Online Resource 5: Smelting experiments with the secondary ores from Mušiston

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Introduction

The advent of bronze metallurgy in Central Asia and elsewhere in the Old World is still an elusive issue. Hardly anything is known about the tin sources that served for the production of the earliest bronzes. One possible scenario is the use of copper ores, which are naturally associated with tin minerals and give a bronze when smelted. Such polymetallic ores are rare throughout Eurasia, but a promising candidate for an early exploitation and bronze production is the copper-tin deposit of Mušiston in Tajikistan. At an altitude of about 3000 metres above sea level, secondary copper minerals such as malachite and azurite are intergrown with secondary cassiterite and hydrostannates like mushistonite, varlamoffite and natanite. The exploitation of the ore body since the 3rd millennium BCE is attested by numerous galleries and radiocarbon dates of charcoal relics from the galleries. The smelting of the secondary ores should theoretically yield natural bronzes, but proof of that was lacking for a long time.

As part of the interdisciplinary research project ‘Zinngewinnung in Mittelasien (ZGMA)’ funded by the Volkswagenstiftung (1997–1999), a series of three smelting experiments were carried out in 1999 with the secondary copper-tin ores from Mušiston by J Lutz and H Herdits. The aim of these experiments was first to test whether these ores are suitable for the production of copper and bronze. For this purpose, a copper-rich (emerald green in colour) and a tin-rich ore (yellow-green in colour) were used for two of the experiments, whereas a mixture of the two served as charge for the third trial (Fig. 2). The original aim was extended during the work of the European Research Council funded project ‘BronzeAgeTin’ (2013–2018), in that it was pursued whether the Mušiston ores can be recognised in the chemical and the isotopic signatures of Central Asian copper-tin alloys of the Bronze Age. Therefore, we analysed the smelting products of the earlier experiments to get an impression of the possible fractionation of tin and copper isotopes in the course of the smelting process. We also wanted to know if the lead isotope composition is changed in any way. This was particularly interesting because the Mušiston slag (see main article) differs significantly from the Mušiston ores in the lead isotope ratios, although it is consistent with the ores in its tin and copper isotope signatures. In the following, the three experiments and their main outcomes are briefly described. A more detailed paper will follow shortly (Berger et al. in preparation).

Experiments: Results and discussion

Smelting experiment 1: Malachite

A hearth or bowl furnace of about 30 cm diameter and 15 cm depth was made in quartz sand for the first experiment (Fig. 1). A quartz tube of 2 cm diameter was inserted at the side as a nozzle so that it was directed slightly downwards and protruded about 10 cm into the hearth. Ventilation was supplied by an air compressor. The hearth was filled with charcoal and lit. After preheating, 1000 g malachite (see Fig. 2a) and charcoal were alternately added and the smelting

