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Sledovi metalurške dejavnosti na keramičnih fragmentih

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Izvleček

Kose dveh keramičnih predmetov, ki so jih domnevno uporabljali v zgodnji metalurgiji, smo pregledali z metodama rentgenske fluorescence in protonsko vzbujenih rentgenskih žarkov. Na notranji površini enega od predmetov smo našli povečane koncentracije bakra, železa, žvepla in sledove arzena. Ti elementi kažejo, da lahko predmet povežemo z metalurgijo bakra iz sulfidnih rud.

Abstract

Fragments of two clay objects, supposedly used in early metallurgy, were examined by the method of X-ray fluoroscence and proton-inducted X-ray emission. The inner surface of one object was enriched in copper iron, sulphur, and traces of arsenic. According to these elements, the object may be related to the copper metallurgy based on sulphide ores.

Keramični kosi, ki pripadajo predmetoma z inventarnima številkama 11852 in 11852 in so podrobneje opisani v prejšnjem sestavku,[1] so verjetno deli posod iz zgodnjega kovinskega obdobja. Kot nadaljnji dokaz za to tezo smo poskusili poiskati materialne ostanke, ki bi pričali o taljenju kovin. Pričakovati smemo, da staljena kovina pusti na steni posod sledove, vsaj tanko plast žlindre z ostanki pretaljene kovine. Deli obeh predmetov so namreč dovolj dobro ohranjeni, da lahko prepoznamo notranje površine, ki so verjetno prišle v stik s staljeno kovino. Povečane koncentracije kovin na notranji površini bi torej pomenile, da so predmeta 11851 in 11852 zares uporabiljali kot orodje v metalurških postopkih.

Z optično emisijsko spektroskopijo so dokazali prisotnost bakra (1-4 %) na notranji površini epilengyelske livarske žlice.[2] S podobno metodo so dokazali rudarsko in topilniško dejavnost s kositrom v osrednji južni Turčiji. Koncentracije kositra v različnih vzorcih žlindre in na stenah keramičnih talilnih lončkov so določili z elektronsko vzbujeno rentgensko fluorescenco in z masno spektroskopijo sekundarnih ionov. Dobljeni rezultati so z veliko verjetnostjo potrdili, da so v pokrajini pridobivali kositer.[3]

Površini obeh predmetov sta bili različnega videza. Kosi predmeta 11851 so bili grafitno sive barve, med notranjimi in zunanjimi površinami ni bilo razlike. Zunanja površina pri predmetu 11852 je spominjala na slabo žgano glino, notranja površina pa je bila prekrita s temno rumenorjavo skorjo, debelo nekaj desetink milimetra. Podobno rumeno skorjo je mogoče videti na ste-

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[1] A. Velušček, T. Greif, *Arh. vest.* 49, 1998, 31-53.

[2] A. Hauptmann, E. Ruttkay, Untersuchung von epilengyelzeitlichen Gusslöffelfragmenten von Bisamberg-Hochfeld, VB Wien-Umgebung, Niederösterreich, *Mitt. Anthr. Ges.* 121, 1991, 182.

[3] A. Adriaens, K. A. Yener, F. Adams, R. Levi-Setti, SIMS analyses of ancient ceramic crucibles and slags from Turkey, v: *Proceedings of the 10th International Conference on Secondary Ion Mass Spectrometry*, Chichester, New York, Weinheim, Brisbane, Singapore, Toronto (1995), 877; A. Adriaens, K. A. Yener, F. Adams, The application of surface analysis techniques to archaeological ceramic crucibles, v: *Proceedings of the 6th European Conference on Applications of Surface and Interface Analysis*, Wiley, Chichester and New York (1996), 123; A. Adriaens, Elemental composition and microstructure of Early Bronze Age and Medieval tin slags, *Mikrochim. Acta* 124, 1996, 89.

nah kamnitega kalupa, ki ga kaže slika 5 v delu pod op. 4, vendar je barva v našem primeru nekoliko temnejša.[4]

