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Chačatur Meliksetyan and Ernst Pernicka

Geochemical characterisation of Armenian Early Bronze Age metal artefacts and their relation to copper ores

Introduction

This paper is based on the trace element and lead isotope analyses of Armenian Early Bronze Age copper-based artefacts and copper ores. Some of this data and discussion were reported in brief earlier.[1]

Metallurgy appears at an early time in the southern Caucasus, and it has long been assumed that this may be related to the presence of dozens of large and small copper deposits. Numerous Eneolithic and Early Bronze Age finds of copper-based artefacts and especially the abundance of arsenical copper and some early tin bronzes have supported this assumption. Trace element concentrations and lead isotope ratios of copper ores and copper-based artefacts are important methods to fill gaps in our knowledge concerning the origin of copper smelted at the beginnings of metallurgy in the territory of Armenia and the southern Caucasus region. They may reveal the dissemination paths of raw materials, particularly copper ores, and/or smelted metal. At the same time the lead isotope abundance ratios in ores also contribute significant information concerning the genesis of some Armenian ore deposits.

Many of the large copper deposits in Armenia were exploited from antiquity until the 19th century.[2] Some of the deposits (Alaverdi, Shamlug, Kapan, Kadjaran, Agarak) are still in operation today. Therefore, in most cases the oxidation zones of the deposits as well as any remains of ancient workings were destroyed. In such a situation geochemical investigations, especially the lead isotope analysis of copper-based artefacts and their comparison with copper ores, are the only reliable methods to identify the early exploitation of these deposits.

All analyses presented in this article were performed in the Institut für Archäometrie at the Technische Universität Bergakademie Freiberg, Germany.

Samples and analytical techniques

Archaeological samples

Specimens of 48 Early Bronze Age metal artefacts and 4 oxidised copper samples from crucibles were selected for this study. All analysed artefacts consist of copper-based alloys. The samples selected for this study cover a long interval of time, from the beginning of the Early Bronze Age until the Middle Bronze Age. A complete list of the analysed metal artefacts, together with their description, metal type and dating is available in *Tab. 1*; *Fig. 1* shows the geographical locations of these finds, combined with the locations of the major copper ore deposits and metallogenic provinces in Armenia.

The samples for this investigation were kindly provided by: The Institute of Archaeology and Ethnography, the Armenian National Academy of Sciences (11 samples, numbers 1–10 and 32 as in *Tab. 1*); Gfoeller Foundation (3 samples, numbers 11–13) the Gyumri Museum of Shirak region (4 samples, numbers 20–23); the Vanadsor Museum of Lori-Pambak region (4 samples, numbers 16–19); the Shengavit Archaeological Site Museum (5 samples, numbers 24–28); Armenian Monuments Corps of the Armenian Board of Historical Sites Conservation (23 samples, numbers 29–31 and 33–52); and finally the State Museum of History of Armenia (2 samples, numbers 14–15).

The archaeological dates in *Tab. 1* follow the Armenian periodization of the Bronze Age suggested by P. Avetissyan and R. Badalyan.[3] It is noteworthy that the spiral ring from tomb 11 of the Talin cemetery (sample FG-010086) turned out to be a true tin bronze with 11% tin (*Tab. 2*). The Talin cemetery dates to the first stage of the Kura-Araxes culture, (end of the fourth to the early third millennium B.C). Artefacts with such a composition are quite rare for this period, and this artefact is one of the earliest known tin bronzes in the region.

The majority of the analysed artefacts belongs to the Kura-Araxes culture. This Early Bronze culture of the mid fourth until the last quarter of the third millennium B.C. covers wide territories of the Armenian Highland, the Caucasus and Anatolia, reaching the Levant and the west central Zagros mountains. The economic basis of the Kura-Araxes culture was farming and cattle-breeding. Many of the Kura-Araxes settlements in Armenia are located at a great distance from the copper ore provinces.

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1 Meliksetian et. al. 2003.

2 Гогинян 1964; Геология Армянской ССР 1967.

