Tainted ores and the rise of tin bronzes in Eurasia, *c*. 6500 years ago

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The earliest tin bronze artefacts in Eurasia are generally believed to have appeared in the Near East in the early third millennium BC. Here we present tin bronze artefacts that occur far from the Near East, and in a significantly earlier period. Excavations at Pločnik, a Vinča culture site in Serbia, recovered a piece of tin bronze foil from an occupation layer dated to the mid fifth millennium BC. The discovery prompted a reassessment of 14 insufficiently contextualised early tin bronze artefacts from the Balkans. They too were found to derive from the smelting of copper-tin ores. These tin bronzes extend the record of bronze making by c. *1500 years, and challenge the conventional narrative of Eurasian metallurgical development.*

Keywords: Eurasia, Serbia, Bulgaria, Pločnik, Belovode, fifth millennium BC, Vinča culture, copper, tin, bronze, metallurgy, compositional analysis

Materials and methods

Analytical work was carried out at the Wolfson Archaeological Science Laboratories, UCL Institute of Archaeology, and the metallographic examination at the Department of Materials,

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Oxford University. Materials for this study were acquired from the Museum of Vojvodina (Gomolava 212) and the National Museum in Belgrade (Pločnik 63), both in Serbia. Samples were cut to size, mounted in epoxy resin discs, ground using abrasive discs (1200 and 2400 grit) and polished using diamond pastes (1µm and 0.25µm). They were examined by reflected light microscopy (OM) before electron microprobe (EPMA) investigation. Both samples were analysed using an accelerating voltage of 20kV, beam current of 50nA, and working distance of 10mm. Analyses were run at nine (Gomolava 212) and ten (Pločnik 63) different areas in the metal, and corrected for accuracy against four different bronze standards (reported in Table S1 below). Metallographic examination was carried out using reflected light microscopy after etching with two different etchants: ammonia hydrogen peroxide (equal proportions of ammonia (NH_4OH), water and 3 per cent H_2O_2) and alcoholic ferric chloride (8g $FeCl_3$, 120ml H_2O, 20ml HCl, 240ml C_2H_5OH).

Table S1. Electron microprobe compositional data of certified reference materials (CRM) for copper alloys (bronzes): IPT10A, UE20, UE52, UE10, given in wt%. All measured values are presented against certified average values for CRMs, with correction values calculated for relative errors above 5 per cent. The averages of all correction values and the correction factor are given in the bottom two lines; the correction factor was applied on the Pločnik 63 and Gomolava 212 analytical data.

	Zn wt%	Cu wt%	Fe wt%	As wt%	S wt%	Sn wt%	Sb wt%	Ni wt%	Mn wt%	Pb wt%
IPT10A	4.64	84.92	0.23	0.00	0.09	4.91	0.08	0.30	0.00	4.39
IPT10A	4.60	84.58	0.22	0.02	0.08	4.41	0.07	0.30	0.00	4.75
IPT10A	4.77	85.03	0.22	0.01	0.08	4.58	0.07	0.31	0.00	4.92
IPT10A	4.61	84.99	0.23	0.01	0.08	5.03	0.08	0.30	0.00	4.66
IPT10A	4.42	84.74	0.22	0.02	0.06	5.03	0.07	0.30	0.00	5.14
IPT10A	4.61	84.25	0.22	0.01	0.08	4.86	0.06	0.29	0.00	4.42
IPT10A	4.65	84.21	0.22	0.02	0.07	4.86	0.06	0.29	0.00	4.37
Average IPT10A	*4.61*	*84.67*	*0.22*	*0.01*		*4.81*	*0.07*	*0.30*		*4.67*
Certified value IPT01A	*4.71*	*85.13*	*0.21*	*0.02*		*4.58*	*0.11*	*0.33*		*4.72*
Absolute error	*-0.10*	*-0.46*	*0.01*	*-0.01*		*0.23*	*-0.04*	*-0.03*		*-0.05*
Relative error	*-2.02*	*-0.54*	*4.54*	*-42.86*		*5.03*	*-36.92*	*-10.09*		*-1.15*
Correction value (above 5%)	**0.05**			**-0.43**		**0.05**	**-0.37**	**-0.10**		**-0.01**