Površine obeh kosov smo premerili z dvema nedestruktivnima metodama, ki temeljita na rentgenski fluorescenci: z običajno rentgensko fluorescenčno analizo (XRF), ki za vzbujanje atomov uporablja kadmijev radioaktivni izvor, in z metodo protonsko vzbujenih rentgenskih žarkov (PIXE). V obeh primerih ioniziramo atome v vzorcu, kar opravimo bodisi z absorpcijo fotonov (XRF), bodisi s protonskimi trki (PIXE). Atomi med rekombinacijo izsevajo karakteristične rentgenske žarke, ki nam omogočajo identifikacijo elementov v vzorcu in tudi njihovo kvantitativno določitev. Izsevane rentgenske žarke smo merili s silicij-litijevim polprevodniškim detektorjem z ločljivostjo 150 eV pri 5,9 keV. Pomembna razlika med obema metodama je bila velikost površine, ki smo jo zajeli pri posamezni meritvi. Pri metodi XRF smo uporabili nekolimiran fotonski snop, s katerim smo obsevali nekaj cm^2 vzorca. Presek protonskega žarka pri metodi PIXE pa je bil le nekaj mm^2. Ta lastnost protonskega žarka nam je omogočila, da smo na površini predmetov preiskali gladka mesta z enakomerno sestavo.

Meritve z metodo XRF smo opravili na vseh površinah, ki so bile dovolj velike in na katerih ni bilo restavratorskega lepila. Rezultati jasno kažejo povečano prisotnost bakra na notranji površini predmeta 11852 (*sl. 1*). Koncentracijo bakra v površinski skorji smo ocenili na 1,5 %, kar je približno tridesetkrat več kot vsebnost bakra 0,05 % v sami glini, ki smo jo izmerili na zunanji površini. Koncentracija bakra v srednjevelikem kosu predmeta 11852 je bila manjša, okrog 0,1 %. Na notranjih površinah 11852 smo zaznali tudi arzen, ki je nečistoča v bakrovih rudah.

Meritve z metodo PIXE smo opravili na dveh največjih kosih predmeta 11852 in na notranjih površinah predmeta 11851. Energija protonov pri prvi seriji meritev je bila 1,4 MeV, vzorce pa smo merili v vakuumski celici. Vzbujene rentgenske žarke smo zaznavali v širokem energijskem območju 3-30 keV, tako da smo lahko merili črte K do antimona. Na notranji površini 11852 smo tudi tokrat opazili močno prisotnost bakra s sledovi arzena in svinca. Razmerje koncentracij, ki smo jih določili na obeh straneh predmeta 11852, je bilo za dober red velikosti večje kot pri meritvah z metodo XRF. Toda ker nismo opravili nobenih referenčnih meritev, nismo mogli določiti absolutnih vrednosti. Pri drugi seriji meritev smo uporabili protonski žarek z energijo 2 MeV v zraku. Absolutne koncentracije smo preračunali glede na koncentracijo argona v zraku, pri čemer smo za referenco uporabili debelo aluminijevo in bakrovo tarčo. Energijsko okno detektorja smo nastavili na območje 1-13 keV. Uporabili nismo nobenih absorberjev za rentgenske žarke, razen 6,4 cm široke zračne reže med tarčo in detektorjem. Taka nastavitev nam je omogočila opazovanje mehkih rentgenskih žarkov, vendar smo s tem zmanjšali občutljivost meritev za trše rentgenske žarke (*sl. 2*). Izmerjene koncentracije glavnih sestavin so negotove za 10 %, slednih elementov pa za faktor dva.

Rezultati (*tab. 1*) kažejo, da notranja površina predmeta 11852 vsebuje precej več bakra, žvepla in železa. Koncentracija železa v skorji je večja za 12 %. Sklepamo, da je snov, ki se je prilepila na glinasto površino, sestavljena iz približno 40 % bakra, 34 % železa in 26 % žvepla. Te koncentracije se dobro ujemajo s sestavo sulfidne bakrove rude, ki v splošnem vsebuje okoli 35 % bakra, 30 % železa in 35 % žvepla.[5]

Pojasnimo še, zakaj z metodama XRF in PIXE dobimo različne koncentracije bakra in železa. V obeh primerih namreč analiziramo vzorec do različne globine. Doseg protonov z energijo 1,5 MeV v glini je okoli 30 μm, atenuacijska dolžina fotonov z energijo 22 keV, ki jih seva kadmijev izvor, pa je okrog 2 mm. Ker je skorja debela le nekaj desetink mm, predstavlja homogeno tarčo samo za protone. Pri obsevanju z rentgenskimi žarki se signali iz skorje pomešajo s signali iz gline pod njo in se tako zdijo šibkejši.

