compositional analysis of metallic residues. Thirteen of the largest metal prills (MA-171261–1 to -13) were investigated, whose individual masses ranged from 2.3 to 26.3 mg (Fig. 3b; Table 1). The total mass of metallic residues throughout the slag was not determined, but based on the 101.2 mg of the 13 specimens, it is estimated to less than 150 mg. Prior to chemical analysis, all samples were mechanically cleaned to remove any non-metallic
component. This was necessary not only for achieving a representative chemical characterisation, but also for an accurate determination of the metal’s isotopic composition. In particular, tin isotopes tend to fractionate between metallic and siliceous phases, as smelting experiments with tin ores have shown (Berger et al. 2018). The metal prills were completely dissolved with mineral acids and the solutions analysed with a multi-collector inductively coupled mass spectrometer (MC-ICP-MS) at the CEZA (Neptune Plus, Thermo Fisher Scientific, Bremen, Germany). Aliquots of the solutions were processed according to the requirements of tin, copper and lead isotope analysis. Details of the preparation and analytical protocols are described in Brügmann et al. (2017a) and Berger et al. (2022). The copper isotope ratios are given in delta notation as δ\(^{65}\)Cu (\(=\delta^{65}\)Cu/\(^{63}\)Cu) in ‰ relative to NIST SRM 976. In the case of tin, the samples were originally measured along with an ultrapure tin metal reference material (Johnson Matthey Puratronic) and eight tin isotope ratios were determined (Brügmann et al. 2017a). These values were recalculated to NIST SRM 3161a reference solution (Brügmann et al. 2017a) and finally subjected to a linear regression analysis in order to obtain δSn values in ‰ per atomic mass unit (‰ \(^{\text{u}^{-1}}\)). This was done to facilitate comparison with other studies. For the sake of completeness, the original tin isotope data (relative to Puratronic) is reported in the electronic supplementary material (Online Resource 3) of this paper, not least to allow comparison with data of our own group formerly using the \(^{124}\)Sn/\(^{120}\)Sn ratio (e.g. Brügmann et al. 2017a; 2017b; Nessel et al. 2019; Berger et al. 2019). In addition to the metal samples, the lead isotope composition was also determined for the slag matrix (MA-171261–14 and -15) on the pulverised material with the same MC-ICP-MS at the CEZA.

### Results

#### Macroscopic description of the slag

The Mušiston slag is a fist-sized object and showed macroscopically neither remains of refractory materials from furnaces or crucibles nor any flow structures typical for tapped slags (Fig. 3). Its external colour is light brown due to sintered soil accretions or iron oxide components. Organic matter survived in cavities and consists mainly of plant roots. The slag matrix itself is of a dull dark grey colour and appears vitreous only in some areas. On fresh fractures, green stains were observed, which were also present in vesicles enclosed by the slag material. Overall, the object is rather heterogeneous with a high amount of porosity (Fig. 4a). Numerous metal prills are distributed throughout the slag, and most of them are smaller than 10 μm in diameter. A small fraction ranges up to 100 μm, and only some of the prills are larger than 1 mm. The colour of the metal varies from copper red to golden yellow. Strikingly, the metal appeared to have been concentrated in some areas of the slag, while others are virtually free of metallic residues (Fig. 4a). In addition, the slag turned out to be magnetic when tested with a hand magnet. As mentioned above, charcoal was found in the form of tiny pieces of up 2 mm in length, which were irregularly distributed within the object.
Metal inclusions

Many metallic inclusions of highly variable size and chemical composition are present in the slag and are concentrated at its centre (detailed description further below). Analyses with SEM–EDX were carried out directly on the polished section on 44 of these prills and revealed three compositional groups (Figs. 5 and 6; Online Resource 1): (1) bronze with tin contents between 0.12 and 10.9%. Besides, considerable amounts of arsenic (0.62–3.2%).

Fig. 4 Optical micrograph of the polished section of the bronze slag as seen under bright field illumination (a, d) and under crossed polars (b–e, c). In (a) bluish sulphides of Cu and Cu–Fe and red-yellow metal inclusions can be discerned from the dark grey coloured slag matrix. The metal-rich centre is clearly demarcated from the metal-poor outer region of the slag sample highlighted by the hatched orange line. (b) and (c) are close-ups of the typical appearance of the outer region and the slag ‘centre’, while (d) and (e) show the sharp transition between both regions (photos: D Berger)
silver (0.16–1.32%) and antimony (0.78–4.3%) are present in almost all of the metal inclusions of this group. Some of them additionally contain iron, zinc and lead, and considerable concentrations of bismuth, up to 18% in one of the prills (Online Resource 1). Group (2) is copper alloys without tin, but with the same alloying elements silver, arsenic and antimony, and occasionally iron, zinc, lead and bismuth. There seemed to be no accumulation of this kind of metal in any particular area of the slag because it occurs together with the prills of the first group. This observation was also true for the metal prills of group (3), which consist of lead. Inclusions of this type are significantly less frequent in the slag and contain only antimony up to 3.5% (Fig. 6e; Online Resource 1). Conspicuously, no metallic tin or high-alloyed bronze with more than 40% tin could be observed in the entire slag.

Groups (1) and (2) were also identified among the 13 metal samples analysed ex situ by EDXRF (Table 1). However, the prills of group (2) contain several hundred µg g⁻¹ tin, which may have been missed by SEM–EDX because the concentration was below the limit of detection of the device. Other trace elements such as selenium, cobalt and nickel were also identified by EDXRF with concentrations up to 500 µg g⁻¹. The high concentrations of selenium are particularly remarkable in this context since the metalloid as a trace element in copper alloys rarely occurs at such high levels. One sample (MA-171261–12) stood out due to distinctly higher concentrations of iron (1.4%), cobalt (0.08%) and nickel (0.56%) than in the other metal samples that came along with an elevated lead content of 12.3% (Table 1).

Depending on their tin concentration, the bronze inclusions are either single- or bi-phased. The largest of the prills for instance showed a dendritic microstructure of primary α-bronze and (α + δ)-eutectoid in the polished section (Figs. 5a and 6a). Its surface is covered by a thin layer of cuprite (Cu₂O) and chalcocite (Cu₂S) above a complex layer of oxidised Cu–Sn–Fe–Sb phases that could not be properly identified (Online Resource 2, Points 37–38). Non-metallic
inclusions have been preserved throughout the microstructure of the bronze and are dominated by sulphides (Cu₂S), in which selenium concentrates (Online Resource 2, Point 168). Similar observations applied to the copper prills, which irregularly contain either Cu₂S (with Se and Te) or Cu₂O inclusions. Moreover, segregations of bismuth associated with silver were documented (Online Resource 2).