	Zn wt%	Cu wt%	Fe wt%	As wt%	S wt%	Sn wt%	Sb wt%	Ni wt%	Mn wt%	Pb wt%
UE20	1.34	87.39	0.28	0.07	0.12	8.41	0.93	0.61	0.07	0.76
UE20	1.32	87.23	0.28	0.08	0.18	8.15	1.07	0.63	0.10	0.93
UE20	1.27	87.46	0.26	0.08	0.16	8.05	1.06	0.61	0.09	0.92
UE20	1.26	86.80	0.26	0.09	0.18	8.58	1.19	0.65	0.09	0.87
UE20	1.29	86.46	0.27	0.09	0.11	9.20	1.04	0.65	0.07	0.79
UE20	1.35	86.76	0.28	0.07	0.16	8.87	0.94	0.62	0.09	0.82
UE20	1.28	87.04	0.29	0.07	0.17	8.20	1.09	0.66	0.11	0.77
UE20	1.26	86.45	0.27	0.08	0.14	8.80	1.14	0.67	0.10	0.79
UE20	1.33	86.61	0.30	0.09	0.15	8.60	1.10	0.68	0.10	0.75
UE20	1.21	85.28	0.27	0.10	0.17	9.74	1.38	0.68	0.10	0.81
UE20	1.33	87.43	0.29	0.09	0.17	7.85	1.01	0.64	0.10	0.82
UE20	1.33	88.00	0.23	0.08	0.10	7.62	0.98	0.58	0.10	0.72
UE20	1.15	85.79	0.29	0.07	0.19	9.37	1.10	0.79	0.06	0.78
UE20	1.18	87.11	0.31	0.08	0.12	8.39	0.91	0.75	0.12	0.78
UE20	1.20	87.97	0.29	0.06	0.11	7.75	0.91	0.74	0.09	0.63
UE20	1.18	86.67	0.27	0.09	0.11	8.70	0.98	0.75	0.08	0.75
UE20	1.17	86.89	0.30	0.09	0.16	8.47	0.91	0.78	0.08	0.75
Average UE20	*1.26*	*86.90*	*0.28*	*0.08*	*0.15*	*8.51*	*1.04*	*0.68*	*0.090.10*	*0.79*

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Certified value UE20	*1.25*	*86.15*	*0.26*	*0.06*	*0.08*	*8.53*	*1.08*	*0.70*	*0.07*	*0.93*
Absolute error	*0.01*	*0.75*	*0.02*	*0.03*	*0.07*	*-0.02*	*-0.04*	*-0.02*	*0.02*	*-0.14*
Relative error	*0.90*	*0.87*	*6.16*	*32.00*	*45.27*	*-0.21*	*-3.58*	*-3.52*	*22.98*	*-17.80*
Correction value (above 5%)	**0.06**			**0.32**	**0.45**	**0.00**	**-0.04**	**-0.04**	**0.23**	**-0.18**

	Zn wt%	Cu wt%	Fe wt%	As wt%	S wt%	Sn wt%	Sb wt%	Ni wt%	Mn wt%	Pb wt%
UE52	5.60	84.42	0.09	0.00	0.03	6.21	0.00	0.31	0.00	2.90
UE52	5.69	83.21	0.08	0.02	0.06	6.02	0.00	0.30	0.00	3.87
UE52	5.68	84.62	0.08	0.01	0.03	5.79	0.00	0.32	0.00	2.78
Average UE52	*5.66*	*84.09*	*0.08*		*0.04*	*6.01*		*0.31*		*3.18*
Certified value UE52	*5.70*	*82.50*	*0.08*		*0.03*	*6.05*		*0.33*		*5.03*
Absolute error	*-0.04*	*1.59*	*0.00*		*0.02*	*-0.04*		*-0.02*		*-1.85*
Relative error	*-0.79*	*1.89*	*3.61*		*38.52*	*-0.70*		*-7.38*		*-58.01*
Correction value (above 5%)	**0.04**				**0.39**	**-0.01**		**-0.07**		**-0.58**

	Zn wt%	Cu wt%	Fe wt%	As wt%	S wt%	Sn wt%	Sb wt%	Ni wt%	Mn wt%	Pb wt%
UE10	0.27	83.59	0.12	0.00	0.02	14.07	0.29	0.87	0.00	0.53