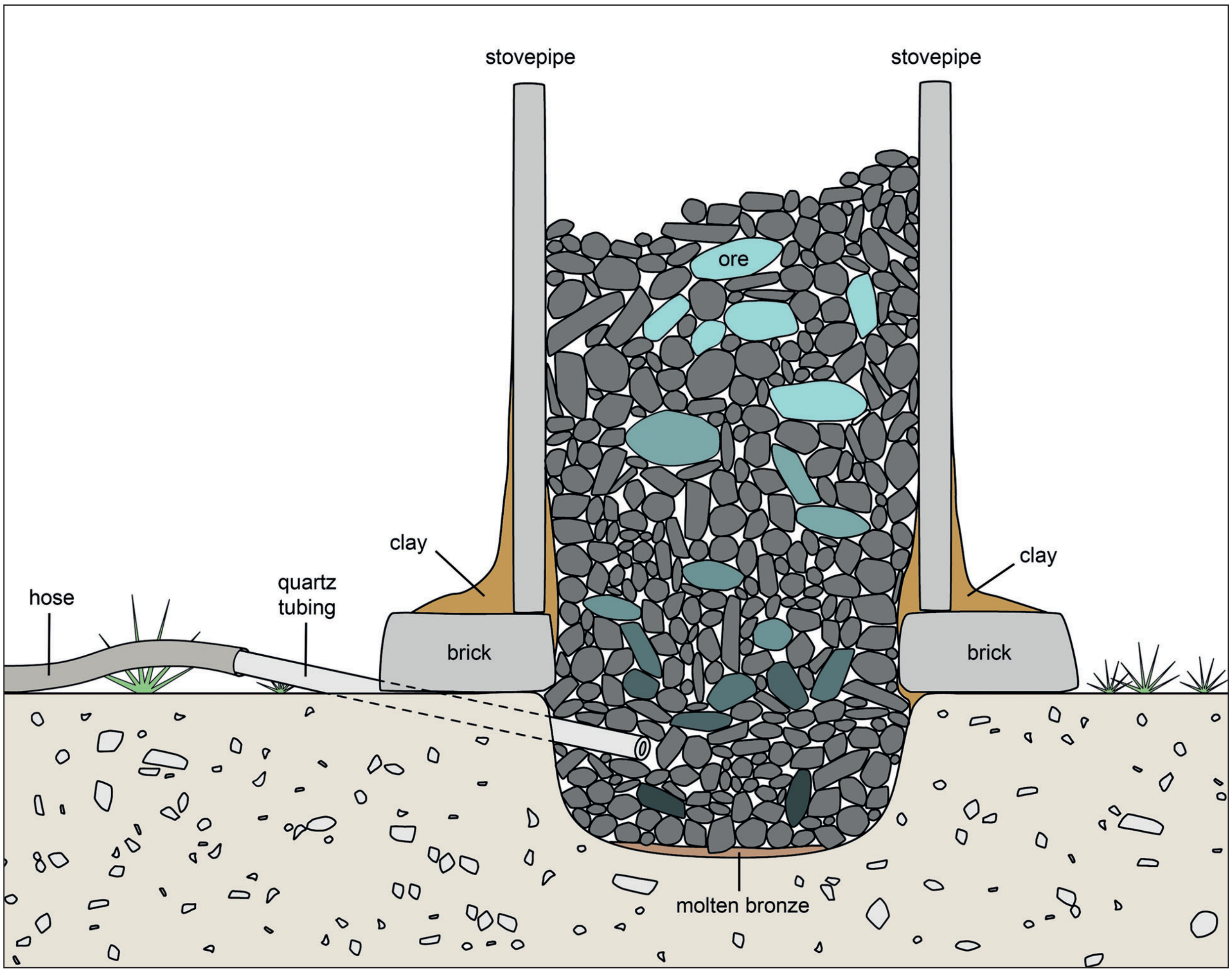

Fig. 1 *Schematic representation of the shaft furnace as it was used in the smelting experiments 2 and 3. For experiment 1, only a simple pit without the shaft was used as hearth (resembling some kind of bowl furnace) for the smelting procedure (image: D Berger).*

operation run for ca. two hours. After cooling and opening the hearth, it was found that the ore was only incompletely reduced. Macroscopically, small copper globules and somewhat larger copper flakes could be seen in a reddish mass of copper oxide. A continuous and larger copper piece had not formed. The reason for the incomplete reduction was most likely the furnace construction with its low height allowing only weak reducing conditions and the fact that the ore trickled through the coarse charcoal too quickly in a region where the temperature was likely not high enough. So even though the experiment was strictly speaking a failure, it nevertheless showed that copper can be extracted from the malachite of the Mušiston deposit. Analyses of several prills with energy dispersive X-ray fluorescence spectroscopy (EDXRF) showed that the smelted metal is a very pure copper with only small amounts of other components. Although the ore contained ca. 2 mass% tin as SnO_2, only a trace of tin was present in the metal. Most of other elements frequently associated with the ores from Mušiston, such as arsenic, antimony, lead and bismuth, are also drastically depleted in the metal with respect to the original ore charge or are practically absent. The only exception is silver. This result is certainly due to the poor reduction conditions in the shallow hearth, where copper and the impurity elements were only partially reduced. In the case of zinc, high evaporation losses occurred because of the low boiling point of the metal.

Fig. 2 *Copper and tin ores from Mušiston that have been used for the smelting experiments (a) and bronze lump (b) and bronze slag (c) obtained from experiment 2 (photos: D Berger).*