Towards the surface of the large bronze prill, there were indications of corrosive attack (Cu₂O corrosion products), which is even more pronounced in other metal prills in the slag. While some metals from groups (1) and (2) exhibited only a superficial alteration, high-temperature corrosion has propagated vividly towards the centre of other prills thereby disintegrating the structure of the metal. Still other prills were completely transformed into corrosion or scaling products, mainly cuprite (Fig. 5).

On nine of the samples extracted from the slag, the isotopic composition of tin, copper and lead was determined. The tin isotopic composition (δSn) of eight prills ranged from −0.097 ± 0.001 to +0.089 ± 0.002 ‰ with a weighted average of −0.023 ± 0.144 ‰ (2SD) (Table 2). The weighted average is considered to be more meaningful than the standard mean value in the present case, as it takes into account the different masses and tin contents of the prills. It corresponds to the theoretical isotopic composition of a bronze that would have been melted from all the metal prills analysed. For the same reason, the weighted averages of the copper isotope composition δ⁶⁵Cu of 0.22 ± 0.64 ‰ (2SD) and the tin content of 5.1 ± 3.9% (2SD) are regarded as more meaningful estimates for the entire metal population of the slag. The copper isotope ratios of individual prills spread from −0.34 ± 0.01 ‰ to 0.69 ± 0.02 ‰, but were predominantly positive (Table 2). Nevertheless, copper isotope ratios are as variable as the tin isotope ratios, which surprisingly also applied to the lead isotope composition of six specimens (Table 2). For example, ²⁰⁷Pb/²⁰⁶Pb ranged from 0.86160 to 0.87197, while ²⁰⁸Pb/²⁰⁶Pb varied from 2.1117 to 2.1361. There seemed to
be no systematic relationship between the different isotope systems (Fig. 7), as is the case for trace elements and the chemical composition (not illustrated).

**Slag matrix and non-metallic components**

The bulk chemical composition of the slag was determined by SEM–EDX applying two methods, and the results are listed in Table 3. Areal analysis of the entire polished section yielded high amounts of Fe$_2$O$_3$ (28.5%), Cu$_2$O (10.1%), ZnO (6.7%), SnO$_2$ (9.5%) and PbO (0.79%) besides common slag components such as SiO$_2$ (31.3%), Al$_2$O$_3$ (3.9%), CaO (5.4%), K$_2$O (1.00%) and MgO (1.45%) (Table 3, slag ‘cross section’). Bulk EDX analysis of the pulverised slag samples (MA-171261–14 and -15) gave comparable compositions only considerably deviating in the content of Fe$_2$O$_3$ (44.9–46.3%), which is higher, and those of CaO (2.12–2.18%), ZnO (0.88–0.95%) and SnO (1.17–1.21%), which are lower compared to the data of areal analysis on the section (Table 3, slag ‘powder’). This discrepancy between powder samples and cross-section as well as between the two powder samples may be explained by the heterogeneous nature of the slag and the differing volumes comprised by the samples. At the same time, the differing chemical compositions can provide clues as to why the lead isotope signatures of the two powder samples differ significantly (Fig. 7b–c; Table 4).

On closer inspection under the microscope, two distinct areas in the slag could be discerned that are not only different in their visual appearance but also in their chemical and mineralogical composition. These regions are called ‘centre region’ (which is metal rich) and ‘outer region’ hereafter (Fig. 4). Viewed under crossed polars, the centre region of the cross-section revealed to be highly crystallised. It has a whitish transparent colour due to the presence of colourless or white crystals and shows many dark spots of opaque minerals (Fig. 4c). The matrix is a Zn–Fe–Al–Si–Ca–Mg–O glass, which varies in chemical compositions at different positions. Exsolution is pronounced, showing mainly melilites with a composition between (ferro)åkermanite (Ca$_2$(Mg,Fe)Si$_2$O$_7$), iron gehlenite (Ca$_2$(Fe,Mg)SiAlO$_7$) and hardystonite (Ca$_2$ZnSi$_2$O$_7$) (Online Resource 2 and 4, points 39–41, 69–70, 143–145, 162–164). Acicular, rhombohedral, tabular or slightly rounded crystals of secondary cassiterite (SnO$_2$) are embedded in the matrix and encircle metallic inclusions (Fig. 6a–d; Online Resource 2 and 4, points 42–43, 52–54, 63–64, 71, 74, 76, 80, 101–106, 110–111). Many of these crystals have hollow cores enclosing glass and occasionally bronze or copper prills (Fig. 6e). In addition, copper and zinc appear to be incorporated in the crystal lattice of SnO$_2$, which is suggested to be a typical feature for secondary cassiterite that formed during the oxidation of bronze (Benvenuti et al. 2003; Renzi and Rovira 2016;
 Therefore, it can be easily distinguished from cassiterite as a primary ore mineral that is commonly free of both constituents.

Among accumulations of cassiterite, euhedral crystals of magnetite were observed (Fig. 6). But rather than consisting entirely of iron and oxygen following the formula Fe^{2+}(Fe^{3+})_2O_4 ('Fe_3O_4'), the bivalent iron position in the spinel seems to be completely substituted by Zn^{2+} ions, less frequently also by Cu^{2+} (Online Resource 2 and 4, points 44–45, 55, 61–62, 68, 79, 87, 100). The trivalent position, on the other hand, might be partially occupied by tin ions, whereby co-incorporation of Fe^{2+} and Sn^{4+} must be assumed to ensure charge balance (Heimann et al. 2010). This zinco-stanniferrous magnetite, (Fe^{2+},Zn)(Fe^{3+},Sn)_2O_4, appears to be a solid solution between franklinite (ZnFe_2O_4) and a nameless tin spinel analogue to the inverse ulvöspinel (Fe_2SnO_4 instead of Fe_2TiO_4; see Heimann et al. 2010). To our knowledge, this kind of spinel has not yet been described.

Fig. 7 Tin, copper and lead isotope compositions of the analysed metal prills of the slag compared to the isotope systematics of hypogene sulphidic (stannite) and supergene oxidic ores from Mušiston. Legend in (b) also applies to (c); the black dot in (a) represents the weighted average of the metal samples (2SD) which has been corrected for the fractionation on smelting by $-0.025 \text{ ‰ u}^{-1}$ (cf. Online Resource 5). The annotation -12, -14 and -15 in (b–c) corresponds to the slag powder samples MA-1761261–14 and -15 as well as the metal sample MA-1761261–12 (diagrams: D Berger; data: G Brügmann, B Höppner).
from ancient slags, which may be due to the mineralogical peculiarities of the Mušiston deposit.