Od slednih elementov v skorji smo odkrili arzen in svinec. Njune rentgenske črte se delno prekrivajo, zato smo za svinec določili samo zgornjo detekcijsko mejo. Koncentracija arzena glede na baker je bila 0,3-2 %, koncentracija svinca pa manjša kot 0,5 %. Tako majhne količine pomenijo, da arzena verjetno niso dodajali v kovino namenoma. Bakra tudi niso zlivali s kositrom, saj smo detekcijsko mejo kositra glede na baker ocenili na 0,6 %. Med drugimi pomembnimi slednimi elementi smo detekcijsko mejo niklja glede na baker ocenili na 0,3 %, antimona pa na 0,7 %. Edino kobalta kot sledi v splošnem nismo mogli zaznati, saj njegova črta K sovpada z železovo črto K. Baker, ki so ga uporabljali v zvezi s predmetom 11852, tako

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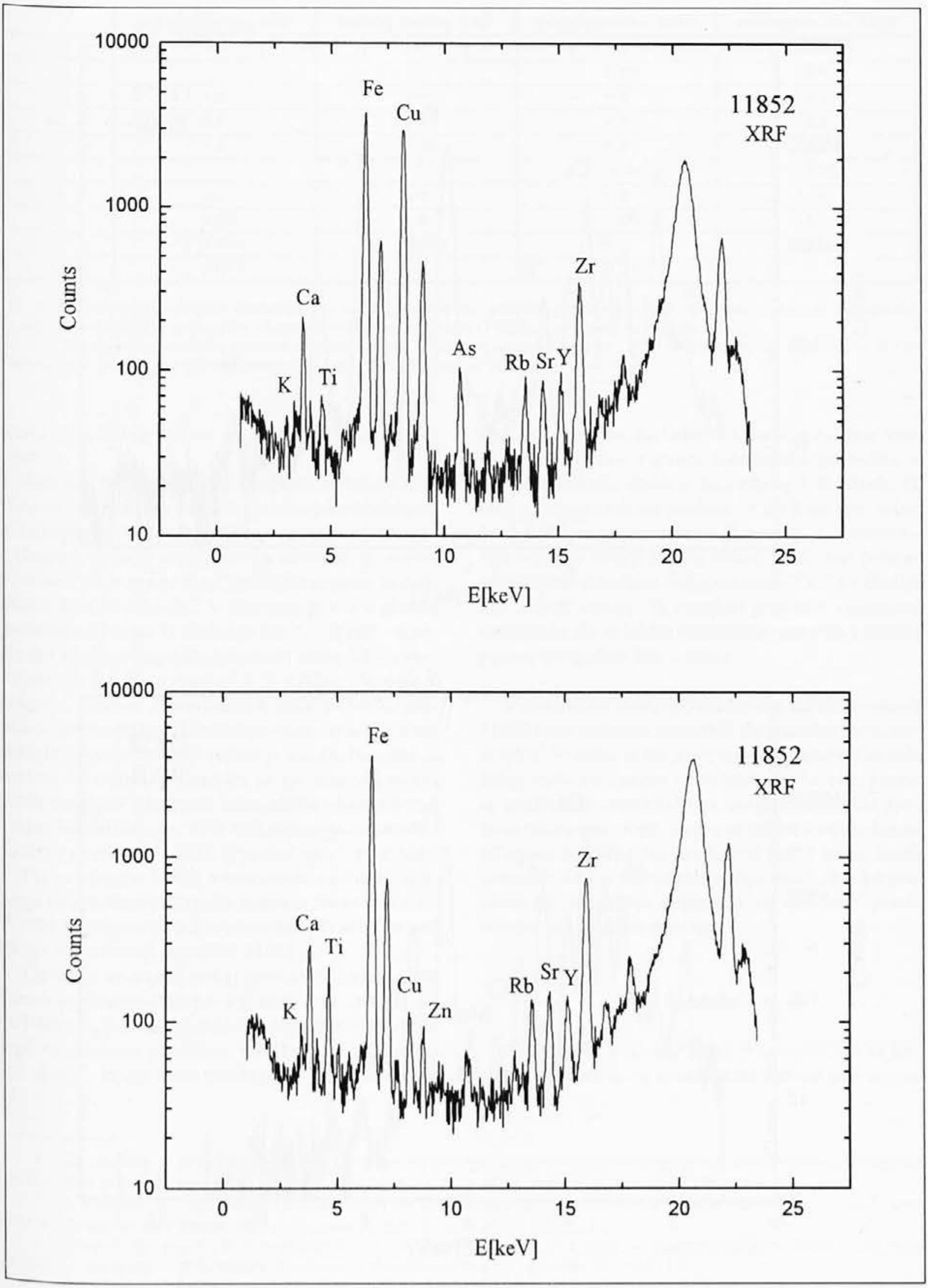
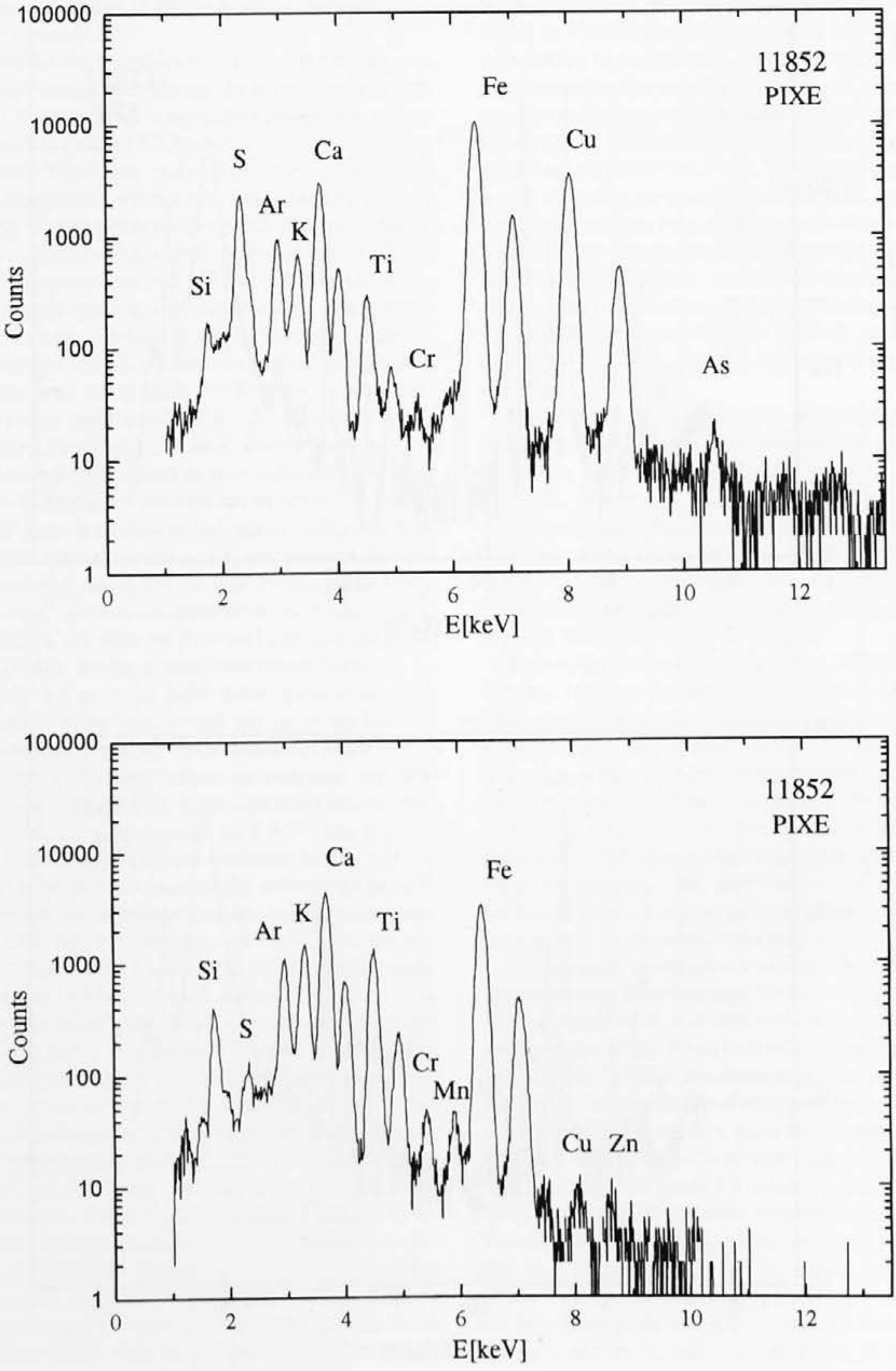
[4] K. Goldman, Bronzegusstechniken in prähistorische Mitteleuropa, v: *Archäologische Bronzen - Antike Kunst, Moderne Technik*, Berlin (1985), 52-58.