Smelting experiment 2: Malachite and tin ores

A shaft furnace was constructed for the second experiment according to Figure 1. This was done as the shallow hearth from the first experiment proved to be unsuitable for a proper ore reduction. After preheating with charcoal, 1000 g of the mixed copper-tin ore was fed into the furnace alternately with more charcoal. To prevent the ore material from trickling through the charcoal too quickly again, the ore was formed into larger lumps using flour and water as organic binder. Both changes in comparison to experiment 1 were probably the reason why after a smelting time of ca. two hours a large smelting cake of ca. 250 g were obtained at the bottom of the furnace (Fig. 2b). A shapeless lump of slag had formed on top of this, which contained further large pieces of metal (Fig. 2c). Analysis of the metal with EDXRF showed the smelting cake and the inclusions to consist of bronze with about 14 mass% of tin. The experiment was thus successful and showed that bronze can be easily produced with the oxidised ores from Mušiston in a co-melting process. However, a significant amount of almost 40 % of tin was lost during the smelt. Judging from the starting material, one would theoretically have expected about 25 mass% tin for the bronze. The same applies to antimony (ca. 0.16 mass%) whose loss was about the same as that of tin, as well as to lead (0.02 mass%) and bismuth (0.03 mass%), which were heavily depleted on the way to the metal. In contrast, the contents of arsenic and silver hardly changed with respect to the original ore batch and came to 0.39 and 0.09 mass%, respectively. The highest loss was observed for zinc, which completely passed into the vapour phase as fume. Remnants of this fume were found in the upper part of the furnace as white tarnish and contained mainly zinc (ca. 64 mass%) and tin (ca. 23 mass%) with small amounts of lead (ca. 4 mass%), bismuth (ca. 3 mass%) and copper (ca. 3 mass%).

In addition to the loss by evaporation, a small amount of ca. 1 mass% tin was lost to slag phase (leading to ca. 0.8 mass% SnO_2 in the slag), which also contained a relatively small amount of Fe_2O_3 (8.8 mass %), but a high concentration of CaO (30 mass%) and SiO_2 (45 mass%) among other typical slag elements (4.5 mass% Al_2O_3, 1.9 mass% MnO, 4 mass% MgO, 3 mass% K_2O, 0.3 % TiO_2, 1.2 mass% P_2O_5). Strikingly, the slag was free of copper and zinc. Due to its chemical composition, the liquid slag had a high viscosity theoretically resulting in poor flow properties and incomplete separation of the metal from the slag. Using the empirical model of Bachmann et al. (1989), the viscosity of the slag was about 22 Pa s at 1200 °C and 5.7 Pa s at 1300 °C, which corresponds to a high viscous slag. Nevertheless, the bronze was able to form a large lump beneath the slag, probably favoured by a high temperature (>1300 °C) in the furnace lowering the slag viscosity.

From the results of the second experiment, it is evident that a considerable amount of 40 % of tin was lost from the original ore, despite the highly reducing conditions in the furnace. This loss had a small but measureable effect on the tin isotope composition of the bronze. The original tin isotope signature of $\delta Sn_{NIST\ SRM\ 3161a}$ of –0.043 ± 0.001 ‰ u^{-1} of the mixed ore changed to –0.017 ± 0.045 ‰ u^{-1} in the metal, corresponding to a fractionation of +0.025 ‰ u^{-1} $\Delta Sn_{NIST\ SRM\ 3161a}$. The copper isotope composition also changed slightly from +0.07 ‰ in the ore to +0.03 ‰ $\delta^{65}Cu$ in the bronze. This amounts to a fractionation of +0.03 ‰ due to the smelting procedure. In contrast to that, only a marginal change in the lead isotope signature from the ore to the bronze could be observed, which is consistent with earlier studies on lead isotope fractionation (Macfarlane, 1999; Stos-Gale & Gale, 2009; Baron u. a., 2009). Thus, smelting the Mušiston ores under the chosen smelting conditions resulted in a slight fractionation of the tin and copper isotopes, while the lead isotopes were not affected. Additionally, most of the elements in the ores were transferred to the metal phase, some of which have been depleted compared to ore and others of which have been transferred without loss.

Smelting experiment 3: Tin ore

The same furnace construction and process parameters as in experiment 2 were used for the smelting of the oxidised tin ore in experiment 3 (see Fig. 2a). Again, 1000 g of ore was added to the furnace and after two hours tin metal had accumulated at the bottom above which a larger piece of slag developed. The tin from this experiment is heavily contaminated by other components as shown by EDXRF analysis. Besides considerable amounts of copper (15–19 mass%), it also contains lead (ca. 0.3 mass%), arsenic (ca. 1 mass%), antimony (ca. 0.4 mass%), silver