The spinel is impregnated with tiny crystals of SnO2 that precipitated during cooling (Fig. 6d). It is additionally associated or intergrown with another Zn-bearing spinel in some places of the slag centre. This spinel (sensu stricto) is not as variable in chemical composition as the magnetite-based variant, but contains the same elements zinc, iron and tin. Zinc is the dominating component besides aluminium and oxygen (Online Resource 2 and 4, points 65–67, 77, 86). The formula of the spinel corresponds to (Mg,Zn,Fe,Sn)Al2 O4, and it is thus a solid solution based variant, but contains the same elements zinc, iron and tin. Zinc is the dominating component besides aluminium and oxygen (Online Resource 2 and 4, points 65–67, 77, 86). The formula of the spinel corresponds to (Mg,Zn,Fe,Sn)Al2 O4, and it is thus a solid solution based variant, but contains the same elements zinc, iron and tin. 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off the melt (Hauptmann 2007, 169–171). Reaction zones could also be observed for agglomerates of alumo-silicates at one location of the outer region of the slag sample (particle size < 50 μm, occasionally up to 250 μm). A reaction zone with elemental gradients is clearly visible (Fig. 11c; Online Resource 2, point 155–156), and it is conceivable that the components were part of the clay lining of a furnace. The bulk chemical composition of the unaltered zone mainly comprises light elements like SiO₂ (46%), Al₂O₃ (22%), CaO (5%), K₂O (5%), MgO (4%), TiO₂ (2%) and 13% Fe₂O₃ (Online Resource 2, point 155). A similar composition was determined for agglomerates of fine-grained alumo-silicates within voids at other locations of the slag (Online Resource 2, points 213, 214, 216). However, they show no signs of reaction with the slag matrix (Fig. 11d). They were thus acquired during burial in the soil, which is also true for striated iron oxide formations at the surface (from weathering).

### Charcoal relics and dating of the slag

Tiny particles of charcoal were documented at different locations within the slag, which were visible with the eye and microscope (Figs. 3c and 12). They reached dimensions up to 2 mm in length and totalled to no more than 2 mg in the entire object. This is a relatively small amount of charcoal; nevertheless, two particles could be analysed by radiocarbon dating. One of them consisted of almost pure charcoal (MAMS-31106–1; 60% C) and yielded a calibrated age of 1882–1524 calBCE (2σ) (Fig. 13). The second piece was heavily contaminated with inorganic soil particles (MAMS-31106–2; 17% C), which could not be removed completely prior to analysis (Fig. 3c). This might be the reason for its somewhat older date of 2846–2143 calBCE (2σ).

Even if the charred material provides only a cursory view (e.g. only transversal sections) due to its small size, residual details of the vascular system of the former wood still allow some conclusions to be drawn about the nature of the tree or shrub from which it originates. On the one hand, several charcoal particles in the microscopic cross-section of the slag show features of a homoxylous structure with radial alignments of (collapsed) tracheids and ray parenchyma cells (Fig. 12c–d). With all due caution, one could deduce from the observations that these charcoal pieces originate from coniferous wood (softwood). On the other hand, there are particles with heteroxylous structural features. They show oval-shaped vessel elements (poles), fibres and parenchyma cells (Fig. 12a–b), which are typical for hardwood (Wiedenhoeft and Miller 2005; Schweingruber 2007). Taken together, there seems to be charcoal stemming from both hardwood and softwood.
Discussion

Cultural allocation

Ancient smelting slags from the pyrotechnical processing of tin ores are among the great rarities of archaeological finds. From all over Eurasia, a maximum of two handfuls of such vestiges are known from prehistoric contexts. The identification of the Mušiston slag as a relic of a tin ore smelting process is therefore an exceptional result. This result is even more important in view of the age: radiocarbon dating of two charcoal flakes from the interior of the slag allows its attribution to the Bronze Age in a time period from 2846 to 1524 cal BCE (2σ). Given the high degree of contamination of the second dated charcoal piece, only the date of the first and much purer piece is considered to be trustworthy. This delimits the age of the slag to between 1882 and 1524 cal BCE (2σ). The rather broad time span compared to standard radiocarbon dating using solid graphite instead of CO₂ gas can be attributed to the small amount of charcoal available for analysis (ca. 50 µg) causing the analytically uncertainty to be much larger (Hoffmann 2016; Hoffmann et al. 2018). However, despite the high analytical errors a possible old wood effect, ¹⁴C dating places the charcoal and hence the slag in the Late Bronze Age (1900–1400 BCE). This result is important and interesting at the same time, as it matches with the dating of charcoal remains excavated within galleries of the Mušiston copper-tin deposit only 4 km upstream the Kaznok River (Alimov et al. 1998; Garner 2015). Together with other archaeological finds (particularly ceramics; also mallets, antler picks, wooden remains), there is strong evidence that people from the Andronovo cultural community, more precisely from the Andronovo-Tazab’jab subgroup (Parzinger and Borroffka 2001; Parzinger 2006; Garner 2015), inhabited or controlled the area around Mušiston and exploited its polymetallic ores. Of course, the absolute age of the slag does not imply a cultural link. However, given the archaeological observation from the site and its direct vicinity, it is most likely the product of a smelting process by the same people. In this respect, it would be a rare pyrotechnical residue from the Bronze Age in the entire region.

The question of local ore smelting

The proximity of the bronze slag to a metal source and especially the matching Cu–Sn characteristics make it very likely that the object originates from the vicinity of the find spot and that smelting activities took place on site. Nevertheless, we felt compelled to verify this by correlating the chemical and isotopic systematics of the slag and its components with those of the ores of the nearby deposit. This point weighs all the more heavily, since the slag piece was just a stray find from the surface. At the same time, the situation can serve as a valuable case study to assess how diagnostic the non-traditional isotope systems copper and tin are in terms of metal provenance.