[5] Glej op. 4.



Sl. 1: Rentgenski spekter notranje (zgoraj) in zunanje površine (spodaj) največjega kosa predmeta 11852, izmerjen z metodo rentgenske fluorescence (XRF).
Fig. 1: X-ray spectra of the inner (top) and outer surface (bottom) of the largest piece of 11852, obtained by the XRF method.



Sl. 2: Enako kot na *sl. 1*, le da je meritev opravljena z metodo protonsko vzbujenih rentgenskih žarkov (PIXE), s protonskim žarkom v zraku.

Fig. 2: The same as in *Fig. 1*, but for the method of PIXE using an external proton beam.

	zunaj/outside, XRF	znotraj/inside, XRF	zunaj/outside, PIXE	znotraj/inside, PIXE
Si	-	-	12.4	9.4
S	-	-	0.15	9.6
K	1.0	1.0	0.9	0.7
Ca	5.0	2.6	2.3	2.6
Ti	1.0	0.16	0.9	0.26
Cr	-	-	0.18	0.20
Fe	4.3	3.4	5.3	17.8
Cu	0.05	1.5	0.012	15.0
As	0.004	0.009	-	0.09
Zn	0.019	-	0.011	-

Tab. 1: Koncentracije izbranih elementov na notranji in zunanji površini predmeta 11852, določene z metodo rentgenske fluorescence (XRF) in protonsko vzbujenih rentgenskih žarkov (PIXE), s protonskim žarkom v zraku.
Table 1: The concentrations of selected elements in the inner and outer surface of 11852 obtained by the methods of X-ray fluorescence (XRF) and proton induced X-rays (PIXE) using an external proton beam.

izvira iz sulfidne rude z arzenom kot glavno nečistočo.

Koncentracije slednih elementov so lahko značilne za posamezno rudo ali produkcijsko obdobje.[6] V Evropi niso našli zanesljive zveze med koncentracijami slednih elemenov in mestom izdelave, potrjena pa je zveza med koncentracijami in produkcijskim obdobjem.[7] V Sloveniji je arzen glavna nečistoča v bronu iz obdobja Ha A.[8] Bakrene kovinske kepice iz egejske bronaste dobe lahko vsebujejo do 4,5 % arzena in 1 % niklja.[9] V našem primeru kovina s predmeta 11852 ni bron, ampak arzenov baker iz sulfidne rude. Izkoriščanje sulfidnih in arzenidnih rud se je začelo že v eneolitskem obdobju, potem ko so po mnenju nekaterih avtorjev[10] izčrpali nahajališča oksidnih rud v karpatskem bazenu. To je tudi najzgodnejša možna datacija predmeta 11852, ki jo dovoljuje vrsta rude.

Pri predmetu 11851 nismo našli razlik v vsebnosti bakra. Koncentracija bakra je bila okoli 0,01 %, kar je primerljivo z vrednostmi, ki smo jih namerili na zunanji površini 11852.

Opravili smo tudi nekaj poskusov z ulivanjem brona v glinaste kalupe. Pri tem smo opazili, da se bakrena žlindra (kovinsko sive barve) močno lepi na glinasto površino. Oblikuje se v žlindrasto skorjo, ki po barvi prehaja od kovinsko sive, kjer je debelejša, do temnookraste in zelene, kjer je tanka in zlita z glino. Koncentracija bakra v okrasto-zelenih delih je bila okrog 9 %. Bron, ki smo ga uporabili za poskus, je bil bakreno-svinčeva litina in je vseboval 8 % svinca. Koncentracija svinca v skorji je bila okrog 11 %, kar pomeni približno desetkrat večje razmerje Pb/Cu v žlindri kot v čisti kovini. Ta rezultat moramo razumeti kot svarilo, da so lahko elementna razmerja v žlindri precej drugačna kot v litini.

V zaključku lahko povzamemo, da so predmet 11852 zelo verjetno uporabili pri metalurškem postopku. V stiku je bil z arzenovim bakrom iz sulfidne rude ali s samo rudo med predelavo. Samo iz analitskih rezultatov ni mogoče določiti njegove podrobne vloge, ali gre za talilni lonček, kalup ali za kaj drugega. Na predmetu 11851 nismo našli nobenih sledov metalurške dejavnosti, kar pa povsem ne izključuje možnosti, da predmet predstavlja nerabljeno posodo.