3 Avetissyan et al. 1996.

	Sample	Description	Composition	Culture and Dating	Site	
1.	FG-010084	Spearhead	Cu, As, Sn	Kura-Araxes culture,EBA I	tomb 12	Talin
2.	FG-010085	Spearhead	Cu, As(Sn)		tomb 10	
3.	FG-010086	Spiral ring	Cu, Sn(Ni)		tomb 11	
4.	FG-020479	Spiral ring	Cu, As, Pb	Kura-Araxes culture, EBA II–III	Harich, burials	
5.	FG-020480	Awl	Cu, As			
6.	FG-020481	Awl	Cu (As,Ni)			
7.	FG-020482	Awl	Cu, As			
8.	FG-020484	Pin	Cu, As			
9.	FG-010089	Spiral bracelet	Cu, As	Kura-Araxes culture, EBA I/II	Chkalovka, tomb	
10.	FG-010088	Spiral ring	Cu	Kura-Araxes culture, EBA II	Mokhrablur, settlement	
11.	FG-020485	Dagger	Cu, As	Kura-Araxes culture, EBA II	Agarak, settlement	
12.	FG-020487	Awl	Cu, As			
13.	FG-020486	Bronze ingot	Cu, Sn	EBA–?		
14.	FG-011848	Axe head	Cu, As	Kura-Araxes culture, EBA I/II	Chance finds, Jrashen (near the Yerevan hoard)	
15.	FG-011876	Adze	Cu, As			
16.	FG-011847	Pin	Cu, As	Kura-Araxes culture, EBA II	Chance finds, Bazum	
17.	FG-011846	Spiral bracelet	Cu			
18.	FG-011875	Dagger	Cu, As	EBA III–?	Chance finds, Vanadsor, Dimac	
19.	FG-011836	Dagger	Cu			
20.	FG-010081	Axe head	Cu(Sn, Ni)	Kura-Araxes culture, EBA	Chance finds, Gyumri (Shirak area)	
21.	FG-010082	Axe head	Cu, As			
22.	FG-010083	Axe head	Cu, As			
23.	FG-011838	Spearhead	Cu, As			
24.	FG-011887	Bracelet	Cu, As	Kura-Araxes culture, EBA III	Shengavit settlement, level IV	
25.	FG-011888	Fragment	Cu, As			
26.	FG-011839	Fragment	Cu, As			
27.	FG-011849	Pin	Cu, As			
28.	FG-011889	Pin	Cu, As			
29.	FG-011834	Copper samples from a crucible	Cu, As		Shengavit settlement, level III	
30.	FG-011835		Cu, As			
31.	FG-011837		Cu, As			
32.	FG-020498		Cu			
33.	FG-011850	Spiral ring	Cu, As	Kura-Araxes culture, EBA II/III	Berqaber (Choghas), kurgan 4	
34.	FG-011857	Oval bead	Cu			

Tab. 1. List of the archaeological artefacts analysed.

	Sample	Description	Composition	Culture and Dating	Site
35.	FG-011891	Spiral ring	Cu (As)	Early Kurgan culture, EBA IV–MBA I	Berqaber (Choghas), tomb 1
36.	FG-011840	Spiral ring	Cu, As		
37.	FG-011892	Spiral ring	Cu, As		
38.	FG-011871	Pin	Cu, As		
39.	FG-011841	Spiral ring	Cu, As		
40.	FG-011842	Spiral ring	Cu, As		
41.	FG-011893	Pin	Cu, As		
42.	FG-011843	Pin	Cu, As		
43.	FG-011852	Spiral ring	Cu, As		
44.	FG-011844	Spiral ring	Cu, As		
45.	FG-011872	Pin	Cu, As		
46.	FG-011873	Spiral ring	Cu, As		
47.	FG-011853	Pin	Cu		
48.	FG-011874	Spiral Ring	Cu, As		
49.	FG-011890	Spearhead	Cu(As)		Berqaber (Choghas) kurgan 1
50.	FG-011855	Arrowhead	Cu, As		
51.	FG-011856	Arrowhead	Cu(As)		
52.	FG-011854	Dagger	Cu, As		

Tab. 1. (continued).