As mentioned above, Mušiston is a polymetallic ore body with an ore assemblage containing copper and tin minerals. The sedimentary host rocks belong to a sequence of Ediacaran to Ordovician schists, Lower Silurian limestones, Upper Silurian to Lower Devonian dolomites and limestones with overlying Upper Devonian (siliceous) schists (Pavlovskii et al. 1995; Alimov et al. 1998, 166; Konopelko et al. 2022). Tectonic activity affected the region in the Lower Carboniferous, Permian and the Jurassic era, but hydrothermal ore formation took place only during the Variscan orogeny (ca. 300–280 Ma). The ore body itself has a large zone of primary mineralisation consisting mainly of stannite (Cu₂SnFeS₄). This sulphide mineral contains copper (28–30%), tin (26–28%) and iron (13%) as major constituents, but also zinc (up to 7%), which can substitute for ca. half of the iron (thus resulting in Cu₂Sn(Fe₀.₅Zn₀.₅)S₄) (Alimov et al. 1998, 166; Konopelko et al. 2022). Stannite occurs massively in veins and veinlets together with quartz and minor and accessory minerals (cassiterite, sphalerite, arsenopyrite, chalcopyrite, pyrite, scheelite, tetraedrite, bouronite, bismuthinite, native bismuth, galena, tetradyminate and rhodostannite). According to Alimov and colleagues (1998), the primary ores were not the focus of the ancient miners; instead, the deposit’s large oxidation zone (200–400 m) with secondary minerals had been exploited (see also Ivanov et al. 1993; Sun et al. 2017; Konopelko et al. 2022). This is confirmed by the mining archaeological observations, which documented Bronze Age galleries exclusively from the supergene region (Alimov et al. 1998; Weisgerber and Cierny 1999; Garner 2013; 2015). Greenish, yellowish to brownish oxidised ores are present there and are admixtures of secondary copper and tin minerals. Malachite (CuCO₃Cu(OH)₂) and residual cassiterite (SnO₂) are the most common compounds, but there is also azurite (2CuCO₃·Cu(OH)₂) and a variety of hydrostannates like mushistonite ((Cu₂Zn,Fesn(OH)₂), varlamoffite ((Sn,Fe) (O,OH)₂), vismirnovite (ZnSn(OH)₂), and natanite

Table 5 Mineralogical phases of the powdered slag sample (MA-171261–14) determined by XRD (data: H-P Meyer)

| Lab. no.       | Object   | Mineralogical phases                           |
|----------------|----------|-----------------------------------------------|
| MA-171261–14   | Slag matrix | Fayalite, cassiterite, Fe-Sn oxide, hardystonite, petedunnite, cuprospinel |
Fig. 8 Elemental distribution maps of the slag comprising its centre and outer regions, which are clearly distinguishable by means of O, Ca, Fe, Zn and Sn. The inset in the optical micrograph (OM) marks the regions shown in detail in Fig. 9. Scale bar applies to each map (mappings: H-P Meyer)
(FeSn(OH)₆)). The relative abundance of the minerals is highly variable: zones with dominating copper minerals were documented as well as zones where tin minerals prevail. However, all kinds of mixtures are possible, and the colour of the ore roughly reflects the proportions of copper and tin minerals (Online Resource 5, Fig. 3). This empirical indicator presumably empowered the ancient miners or metallurgists to select exactly those ores that were sought for their purposes: either emerald green ores to produce copper metal or olive-green and yellow ores to obtain bronze and (impure) tin. Smelting experiments with the respective ores showed that all three products are possible by just selecting or mixing the raw materials on the base of the colour aspect (Online Resource 5). The smelting of the supergene ores themselves is in general easy to achieve in a single step, just like the smelting of malachite from other deposits (cf. Tylecote et al. 1977). The primary stannite on the other hand required roasting before it could be smelted. Moreover, the proportions of copper and tin even in the roasted charge are such (1:1) that only high-alloyed tin bronzes would be the product. Hence, oxidised ores offered apparent advantages over the primary ones. However, if a mixture of stannite and secondary copper-rich ore from Mušiston was processed following a co-smelting procedure (analogous to the co-smelting experiments with malachite and fahlores by Martinek 2011), then bronzes with moderate tin contents were possible without prior roasting of the stannite.

Due to Mušiston’s polymetallic nature with ores rich in elements like iron, zinc, arsenic, silver, antimony, lead and bismuth (Alimov et al. 1998, Tabelle 2; Online Resource 6), and on base of the smelting experiments (see Online Resource 5), it can be expected that the produced metals also contain these elements as impurities. This is actually observed in the chemical composition of prills and droplets in the slag. When compared with the chemical data of secondary ore samples from the site normalised to Cu + Sn, good match is observed for most elements, especially for arsenic, antimony, silver, lead and bismuth (Fig. 14a–b, d). Poorer agreement is observed for the stannite ore instead. The high concentrations of zinc and selenium in the metal (Fig. 14c) can be considered as an additional indication for the use of local ore, since primary and secondary mineralisation is exceptionally rich in zinc and contain also appreciable selenium (Alimov et al. 1998; Online Resource 6). The same

Fig. 9 Detailed view (OM) and elemental distribution maps of the slag comprising the centre and outer regions of the slag as marked in Fig. 8. Scale bar applies to each map (mappings: H-P Meyer)
A conclusion can be drawn from the association of zinc, tin and copper in the slag matrix.

Additional evidence concerning the origin from local ores is provided by the isotopic composition. The weighted mean $\delta^{119}$Sn of $-0.023 \pm 0.144 \% e$ u$^{-1}$ of the prills is well within the isotopic range of the Mušiston ores and very close to their average, even when a fractionation of about $+0.025 \% e$ u$^{-1}$ towards heavier isotopic compositions during the smelting is considered (Fig. 7a). This empirical value was determined by the experimental smelts of the secondary ores from Mušiston and is in good agreement with former smelting experiments with cassiterite (Berger et al. 2018; forthcoming; Online Resource 5).

Strictly speaking, the smelting of the Mušiston ores must be understood as a co-smelting procedure of naturally associated copper and tin minerals. That is why the pyrometallurgical impact on the isotopic composition of copper has also to be accounted for. In the co-smelting experiment mentioned above, we observed only a slight fractionation of copper isotopes of $+0.03 \% e$ relative to the original ore charge (Online Resource 5; Berger et al. in preparation). Applying this insignificant degree of fractionation to the mean $\delta^{65}$Cu value of the metal prills ($0.22 \pm 0.64 \% e$) does hence not obscure provenance. The value would be still within the isotopic field of the local ores and very close to their average composition (Fig. 7a). At the same time, however, neither the copper nor the tin isotope composition does provide any clues on whether secondary oxidic or primary sulphidic ores were used. The $\delta^{65}$Cu and $\delta^{119}$Sn variations of both ore types are very similar and overlap completely (Fig. 7a, Online Resource 6). This observation is contrary to the common belief that the copper isotope composition is a helpful tool in that it allows a discrimination between hypogene and supergene copper ores. Simply speaking, $\delta^{65}$Cu values of around zero are characteristic for primary (hypogene) sulphides, while secondary (supergene)
sulphides in the cementation zone are predominantly negative in δ⁶⁵Cu and secondary (supergene) oxides are positive (e.g. Markl et al. 2006; Klein et al. 2010; Jansen et al. 2018). Even though we do not yet have a reasonable explanation for the situation in Mušiston, it will most likely not compromise the general applicability of copper isotopes. Other copper deposits usually exhibit much better differentiation between mineral species in the copper isotope composition.