UE10	0.22	82.98	0.12	0.00	0.02	14.68	0.28	0.91	0.00	0.54
UE10	0.34	83.04	0.13	0.01	0.02	14.49	0.28	0.93	0.00	0.54
UE10	0.27	83.59	0.13	0.01	0.02	14.04	0.29	0.91	0.00	0.50
UE10	0.29	83.37	0.12	0.01	0.02	14.22	0.29	0.90	0.00	0.53
Average UE10	*0.28*	*83.31*	*0.12*		*0.02*	*14.30*	*0.29*	*0.90*		*0.53*
Certified value UE10	*0.28*	*82.90*	*0.11*		*0.01*	*14.70*	*0.37*	*1.01*		*0.29*
Absolute error	*0.00*	*0.41*	*0.01*		*0.01*	*-0.40*	*0.08*	*-0.11*		*0.24*
Relative error	*-0.65*	*0.50*	*11.86*		*7.84*	*-2.81*	*-29.73*	*-12.15*		*45.50*
Correction value (above 5%)	**0.12**				**0.28**	**0.03**	**0.30**	**0.12**		**0.45**
Average correction value	***0.07***			***-0.05***	***0.37***	***0.00***	***-0.23***	***-0.08***		***-0.08***
Correction factor	0.93			1.05	0.63		1.23	1.08		1.08

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On the occurrence of stannite and stannite-rich copper ore

According to the principal textbook on ore minerals (Ramdohr 1980: 549–62), stannite is 'not uncommon' but widespread; it is almost always intergrown with chalcopyrite, and often with fahlore. The entry for stannite runs to more than a dozen pages, an indication of the significance of this mineral, even if it is not commonly found in mineral cabinets and exhibitions: "[g]rain shape: stannite very rarely forms well developed crystals, much more commonly very irregular space fillings between older minerals and films on these, or where present in larger quantities..." (Ramdohr 1980: 553). Since most mineral collections prefer well-formed crystals, stannite is rare in these; however, as an ore-forming mineral it is present world-wide, and "not uncommon in many...hydrothermal deposits...stannite is widely and regularly distributed in the sulphide fraction of almost all ore deposits of this type" (Ramdohr 1980: 560, section IX, Paragenetic position).

Of particular significance to our argument for a mixed stannite-chalcopyrite ore are statements on p. 554: "[e]ven the common chalcopyrite fracture fillings in and between stannite grains are oriented to these grains", and at the top of p. 557: "[m]yrmekitic intergrowths with chalcopyrite are widespread of greatly differing grain sizes...". Here and on numerous other occasions, Ramdohr spells out the close relationship of chalcopyrite, stannite and fahlore: both structurally and as intergrown minerals in numerous ore deposits. This is evident for instance at the bottom of p. 557: "[c]areful investigation has, however, demonstrated their widespread occurrence"; and p. 558: "[i]t has recently become evident that isostannite in particular is very widespread". This goes together with the statement on p. 550: "VI. Fabric. ... Study of a very large number of specimens from the whole world shows...". See finally also the long list of investigated occurrences under section X at the bottom of p. 560 and top of p. 561.

This evidence demonstrates that stannite, in the geological context of tin-rich provinces such as Bolivia, the Bohemian Erzgebirge, Japan and the Balkans, is a 'not uncommon' mineral, regularly intergrown with chalcopyrite and fahlore, and is widespread. This intergrowth/paragenesis of stannite and chalcopyrite is in our view the reason for the variable tin content and the fact that the metal smelted from such mixed ores does not remotely reach the theoretical content of 30 per cent tin of pure stannite. Already a generation ago, Wertime (1978) suggested that the role of stannite in the emergence of tin bronzes has been underestimated, and pointed out that the smelting of stannite would have yielded a natural bronze. Wertime (1978: 2) states that "...stannite fits the hypothesis that metallurgy was born in a polymetallic setting, where interfluxing and interalloying of ores could occur. This would most generally be a gossan cap on a copper deposit, also containing arsenopyrites and lead-silver". Charles supported this assumption: "...it [stannite] may have been the first primary source of tin to be alloyed with copper" (Charles 1978: 28).

It might be argued that such a complex mineral cannot be smelted easily—here, we refer to the cases of the famous 'A-type metal' of the British Early Bronze Age, linked to the fahlore-chalcopyrite ore body of Ross Island (Northover *et al.* 2001: 26, 29), and the demonstrated Early Bronze Age fahlore smelting in Brixlegg, Austria, (the earliest copper smelting evidence in Central Europe; Hoppner *et al.* 2005; see also Krismer *et al.* 2012), or the Chalcolithic copper smelting at Cabrières in southern France (Bourgarit *et al.* 2003; Bourgarit 2007), pre-dating in all cases the 'normal' malachite/chalcopyrite-based copper smelting of later periods. Thus the use of complex minerals/fahlores at the very beginning of copper smelting was a pan-European phenomenon.

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