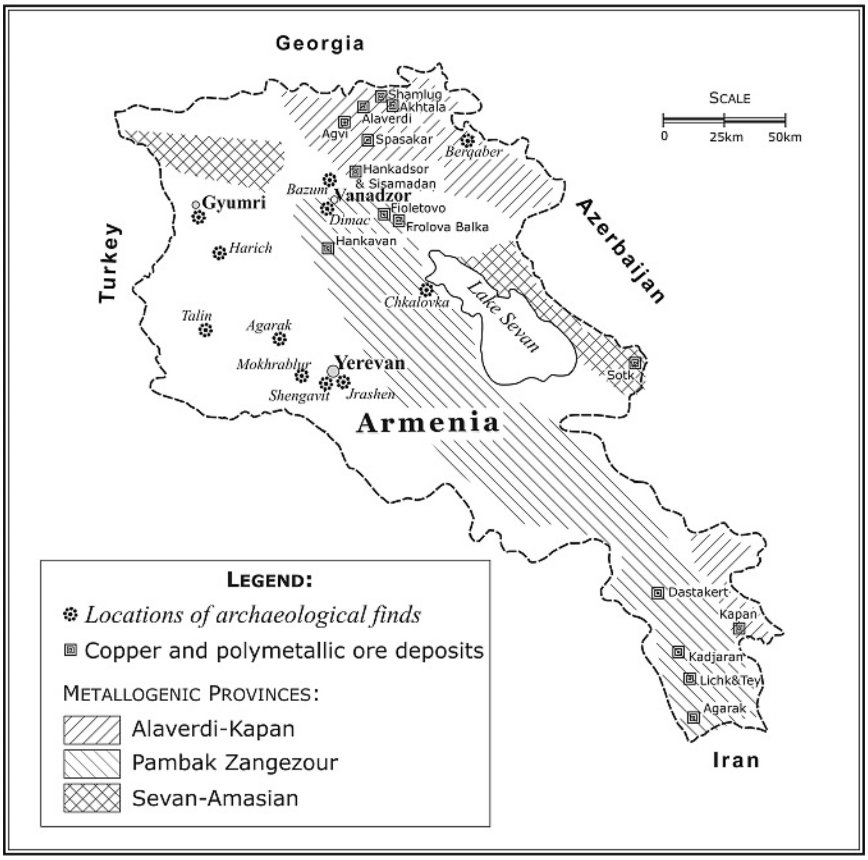

Fig. 1. A schematic map of the Republic of Armenia, showing the metallogenic provinces, the origins of the archaeological artefacts and the locations of the copper deposits investigated in this study.