Given the finding in Mušiston, the few values in δ⁶⁵Cu of below zero in some of the prills (see Table 2) do thus not
necessarily indicate the presence of stannite as do primary copper sulphides in other copper mineralisation. Such variations in the copper isotope composition — as well as that of tin — in the metal phase can be a result of insufficient metal homogenisation and related reservoir effects during the smelting process (Berger et al. 2018; forthcoming). The low amount of sulphide inclusions in the metal and the slag matrix, however, can be regarded as an indicator for the smelting of oxidised rather than primary ores, as also does the presence of selenium in the metal. Would stannite really have been the feedstock for smelting after a previous roasting step, selenium would have been lost largely. Its oxide form \((\text{SeO}_2)\) is highly volatile and evaporates during an oxidising roast (e.g. Taskinen et al. 2011; or cf. Online Resource 6, MA-154255b, roasted ore). The presence of some copper and copper-iron sulphides in the slag does not contradict this conclusion. It is known from oxidised secondary copper ores that they often contain minor to substantial amounts of sulphide relics, which can be transferred into the metal phase or remain with the slag (Tylecote 1976; Craddock 1988).

If the combination of the chemical and the copper and tin isotope characteristics is clearly indicative of the Mušiston deposit, one would expect the lead isotopes to support the use of local ores all the more. This is obviously not the case.

**Fig. 13** Calibrated radiocarbon curves of two charcoal flakes (diagrams: R Friedrich using OxCal)
Not only do the lead isotope ratios of six metal prills vary greatly, they are also much less radiogenic than the parent ores (Fig. 7b–c). The same is true for the slag matrix with a similar (MA-171261–14) or even less radiogenic lead isotope signature (MA-171261–15) than the metal phase (Table 5). Such a deviation is surprising and cannot be explained by isotope fractionation processes. Smelting experiments have as yet indicated no or only minor influence of pyrometallurgy on the lead isotope ratios (cf. File S5; Budd et al. 1995; Macfarlane 1999; Stos-Gale and Gale 2009; Baron et al. 2009; Cui and Wu 2011) provided lead contents in ores are high. Otherwise, contamination with process components can take place (Rademakers et al. 2020). Similar observations with deviating isotope ratios between ores and slags as in our case have recently been reported by Pernicka and co-workers (2016) and Merkel (2016, 248–249). According to Pernicka et al. (2016), the separation of uranium phases and radiogenic lead during ore dressing could be a possible reason for the isotopic shift. Another reason could be the addition of flux material containing lead having a different isotopic signature. Since the high quality and massive occurrence of the Mušiston ores...
would have required only minor beneficiation, the second explanation appears more reasonable. However, lead contamination by the refractories or the fuel must also be kept in mind.

**Process parameters and smelting technology**

**Fluxing and the source of lead contamination**

The two options raised in the final sentence of the last paragraph do not seem to be viable explanations for the source of lead contamination given the generally high lead concentration in the oxidised ores from Mušiston (average $0.52 \pm 1.30\% \text{ PbO}$; Online Resource 6). Both the clay material used for constructing a furnace or crucible and the charcoal used in smelting are usually low in lead. Thus, the addition of a flux can be considered a more likely source of extraneous lead input to the system (Tylecote et al. 1977). Intentional fluxing could be indicated by the high level of $\text{Fe}_2\text{O}_3$ of 46% in the bulk slag. This is per se not much more than in other Bronze Age copper slags and in the few early tin slags. Comparable contents of iron were reported from contexts of the developed Bronze Age from elsewhere (Bachmann and Rothenberg 1980; Bachmann 1982; Tylecote et al. 1989; Chirikure et al. 2010; Heimann et al. 2010; Hauptmann 2007; Addis et al. 2016; Figueiredo et al. 2018; Li et al. 2019). The question of intentional fluxing with iron oxides (hematite, limonite, goethite) is hence not straightforward to answer, especially since the original ore charge and the process components like refractories are almost completely missing in the present case. In addition, the Mušiston ores contain appreciable amounts of iron (see Online Resource 6), which could lead to a high iron content in the slag. Thus, the ore can in theory be self-fluxing, given additionally the calcium-bearing sedimentary host rocks of the deposit (Ivanov et al. 1993; Alimov et al. 1999; Konopelko et al. 2022). However, iron is mainly associated with tin-rich ores in the cementation zone exhibiting $\text{SnO}_2/\text{Fe}_2\text{O}_3$ ratios of ca. 3–6, while the iron contents in malachite-dominated assemblages are very low ($\text{Cu}_2\text{O}/\text{Fe}_2\text{O}_3 = 70–400$) (Online Resource 6). Therefore, if we assume an intended tin content of about 10% in the final bronze and most of the iron is introduced with the tin component (cassiterite, hydrostannates), the original ore charge should have contained ca. 13% $\text{SnO}_2$ and not much more than 2–4% $\text{Fe}_2\text{O}_3$. This iron should mainly partition into slag, which would result in a concentration of ca. 30–45% if the amount of gangue is between 5 and 10% (gangue to $\text{Fe}_2\text{O}_3$ ratio < 3). If the charge was richer in gangue and/or the refractories and fuel contributed to the chemistry of the slag, the iron content in the slag would have changed considerably towards lower quantities. This is to be expected since the iron contents of ceramics and fuels are often relatively low (balance to $\text{Fe}_2\text{O}_3$ ratios between 10 and 20; e.g. Wolff 1871, 117–128) and the overall contribution of the components to slag formation is high (Thomas and Young 1999). Accordingly, it is hardly possible to achieve slags with iron concentrations of more than 40% $\text{Fe}_2\text{O}_3$ with the local ores alone, and intentional fluxing with iron minerals is very likely. This is, of course, only a mind game that ignores many details. In view of the missing process parameters and smelting components, this estimate is practically the best explanation we can offer.

However, further clues for the above interpretation are provided by the heterogeneous texture and properties of the slag sample. The different chemical and mineralogical compositions observed in the distinct areas of the slag indicate poor homogenisation and equilibration during the smelting process as expected for hearth slags (Hauptmann 2007). The heterogeneous texture and properties of the slag sample indicate poor homogenisation and equilibration during the smelting process as expected for hearth slags (Hauptmann 2007).