(0.4–0.8 mass%), bismuth (ca. 0.5 mass%) and iron (2–10 mass%). These are mainly the elements (except copper) that were not dissolved during the weathering of the sulphidic primary ore mineral stannite and remain together with tin as residuals in the original stannite veins. The copper and silver contents are significantly higher in the metal than the ore analysis would suggest. This is again due to a high loss of 35 % of the main element tin during smelting, resulting in a relative enrichment of the noble elements copper and silver. Lead and bismuth were also slightly enriched. Arsenic and antimony behaved similarly to tin, while zinc again evaporated almost completely. The isotopic composition of the tin also changed slightly in this experiment from of -0.041 ± 0.001 ‰ u^{-1} to -0.025 ± 0.010 ‰ u^{-1} $\delta Sn_{NIST\ SRM\ 3161a}$ with a fractionation $\Delta Sn_{NIST\ SRM\ 3161a}$ of about +0.016 ‰ u^{-1} relative to the original tin ore. This value is comparable to that of experiment 2.

Also comparable with experiment 2 is the composition of the slag. It contains the same elements as the slag of experiment 2, but the tin content was significantly higher (6.4 mass%) as also was the content of iron (29 mass%). This shows that the iron is mainly introduced with the tin ore. In addition, the concentrations of CaO (17.5 mass%) and SiO_2 (45 mass%) are lower than in experiment 2, while other elements are in the same order of magnitude (3 mass% Al_2O_3, 1 mass% MnO, 2.2 mass% MgO, 2.3 mass% K_2O, 0.2 % TiO_2, 0.8 mass% P_2O_5). The slag thus had a lower viscosity of about 15 Pa s at 1200 °C and 4.1 Pa s at 1300 °C.

Conclusions

The smelting experiments show that it is possible to produce relatively pure copper as well as bronze and tin with a high proportion of impurities with the oxidised ores from Mušiston. The contents of impurity elements such as arsenic, silver, antimony, lead and bismuth correlate positively with the tin content in the metal, as these elements are mainly associated with tin minerals in the oxidation zone of the Mušiston deposit. By carefully selecting green copper-rich and yellowish-green tin ores, it was thus possible to control the composition of the metals produced, possibly by mixing the different coloured ores (Fig. 3). The loss of some elements, especially tin and zinc, are rather large during the smelting process, which causes small fractionation towards heavier isotopic compositions of tin, but also copper, while the lead isotope ratios are not affected.

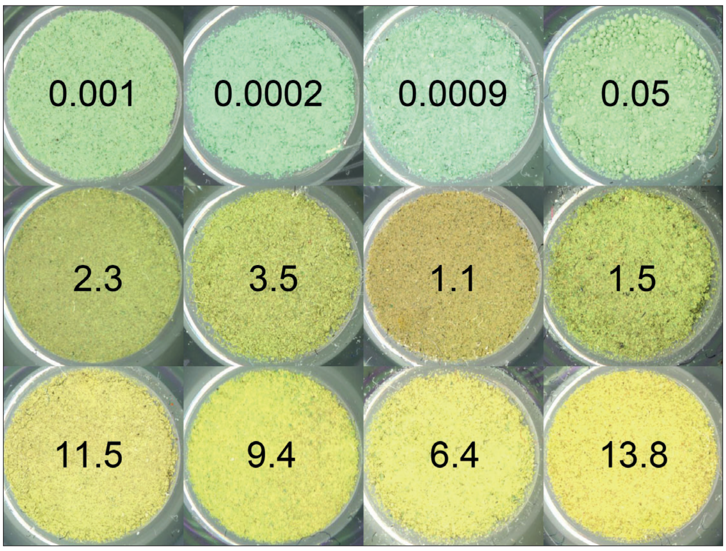

Fig. 3 *Colour range of the oxidised ores from Mušiston and their corresponding Sn/Cu ratios. The first row shows greenish malachite ores, while the other two show more yellowish ores due to their higher tin contents and their predominating mineral species, mainly hydrostannates and cassiterite (image: D Berger).*

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This electronic Supplementary Material is part of the article Berger D, Brügmann G, Friedrich R, Lutz J, Meyer H-P, Pernicka E, Shiny bronze in glassy matter: An inconspicuous piece of slag from the Bronze Age mining site of Mušiston (Tajikistan) and its significance for the development of tin metallurgy in Central Asia, Archaeological and Anthropological Sciences, https://doi.org/10.1007/s12520-022-01606-2, corresponding author: Berger D, Curt-Engelhorn-Zentrum Archäometrie Mannheim, daniel.berger@ceza.de