Sample	Cu %	Fe	Co	Ni	Zn	Pb	Bi	Sn	As	Sb	Se	Te	Au	Ag	Site
FG-010084	96	800	330	490	*160*	300	260	*13 500*	16 900	*540*	*7,1*	< 80	< 100	4 600	Talin
FG-010085	96	< 500	140	700	*200*	500	130	*7 100*	20 900	278	11	< 80	200	1 660	
FG-010086	89	1500	390	3400	*340*	2100	130	110 000	4 000	320	30	< 80	< 100	2 000	
FG-020479	82	< 500	< 50	470	< 1000	43000	< 50	< 50	130 000	760	< 50	< 80	400	2 490	Harich
FG-020480	98	< 500	< 50	300	< 1000	300	< 50	< 50	21 500	170	< 50	< 80	< 100	1 590	
FG-020481	98	< 500	< 50	3000	< 1000	200	< 50	< 50	10 000	< 50	60	< 80	300	620	
FG-020482	92	< 500	< 50	1240	< 1000	400	< 50	< 50	72 000	80	140	< 80	100	910	
FG-020484	97	900	< 50	510	< 1000	300	< 50	310	24 400	680	360	< 80	100	540	
FG-010088	83	< 500	< 50	*215*	*240*	100	< 50	*440*	2 700	201	*5,6*	< 80	200	*350*	Mokhrablur
FG-010089	96	< 500	< 50	*157*	*110*	3200	< 50	*1 400*	23 000	*240*	*10,7*	< 80	< 100	1 030	Chkalovka
FG-020485	97	< 500	< 50	< 100	< 1000	200	< 50	< 50	26 200	250	< 50	< 80	< 100	430	Agarak
FG-020486	97	< 500	140	470	< 1000	5200	< 50	30 000	870	180	< 50	< 80	< 100	390	
FG-020487	99	< 500	< 50	180	< 1000	200	< 50	< 50	10 400	400	< 50	180	200	360	
FG-011848	92	1 200	< 50	320	2000	300	130	< 50	68 000	130	50	330	300	250	Jrashen
FG-011876	93	3 600	< 50	270	2000	300	70	< 50	65 000	260	< 50	80	< 100	950	
FG-011847	98	1 400	< 50	< 100	< 100	< 100	50	180	13 000	230	< 50	< 80	< 100	120	Bazum
FG-011846	99	1 100	< 50	< 100	< 100	< 100	50	< 50	7 600	410	< 50	< 80	< 100	440	
FG-011875	97	1 200	60	< 100	< 100	2200	90	860	12 600	5900	< 50	210	200	280	Dimac
FG-011836	99	3 900	230	620	< 100	500	50	660	1 830	640	90	< 80	100	310	
FG-010081	98	5 200	590	2500	*94*	600	< 50	6 000	60	303	100	< 80	200	1 710	Gyumri
FG-010082	96	1 600	170	530	*430*	< 100	< 50	*1 420*	18 400	350	11	< 80	< 100	2 910	
FG-010083	96	1 500	140	860	*290*	200	< 50	*290*	17 200	84	39	< 80	100	720	
FG-011838	98	900	< 50	< 100	< 1000	600	500	< 50	21 300	< 50	100	< 80	< 100	100	
FG-011887	72	170 000	480	610	< 1000	1200	1160	< 50	102 000	700	< 50	< 80	400	< 50	Shengavit – Artefacts
FG-011888	76	32 000	< 50	< 100	< 1000	1200	50	100	201 000	410	160	90	200	< 50	
FG-011839	93	7 700	< 50	< 100	< 1000	1400	50	70	58 000	2720	< 50	< 80	< 100	< 50	
FG-011849	90	8 100	< 50	340	1000	< 100	50	560	87 000	830	840	< 80	2000	< 50	
FG-011889	93	7 400	100	120	< 100	600	50	< 50	55 000	1150	< 50	< 80	200	210	
FG-011834	72	75 000	270	390	< 100	4800	50	140	197 000	600	< 50	< 80	500	150	
FG-011835	81	60 000	< 50	700	< 100	1000	50	510	12 200	1000	< 50	140	< 100	280	Shengavit – Copper samples from a crucible
FG-011837	79	96 000	< 50	< 100	< 100	1200	50	< 50	112 000	450	< 50	100	200	< 50	
FG-020498	98	8 100	< 50	530	< 1000	600	< 50	< 50	7 400	180	< 50	< 80	100	170	
FG-011850	95	900	< 50	< 100	< 1000	< 100	50	< 50	49 000	140	< 50	< 80	< 100	340	Berqaber (Choghas)
FG-011857	99	< 500	< 50	< 100	< 1000	< 100	110	< 50	6 400	< 50	< 50	< 80	< 100	50	
FG-011890	99	1 300	< 50	< 100	< 1000	100	50	< 50	11 100	50	< 50	< 80	< 100	410	
FG-011891	99	< 500	< 50	< 100	< 1000	< 100	80	100	10 200	< 50	110	< 80	200	< 50	
FG-011840	96	< 500	< 50	260	< 1000	400	90	< 50	33 000	480	< 50	< 80	< 100	340	
FG-011892	98	< 500	110	< 100	< 1000	< 100	290	< 50	17 600	390	350	< 80	500	110	
FG-011871	98	< 500	< 50	< 100	< 1000	200	50	< 50	20 900	690	60	< 80	200	250	
FG-011841	97	< 500	< 50	330	< 1000	200	50	< 50	26 000	250	70	< 80	< 100	230	
FG-011842	98	< 500	< 50	< 100	< 1000	200	50	< 50	26 000	650	< 50	< 80	< 100	250	
FG-011893	98	< 500	< 50	< 100	< 1000	< 100	50	100	18 900	570	70	< 80	< 100	340	
FG-011843	95	700	< 50	180	< 1000	< 100	50	< 50	47 000	430	110	< 80	100	270	
FG-011852	98	< 500	< 50	< 100	< 1000	300	50	260	18 200	360	120	< 80	200	130	
FG-011844	97	1 000	< 50	< 100	< 1000	200	50	< 50	19 700	450	90	< 80	< 100	160	
FG-011872	98	< 500	< 50	< 100	< 1000	< 100	50	< 50	20 800	590	60	< 80	200	300	
FG-011873	96	< 500	< 50	240	< 1000	300	260	< 50	36 000	140	110	< 80	200	280	
FG-011853	99	< 500	< 50	< 100	< 1000	2100	410	120	7 200	57	< 50	< 80	100	340	
FG-011854	98	< 500	< 50	< 100	< 100	< 100	50	< 50	23 400	49	60	< 80	< 100	250	
FG-011874	97	1 600	130	< 100	< 1000	200	50	< 50	24 000	720	< 50	< 80	100	< 50	
FG-011855	98	< 500	< 50	< 100	< 1000	< 100	50	< 50	16 100	50	70	< 80	100	240	
FG-011856	99	600	< 50	< 100	< 1000	100	50	< 50	10 000	500	80	< 80	< 100	770	