**Fig. 15** Normalised chemical composition of the slag matrix from the centre and the outer regions of the bronze slag reported in mass% (diagram and data: D Berger)
While the outer region is much richer in iron than the slag centre (52 vs. 16% Fe₂O₃), for zinc and tin, the reverse zonation is observed (1.4 vs. 12% ZnO, 1.6 vs. 20% SnO₂) (Figs. 8, 9 and 15). The high contents of both metals in the centre compared to the slag’s outer region promoted the formation of zinc- and tin-bearing phases like willemite, cassiterite and zinco-stanniferous magnetite apart from the numerous metal inclusions containing zinc and tin. This obviously occurred in preference over the corresponding phases fayalite and magnetite. It must be attributed to a sufficiently high concentration of both zinc and tin, and especially the former enforces the formation of discrete compounds when a certain level is exceeded. In case of fayalite, the crystal can dissolve up to 9% ZnO. Everything beyond leads to the formation of willemite, which in turn can dissolve a lot of FeO (20%) (Bachmann 1982, 14).

The predominance of zinc and tin (compounds) in the centre of the slag sample together with the numerous metallic inclusions limits the zone of ore reaction to this region (cf. Figure 4a), and it is likely that we are faced with some kind of batch smelting (Hauptmann 2007, 167). According to this scenario, ore nodules and flux material reacted more or less separately at different areas of the reaction volume. Consequently, the chemical composition of the slag centre is more close to that of the original ore charge than its outer region. In this case, the high iron content in the outer region cannot derive exclusively from the ore, nor is it possible that it stems from the lining. The small fraction of lining observed in the cross-section (Fig. 11c; Online Resource 2, point 155) exhibits only low iron contents (13% Fe₂O₃), which increase across the reaction zone towards the slag (19% Fe₂O₃). The same conclusion can be drawn from the low iron contents of the adhering aluino-silicates within vesicles (9–10% Fe₂O₃; Online Resource 2, point 213–216). Although they did not react with the molten slag, their chemical composition can be considered a local fingerprint, which should be close to that of the clay used for the construction of a furnace. In summary, we assume deliberate fluxing with iron oxides with the aim of improving the properties of the slag.

The elevated levels of iron (1.4%) and lead (12.3%) as well as the unusual concentrations of cobalt (0.08%) and nickel (0.56%) in one of the bronze prills (MA-171261–12) could be additional evidence for the fluxing theory. The impurity pattern cannot properly be traced to the oxidised tin and copper ores from Mušiston. They are extremely low in cobalt and nickel (Online Resource 6). However, both elements are frequently associated with iron ores in moderate to high concentrations (e.g. Photos 1989 with further references; Tylecote 1992, 49–52). At the same time, the prill is characterised by the lowest radiogenic lead isotopic composition of the entire sample set, which might imply the strongest contamination with extraneous lead. If the flux had a different lead isotope signature and a high lead content, e.g. due to the presence of galena (possibly suggested by the lead inclusions in the slag), the isotopic shift between ores and smelting products towards less radiogenic ratios could be explained. Since the lead isotope compositions of the slag matrix and the metal prills define a linear trend with the Mušiston ores in the 207Pb/206Pb and 208Pb/206Pb ratios (see Fig. 7b), the source of the flux may probably be sought in the immediate vicinity of the deposit. The deviation in the 204Pb-normalised isotope ratios indicates a common lead contaminant (see Fig. 7c). One possibility could be an iron-rich gossan or leached capping at the top of the Mušiston ore body itself, of which nothing remained today (the area is exposed to extensive erosion), or the addition of carefully selected iron minerals (Pavlovskii et al. 1995; Garner 2013; Konopelko et al. 2022). If we accept that our set of ore samples must not be representative for the entire mineralisation (29 samples with lead isotope data in total), and only accounted for copper- and tin-bearing ores, then the least radiogenic isotope signatures could have been missed. Another option would be a remobilisation of lead during an overprint of the ore body producing e.g. galena-bearing ores with a different lead isotope signal. However, there seems to be no geological indication for this alternative (Pavlovskii et al. 1995; Konopelko et al. 2022). Given the possibilities discussed above, the relationship between metal phases, the slag and the ores cannot be unambiguously resolved, but alteration of the lead isotope composition due the addition of an iron-rich flux material is a reasonable explanation. At the same time, this observation shows once again how complex provenance research with lead isotope ratios can be. If fluxing with lead-containing iron oxides was indeed a common practice in the smelting of the Mušiston ores, interpretations of metal artefacts regarding origin could be severely compromised — especially when low-lead ores such as malachite were used (Online Resource 6).

**Smelting conditions**

By adding a flux, the Bronze Age metallurgists probably tried to influence the melting temperature and viscosity of the slag. Judging from the highly heterogeneous texture with chemically and mineralogically different reaction zones, one may get the impression that the aim was missed or at least not fully reached. The reason for this is not evident at first glance, but it may have had significant impact on the separation of the metal from the liquid slag. The temperatures and reducing conditions were obviously high enough to produce metallic bronze. However, the countless metal prills in the centre of the slag sample suggest that the viscosity of the molten slag was not low enough to ensure a thorough phase separation.
To estimate the slag viscosity, we can use its chemical composition and the method proposed by Bachmann et al. (1989), which is based on experimental measurements on modern slag replications (Table 3). Their model calculates a viscosity index \( K \), which is the ratio of the concentrations of viscosity-reducing (in the numerator) and viscosity-increasing slag constituents (in the denominator). Since the present slag contains significant amounts of ZnO, CuO, PbO and SnO, which affect viscosity, we combine the calculation of Bachmann and co-workers (1989) with the knowledge gained from later studies on zinc-, lead- and tin-bearing slags (Ströbele et al. 2010; Chirikure et al. 2010; Heimann et al. 2010; Young and Taylor 2015):

\[
K = \frac{CaO + MgO + FeO + MnO + TiO_2 + Na_2O + K_2O + ZnO + CuO + PbO}{SiO_2 + Al_2O_3 + SnO}
\]

Using the viscosity index and the temperature \( T \) (in °C), the viscosity \( \eta \) (in Pa s) of the molten slag can be estimated with the following formula:

\[
\ln \eta = 26.46 - 23.67(0.001T) - 3.12K + 0.59K^2 + 3.84(0.001T)^3
\]

Principally, the higher the viscosity index \( K \), the lower the viscosity \( \eta \) and the more fluid is the slag at a given temperature. Applying the above approach yields 1.6 Pa s at 1200 °C and 0.4 Pa s at 1300 °C for the iron-rich region of the slag. These values are typical for low viscous slags such as those to be tapped during a smelting process (Rehder 2000, 111). In contrast, the viscosity of the centre amounts to 12.5 Pa s at 1200 °C and 3.4 Pa s at 1300 °C. The latter thus represents a much higher viscous slag portion, which could neither be tapped off nor allowed it a proper sagging of metal drops (Rehder 2000, 111; Addis et al. 2016). Nonetheless, the smelting experiments with the ores from Mušiston demonstrated that coalescence of metal drops was still possible despite an unfavourable slag viscosity (5.9 Pa s at 1300 °C; Online Resource 5). Larger pieces of bronze within or underneath the slag may therefore well have been the outcome of the smelting operation of the archaeological slag.