Zahvale

Avtorja sta hvaležna Nevi Trampuž Orel za koristne nasvete in za pomoč s strokovno literaturo.

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[6] S. J. Fleming, C. P. Swann, Recent applications of PIXE spectrometry in archaeology, part I: Observations on the early development of copper metalurgy in the Old World, *Nucl. Instr. Meth. Phys. Res.* B75, 1993, 440-444.

[7] N. Trampuž Orel, Spectrometric Research of the Late Bronze Age Hoard Finds, v: *Hoards and Individual Metal Finds from the Eneolithic and Bronze Ages in Slovenia* II, Kat. in monogr. 30 (1996), 165.

[8] Trampuž Orel (op. 7); N. Trampuž Orel, M. Doberšek, D. J. Heath, V. Hudnik, Archäometallurgische Untersuchungen an Sicheln aus spätbronzezeitlichen Hortfunden Sloweniens, *Praehist. Zeitschr.* 71, 1996, 176.

[9] N. H. Gale, A. Papastamataki, Z. A. Stos-Gale, K. Leonis, Copper sources and copper metallurgy in the Aegean Bronze Age, v: *Furnaces and smelting technology in antiquity*, Brit. Mus. Occasional Papers 48, 1985, 81.

[10] B. Jovanović, Smelting of copper in the Enelolithic Period of the Balkans, v: *Furnaces and smelting technology in antiquity*, Brit. Mus. Occasional Papers 48, 1985, 117.

Traces of metallurgic activity on clay fragments

Summary

The ceramic objects numbered 11851 and 11852, described in detail in the preceding paper,[1] are probably fragments of vessels used in early metallurgy. The evidence for this assumption may be corroborated if some material indication of the melting process by were found. One can certainly expect that molten metal would leave some traces on the surface of a vessel, at least a thin layer of slag bearing the applied metal. The fragments of both objects were sufficiently well preserved for recognizing their inner surfaces which presumably made contact with the melted metal. Finding these surfaces enriched in metal would then strongly suggest that the objects 11851 and 11852 were indeed used as metallurgic tools.

Optical emission spectroscopy was used to prove the presence of copper (1-4 %) on the inner surfaces of the epilengyel casting spoon.[2] A similar method was applied to demonstrate tin mining and smelting activities in the central part of southern Turkey. The concentration of tin in different slag samples and walls of the ceramic crucibles were determined by electron induced X-ray spectroscopy and secondary ion mass spectroscopy. According to the results obtained, tin metallurgy in the area was found to be highly probable.[3]

The surfaces of the two objects had varying appearances. Fragments of the object no. 11851 were of a graphite-gray colour, with no difference between the inner and outer surface. The outer surface of object no. 11852 resembled semi-burnt clay, but the inner parts were covered by a dark yellowish-brown crust several tenths of a mm thick. A similar yellow layer can be seen on a stone mould shown in *fig. 5* of ref. 4, though the colour was darker in the present case.[4]

The fragment surfaces were probed by two non-destructive techniques which are based upon X-ray fluorescence: the standard X-ray fluorescence analysis (XRF) which used a cadmium radioactive source for excitation, and the proton induced X-ray emission (PIXE). For both methods, the sample atoms are ionized either by photon absorption (XRF) or proton impact (PIXE). During recombination, the atoms emit characteristic X-rays which provide identification and quantitative estimates of the target elements. The emitted X-rays were detected by a Si(Li) semiconductor detector of 150 eV/5.9 keV resolution. Both methods essentially differed in the size of the investigated area. For the XRF method we used an uncollimated photon beam which irradiated several cm^2 of the sample. For the PIXE, the beam area was a few mm^2. This feature of the proton beam enabled us to test smooth and homogeneous parts of the object surface.

The XRF measurements were executed on all surfaces of the two objects which were sufficiently large and free of restoration glue. The results clearly indicate copper enrichment on the inner surface of object no. 11852 (*Fig. 1*). The concentration of copper on the surface of the crust was estimated to be about 1.5 %, which is by a factor of 30 more than the copper content of 0.05 % in the raw clay, as measured at the outer surface. The copper concentration on the medium sized fragment of object no. 11852 was smaller, about 0.1 %. The inner surface of object no. 11852 was also enriched with arsenic, an impurity in copper ores.