Tab. 2. Chemical compositions of the analysed artefacts. Cu concentrations of all samples are given in weight percent, all others in ppm. Values in italics indicate determination with NAA. All other element concentrations were determined with XRF.

But in spite of this, a wide range of metal wares and many indications for metalworking were found in these settlements. Particularly, in the settlements of the Shirak plateau (Harich, Karnut and others) and the Ararat valley (Jrahovit, Mokhrablur, Arevik and others) casting moulds, crucibles, vessels and fragments thereof with remains of copper were found. A variety of metals was used during the Early Bronze Age: for instance, pure copper, lead, gold, silver and copper-based alloys – arsenical copper, tin bronze, and tin-arsenic bronzes. The archaeological samples analysed in this study represent almost all types of artefacts, one ingot and copper from crucible walls. It is noteworthy that that artefacts derive not only from settlements and burials, but also from the unique Yerevan hoard containing 19 objects. The selection of the archaeological samples was somewhat accidental. Some of the artefacts originate from recent excavations (Talin, Chkalovka, Agarak, Berqaber), and some are from museums (Gyumri, Jrashen) and have already been analysed by OES.[4] However, precise INA, RFA and ICP-MS Pb isotope analyses were performed for the first time.

Geological samples

A total of 41 representative samples were selected from 17 major copper deposits. The sampling of copper ore deposits was carried out by the Institute of Geological Sciences in the Armenian Academy of Sciences. The selected ore samples consisted mainly of the copper minerals chalcopyrite, malachite and azurite. In order to check the homogeneity of the lead isotope ratios in different minerals and mineralization stages within an ore deposit, samples of galena or mixed galena-chalcopyrite concentrates (Kadjaran, Shamlug and Sotk) were included.

Fioletovo is a unique copper ore deposit in the territory of Armenia, in which it is possible to prove the extraction and enrichment of copper ore in the Early Bronze Age using archaeological methods. In the village of Fioletovo and the copper deposit with the same name an Early Bronze Age settlement was found and first recorded by A. Mnatsakanian and E. Khanzadian.[5] During 1962–1964 a special expedition for the study of ancient mining was undertaken under the direction of S. Goginian. Thereby, dozens of 1–10 m large open pits, holes and associated burrows across the strike of ore bodies were discovered and investigated. The excavators also remarked upon the presence of two sloped galleries with the remains of timbering.[6] During 1996–1997 joint investigations of A Karakhanyan, (Institute of Geological Sciences, Armenian NAS), R. Badalyan and P. Avetisyan (Institute of Archaeology and Ethnography, Armenian NAS) confirmed the presence of copper rich ore on the surface as well as the remains of ancient mining on the Fioletovo hill. During the sinking of a prospection hole a layer containing crushed copper ore and archaeological material was discovered. The archaeological finds from Fioletovo can be dated typologically to the final stage of the Kura-Araxes Culture (26–22 century B.C). Also in 1999 A. Gevorgyan conducted excavations in Fioletovo and found copper mineralisations and the remains of ancient mining, thus confirming that the settlement specialized in copper mining and ore-dressing.[7]

Analytical techniques

Neutron activation (NAA) and X-Ray fluorescence (XRF) analyses were used to determine the major and trace element composition of the artefacts. The chemical composition of the ore samples was determined by NAA. The methodical aspects of the neutron activation analysis of copper-based archaeological artefacts used in this study are described in detail by E Pernicka and I. Kuleff.[8]

For analysis with ICP-MS, approx. 10 mg samples in the form of metal shavings from artefacts were dissolved with half-concentrated HNO_3 in an ultrasonic bath. For lead separation nitric acid solutions of the samples were evaporated to dryness and redissolved in 2N hydrochloric acid. Lead was separated from the samples in 0.5 ml ion exchange columns using DOWEX™ ion exchange resins. The preparation of samples for ICP-MS was performed in a glass 1000 clean laboratory. All chemical reagents used for chemical preparation were of ultrapure grade. All used containers, test tubes and vessels were rigorously cleaned to avoid possible contamination of samples.