In addition to differences in viscosity, the varying chemistry must also have led to different solidification temperatures in various slag regions. A rough estimate can be made with appropriate phase diagrams. Because the present slag, as many others from the Bronze Age, formed far from equilibrium conditions, the following can only be a very rough approximation (Hauptmann 2007; 2020; Bourgari 2019). Moreover, ternary phase diagrams account for only a limited number of components (usually the main components), thus neglecting others (mainly minor components). However, the method is useful for estimating differences between the distinct areas. According to the diagram in Fig. 16 (blue dot), the liquidus temperature of the slag melt in the outer region with its fayalitic composition should be slightly above 1100 °C. As noted, this is an approximation and the presence of additional components such as MgO (temperature-increasing), Na₂O, K₂O, Cu₂O and PbO (temperature-decreasing) may change this estimate significantly (Hauptmann 2007; Ströbele et al. 2010). Because of the complex chemical composition of the slag centre and the lack of corresponding phase diagrams (accounting for SiO₂, FeO, CaO, ZnO and SnO) it is even more difficult to provide a proper estimate of its melting temperature. Using the diagram as before, however, the melting point of the centre region was considerably higher than for the outer, fayalitic zone (Fig. 16, red dot). The presence of willemite, which crystallises first out of the melt due to its higher melting temperature compared to that of fayalite, also supports a higher melting temperature in the centre (Bachmann 1982, 14; Jak et al. 2000). Thus, a liquidus temperature of between 1200 and 1300 °C could be realistic, especially when the high percentage of additional components (MgO, SnO) is considered. This estimate also suggests quite high working temperatures of about 1300 °C.

The observations described above suggest that the slag was not tapped off, although the composition of some slag regions as well as the process temperatures would probably have allowed an unhindered outflow from the furnace. Yet incomplete equilibration and mixing of the liquid material as well as early solidification prevented tapping. We do not know the structure nor the type of the actual furnace. However, following Bachmann and Rothenberg (1980), a rather small furnace could be inferred from the properties...
of the slag at first glance, because small reactors are more susceptible to process-related oscillations that lead to inhomogeneities in the composition and temperature.

The morphology of the fayalite and magnetite crystals appears to be in conflict with this interpretation, as it allows an estimation of the cooling rate of the slag. The majority of the fayalite has skeletal or ‘hopper’ habitus with hollow cores (Figs. 10, 11 and 12) indicating slow cooling between 40 and 80 °C h⁻¹ (Donaldson 1976; Faure et al. 2003; Addis et al. 2016; Bourgarit 2019). This common conclusion in the study of ancient slags was recently challenged by Pearce et al. (2021) and somewhat earlier by Ettler et al. (2009). They point to the fact that the morphology as a result of the cooling rate — studied in detail by Donaldson (1976) — only apply to forsterite (Mg₂SiO₄). In case of fayalite (Fe₂SiO₄), the described morphology can develop at higher cooling rates of some hundreds °C h⁻¹. Because only fayalite is present in the Mušten slag, a quicker cooling of the slag within the furnace is thus likely. Nevertheless, the cooling rate could have been locally much lower, as inferred from large euhedral fayalite crystals at some positions (Figs. 4b and 12c; Donaldson 1976).

The predominant granular morphology of magnetite or zinco-stanniferous magnetite over dendritic growth characteristics nevertheless attests that the cooling could not have been too fast (Burger 2008, 97–98), as does the presence of mellilites ((ferro)âkermanite–iron gehlenite–hardsjtonite) in the centre region (Ettler et al. 2009; Vanaecker et al. 2014). Crystal zoning, which would otherwise be an indication of growth under changing temperature conditions, is completely absent (Addis et al. 2016; Bourgarit 2019). The observations thus confirm the general impression of slag solidification within a furnace without any signs of tapping, but moderate cooling and missing chemical zoning of olivines and spinels might suggest a larger reaction volume.

Another important question regarding process reconstruction concerns the furnace gas atmosphere. Conspicuously, it must have been reducing enough to produce metallic bronze, since many metal prills but no original and unreacted ore components (except for quartz) are present. A strongly reducing atmosphere can also be inferred from the presence of fayalite (Fe²⁺) that formed in the iron-rich region of the slag. Yet, there is also evidence for intermittent or locally less reducing conditions due to an increase in the oxygen partial pressure. For example, there are accumulations of magnetite in the outer region of the slag sample (Figs. 10b and 12b) resulting from the decomposition of the neighbouring fayalite crystals. Most likely, oxidation occurred during cooling of the melt in the course of which primary fayalite was partly dissolved by the still liquid slag melt. As the cooling process continued, magnetite was precipitated from the melt (Henderson 2000; Hauptmann 2007). A similar process might have occurred in the centre region, but there zinco-stanniferous magnetite shows exsolution of cassiterite (Fig. 6). The latter is also concentrated around metal inclusion and can be regarded as an indicator of more oxidising conditions (Rademakers and Farci 2018; Montes-Landa et al. 2020). Furthermore, the copper and bronze prills in the centre region either exhibit oxidised rims (consisting of cuprite and Cu–Sn–Fe–Sb oxides) or were completely converted into scale products due to a corrosive high-temperature attack. Cuprite inclusions within the prills show that they precipitated from the liquid metal. All these observations are important for the reconstruction of the underlying smelting process, as they demonstrate that the furnace atmosphere was not stable and varied locally throughout the entire smelting process.

The different types of metal inclusions limited to the slag centre may provide clues for localised reaction zones of ore batches. The type of metal prills and the composition of the slag might also provide constraints on the composition of the charge. The remarkable absence of metallic tin or high-alloyed bronze (˃40% Sn) does not point to a high proportion of cassiterite in the ore charge (cf. Online Resource 1). Such tin-rich products were identified in experimental smelts with mixtures of cassiterite-rich and malachite ores or cassiterite and metallic copper (Rovira et al. 2009; Rademakers and Farci 2018). Hence, the original charge must have contained a (natural?) mixture of copper-dominated minerals like malachite, mixed copper-tin-zinc-iron ores, most likely mushistonite ((Cu,Zn,Fe)Sn(OH)₆) along with some sulphide minerals (chalcoite, bornite, stannite etc.). In addition, compounds containing arsenic, antimony, silver, lead and bismuth as well as gangue rich in calcium (the slag centre is Ca-rich; Fig. 9) were certainly present. Bronze prills could thus reflect co-smelting of copper and tin-bearing minerals, whereas metallic copper might originate from localised reduction of copper minerals.