The PIXE measurements were performed on the two largest pieces of object no. 11852, as well as on the inner surfaces of object no. 11851. In the first set of measurements, the bombarding proton energy was 1.4 MeV and the samples were inserted into the vacuum chamber. The induced X-rays were detected in a broad energy window of 3-30 keV which allowed detection of K lines up to antimony. Again a strong presence of copper containing traces of arsenic and lead was determined on the inner surfaces of object no. 11852. The ratios of concentrations determined on both sides of object no. 11852 were more than an order of magnitude larger than for the XRF measurements. Since no reference data was measured, we were not able to evalute absolute concentrations. A second set of measurements was then performed using a 2 MeV external proton beam. The absolute concentrations were evaluated with respect to the argon signal from the air, using thick aluminum and copper targets for reference. The energy window was set to 1-13 keV. No X-ray absorbers were used, except a 6.4 cm air gap between the target and the detector. This arrangement enabled the observation of soft X-rays, but reduced the sensitivity for X-rays of higher energies (*Fig. 2*). The deduced concentration was variable by 10 % for major components, though by a factor of two for the traces.

The results (*Tab. 1*) indicate that the inner surface of object no. 11852 is markedly enriched in copper, sulphur, and iron. The concentration of iron in the crust is increased by 12 %. We may deduce that the material stuck to the clay surface consists of 40 % copper, 34 % iron, and 26 % sulphur. These concentrations closely agree with the composition of the sulphide copper ore which generally contains about 35 % copper, 30 % iron, and 35 % sulphur .[5]

The differences in copper and iron concentrations obtained by the XRF and PIXE methods may be explained by the different depths of the analyzed material. In clay, the range of 1.5 MeV protons is about 30 μm, and the attenuation length for 22 keV photons from the cadmium source is about 2 mm. As the crust is a few tenths of a mm thick, it represents a homogeneous target for protons only. For 22 keV X-rays, the signals from the crust are intermingled with those from the underlaying clay and thus appear less intense.

The trace elements found in the crust were arsenic and lead. Their X-ray lines partly overlap, so only the upper concentration limit was determined for lead. The concentration of arsenic relative to copper was 0.3-2 %, and the respective concentration of lead was smaller than 0.5 %. Due to these low levels, arsenic was probably not added to the cast metal deliberately. The copper was also not alloyed with tin since the detection limit for tin with respect to copper was estimated to be 0.6 %. Among other important trace elements, the detection limits for nickel and antimony with respect to copper were estimated to be 0.3 % and 0.7 % respectively. Only cobalt was not detectable at all since its K line coincides with the K line of iron. The copper used with the object no. 11852 thus evidently originates from the sulphide ore with arsenic as the predominat impurity.

The trace element concentrations may be characteristic for a particular ore and production site.[6] In Europe, the relation between the trace element concentrations and the production site was found to be unreliable, but the correlation exists between the concentrations and the production period.[7] In Slovenia, arsenic is the predominant impurity in bronze during the Ha A period.[8] Copper prills belonging the Aegean Bronze Age may contain up to 4.5 % of arsenic and 1 % of nickel.[9] In our case, the metal of object no. 11852 is not bronze but arsenic copper from the sulphide ore. The exploitation of sulphide and arsenic ores began already in the Eneolithic period, and according to some authors[10] after the exhaustion of the oxide ores in the Carpathian basin. This is the earliest possible dating of the object no. 11852, as permitted by the ore type.

No copper enrichment was found on the object no. 11851. The copper concentration was about 0.01 %, which is comparable to the values at the outer surfaces of object no. 11852.

We have also performed bronze casting experiments with clay moulds. It was found that the copper slag (which was of a metal-gray colour) sticks heavily onto the clay surface. A crust of copper slag was formed which varied in colour from metal-gray where it was thick, to dark ochre-green where it was thin and diffused in the clay. The copper concentration in the ochre-green parts was about 9 %. The bronze used for the experiment was a copper-lead alloy and contained 8 % of lead. The lead concentration in the crust was about 11 %, which represents an increase by a factor of ten with respect to the copper concentration. This result implies a precaution that the elemental ratios in the slag may be notably different from those in the cast metal.

In conclusion, the object no. 11852 was very probably used in a metallurgic process. It came into contact with the arsenic copper from the sulphide ore, or with the ore itself during the smelting process. From the analytic results alone it is not possible to determine its functional use, whether it was a crucible, mould, or something else. No traces of metallurgic activity were found on the object no. 11851, which, however, does not exclude the possibility that this object represents an unused vessel.

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