The tin-copper deposit of Mušiston: Source for ancient tin bronzes

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The ore deposit of Mušiston (Zerafshan valley), Tajikistan, is unique in that stannite is the princple primary ore mineral which is associated with accessory sphalerite and chalcopyrite. The primary ore contains up to 15 wt.% of copper and tin. Weathering produced a large oxidation zone which contains secondary ore minerals such as mushistonite, varlamoffite, natanite, malachite and cassiterite, and is enriched in tin (\leq 35 wt.%). Smelting of such ores would straightaway produce tin bronze which was highly valued in ancient cultures. Archaeological evidence has shown that the deposit was already exploited during the second half of the 3rd and the first half of the 2nd millennium BC in the so called Andronovo-Tazabag'iab culture [1].

Tin and lead isotope analysis as well as trace element studies were carried out on ore samples and archaeological artefacts using MC-ICP-MS [2], NAA and XRF. The isotopic composition of stannite in terms of $\delta^{124/120}$ Sn ranges from -0.38 to -0.14 ‰, with an average of -0.23 ± 0.17 ‰ (2SD). The isotopic composition of secondary ores is somewhat lighter with values ranging from -0.40 to -0.22 ‰ and an average of -0.30 ± 0.11 ‰ (2SD). These values are significantly lighter than those of cassiterites from the eastern Pamir region (+0.27 ± 0.41 ‰ (2SD)) and from Afghanistan (-0.06 ± 0.32 ‰ (2SD)).

 $\delta^{124/120}$ Sn ratios of archaeological tin bronzes found in the vicinity of Mušiston overlap with those of the tin ores and range from -0.33 to +0.41 ‰. While artefacts with heavy isotopic compositions (> 0 ‰) could not have been manufactured with Mušiston ores, some bronzes have similar light tin isotope compositions. Tiny bronze prills from a piece of slag found not far away from the deposit has on average a $\delta^{124/120}$ Sn value of -0.18 ‰ \pm 0.54 ‰ (2SD). Combined with the matching lead isotopes ratios and chemical composition, a close relationship between the smelting product and the ore can be established. Such an affiliation is also observed for some finished bronze objects from the 17th to the 13th centuries BC, but lead isotope measurements are still pending.

[1] Garner (2015) in Hauptmann and Modarressi-Tehrani, Der Anschnitt, Beiheft 26, 135–143. [2] Brügmann et al. (2017) Geostand. Geoanal. Res. doi:10.1111/ggr.12166.