However, given the fluctuating oxidising conditions, a decrease of the tin concentrations in the metal after the reduction process has to be considered. Tin loss, moreover, has to be expected during the smelting operation in any case. If the smelter’s goal was to produce a bronze with about 10% of tin, the actual concentration in the entire metal population of between 5.1% (XRF data) and 5.0% or even lower (SEM data) would suggest an overall tin loss of 40–60% to the slag and the atmosphere. Although one has to be careful with an estimation of the alloy composition from metal droplets in a slag, it can be regarded a realistic estimate. Low recovery rates are characteristic for prehistoric and particularly for Bronze Age tin smelting (Tylecote et al. 1989; Timberlake 1994; Friede and Steel 1976; Earl 1986; Yener et al. 2003; Krismer and Tropper 2010; Berger et al. 2018; Berger forthcoming; cf. Online Resource 5). In contrast to tin, loss of copper to the slag was rather small, at least much less than...
for the smelting during the early stages of extractive metallurgy (Hauptmann 2007; 2020). With about 12% by mass Cu₂O in the centre region of the slag, the loss is well within the range of Early Bronze Age copper slags, but higher than for slags from the Late Bronze Age onwards (Bachmann 1980; Bachmann and Rothenberg 1980; Hauptmann 2007; Rehren et al. 2012; Erb-Satullo et al. 2015; Addis et al. 2016; Bourgarit 2019). In combination with the proposed iron oxide fluxing, the copper content and the reconstructed process conditions suggest a developed smelting technology that fits into the metallurgical traditions of the mid-2nd millennium BCE.

### Conclusion

The investigation of a single piece of slag found near the polymetallic copper-tin deposit of Mušiston sheds new light on the beginning of bronze metallurgy in Central Asia and helps to answer questions regarding the ‘tin mystery’ (Madin 1998). Tiny remnants of charcoal from inside the object allow the dating of the slag to the Central Asian Late Bronze Age (1900–1400 BCE). The chemical and the tin and copper isotope signatures definitely link the slag to the tin- and copper-bearing ores of Mušiston. This result is of tremendous cultural historical importance and in no way challenged by the non-matching lead isotope ratios of the slag matrix and the embedded bronze prills. It is likely that the lead isotope composition was altered by a deliberate addition of flux material to the ore charge. The importance of the present findings also goes far beyond the mere evidence of the exploitation of an ore deposit in the Bronze Age. Based on a multi-analytical approach, it was possible for us for the first time to reconstruct the use and the smelting of tin ores in the immediate vicinity of a tin source. The present results thus extend the findings of earlier mining archaeological investigations of the Mušiston deposit (Cieri ny 1995; Alimov et al. 1998; Cieri ny and Weisgerber 2003; Garner 2013; 2015) by providing evidence not only of the exploitation but also of the pyrometallurgical processing of copper-tin ores. The preliminary reconstruction of a mixture of softwoods and hardwoods as fuel for the smelting suggests that the ancient metallurgists used native mountain shrubs or trees, whatever they could find. Especially at altitudes above 2000 m above sea level, coniferous plants like dwarf pine as well as mountain ash or elm allegedly flourished in the mountains surrounding the Zeravšan valley during the Bronze Age (Spengler and Willcox 2013). The area around Mušiston is still loosely forested today (mainly with dwarf pines), so the local smelting of ores during the Bronze Age was certainly possible from that point of view. However, the question regarding the extent of smelting is open, since large-scale smelting activities required vast quantities of wood or charcoal. In a mountainous region, such resources may have been limited, therefore one may rather assume smelting on a small scale, probably with the aim of testing the suitability of the mined ores for the production of bronze. The need for such tests is obvious: the polymetallic nature of the deposit with its variously composed copper-tin ores make it difficult to predict the composition of the final bronze. This issue is exacerbated by the technique of co-smelting, which is generally accepted to produce copper-tin alloys with hard-to-predict tin contents (Rostoker and Dvorak 1991; Rovira et al. 2009; Montes-Landa et al. 2020). As the smelting of Mušiston ores is inevitably a co-smelting process, a prior testing of the ore’s potentiality would have been extremely beneficial: by testing the ores on site, a great deal of effort and expense by transporting unsuited material to the plains of the Zeravšan valley could be avoided. Incidentally, this could also be the reason, why there are still significant remains of oxidised ores in the old galleries of the deposit (Garner 2013, 129–131). Normally, ore veins were followed to their end and fully exploited. However, if the resulting bronze from this ore was of inferior quality or of unsuited composition, the ancient miners might have lost interest in the vein.

Although we suppose that the slag is the result of experimental smelting, the underlying smelting technology was certainly a developed one. The formation of the slag is difficult to trace in this respect. Since neither residues of the original ore charge, technical ceramics like a furnace or a crucible nor the complete amount of slag were found, we cannot determine the proportion of these components controlling the chemical and mineralogical characteristics of the slag. It is also difficult to estimate the contribution of the fuel, since only minute residues of it have been documented. However, from the properties and the chemistry of the slag we can infer a developed smelting technology because the ores were most likely processed with the addition of an iron oxide flux. Such a practice has been documented from other Bronze Age sites (e.g. Timna, Israel and Faynan, Jordan; Tylecote et al. 1977; Bachmann and Rothenberg 1980; Hauptmann et al. 1992), but it was not yet known from Central Asian metallurgy of that time. The smelting itself was probably carried out in a medium-sized furnace and supposedly produced larger pieces of bronze metal, only a small portion of which survived as enclosed prills. Of course, we are not aware of the dimension of the furnace and the success of the smelting operation, but from the viewpoint of the ancient metallurgist, a bronze with ca. 5% tin could have been a satisfactory result. Accordingly, the parental ores could have been the base for a metal production on a larger level, be it on site in a seasonal mining camp or farther away in the settlements in the more hospitable valley of the Zeravšan River. In the future, we will explore this topic even deeper by determining the chemical and the
isotopic composition of Central Asian bronze artefacts from the Bronze Age and comparing them with the ore data collected here. This will be the final piece of the puzzle to complete the picture of the prehistory of the Mušiston deposit, starting with its exploitation, the processing of its ores and ending with its integration into the cultural and economic landscape of Central Asia and beyond.

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Data availability All data used for the study is included in this paper or in the Supplementary Material. All materials are stored at CEZA, Mannheim, Germany.

Declarations

Ethics approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

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