The isotope analyses of both the ores and the artefacts were performed with inductively coupled plasma: mass spectrometry with a VG Elemental AXIOM, a double focussing magnetic sector-based multiple collector inductively coupled plasma mass spectrometer (MC-ICP-MS) using the protocol of E. Niederschlag et al.[9] All analyses were continuously compared with certified international analytical reference materials.

Altogether 52 RFA, 36 NAA and 91 ICP-MS analyses of Armenian Early Bronze Age metal artefacts and representative samples of main copper deposits were performed.

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4 Геворгаян 1980.
5 Mnatsakanian 1965; Khanzadian 1967.
6 Гогинян 1964.
7 Gevorgyan / Palmieri 2001.
8 Pernicka 1984; Kuleff / Pernicka 1995.
9 Niederschlag et al. 2003.

Metallogenic province	Deposit	Geological age	Type
Alaverdi-Kapan	Akhtala	Late Jurassic – Early Cretaceous	Volcanogenic massive sulphides (Copper and poly-metallic ores)
	Alaverdi	Late Jurassic – Early Cretaceous	
	Shamlug	Late Jurassic – Early Cretaceous	
	Agvi	Middle Eocene	
	Spasakar	Middle-Late Eocene	
	Hankadzor and Sisamadan	Middle Eocene	
	Kapan	Late Jurassic – Early Cretaceous	
Pambak-Zangezour	Agarak	Late Oligocene Neogene	Porphyry and vein (copper-molybdenum ores)
	Kadjaran		
	Dastakert		
	Lichk and Tey		
	Frolova Balka and Fioletovo	Middle-Late Eocene	Vein (copper)
	Hankavan	Middle-Late Eocene	Porphyry, vein and skarn (copper-molybdenum)
Sevan-Amasian	Sotk	Late Oligocene-Neogen	Vein (gold, polymetallic)

Tab. 3. Some characteristics of the major copper ore deposits of Armenia.

For 8 metal artefacts (FG-010084, FG-010085, FG-010086, FG-010088, FG-0100893 FG-010081, FG-010082, FG-010083) both NAA and RFA were used to determine major and trace elements concentrations. The correlation between the results for Sn, As, Sb, Zn and Se is very good, but NAA results were used for diagrams and discussion as they are more precise at low concentrations.

Geochemical characterisation of metal artefacts and ores

The major and trace element concentrations of the artefacts are summarized in *Tab. 2*. The artefacts from the Shengavit settlement were partly oxidized, and it is not clear whether the high concentrations of iron are due to contamination, or whether we have copper smelted at very high temperatures, during which some iron may be taken up by the copper. Artefacts from Gyumri (chance finds in the Shirak area) and Jrashen (near the Yerevan hoard) have already been analysed using optical emission spectrometry (OES) in the Institute of Archaeology and Ethnography, Armenian NAS during 1970–1980.[10] The results of these analyses and the present data are generally in good agreement, but there are also some major discrepancies, especially for concentrations of As, Sn, Sb, Ni and Co in some of the artefacts.

The artefacts studied, can be divided into five main chemical groups:

1. pure *Cu* (spiral ring from Mokhrablur, bracelet from Bazum, dagger from Dimac and oval bead and pin from Berqaber, samples, FG-010088, FG-011846, FG-011836, FG-011857, FG-011853 respectively);
2. *Cu* + *As* (the majority of the analysed artefacts and copper samples from crucibles);
3. *Cu* + *As* + *Sn* (spearheads from Talin, samples FG-010084, FG-010085);
4. *Cu* + *Sn* (spiral ring from Talin, sample FG-010086 and bronze ingot from Agarak, sample FG-020486);
5. *Cu* + *As* +*Pb* (spiral ring from Harich, sample FG-020479).

10 Геворгян 1980.

Sample	Cu %	Ni	As	Sb	Se	Sn	Zn	Ag	Ore Deposit
FG-010090	22,3	38	62	2,4	91	43	2 480	58,2	Agarak
FG-010091	5,1	26	540	43,2	28	32	4 500	21,9	
FG-010092	9,4	8,1	9,7	1	17	18	130	3,5	
FG-010093	1,6	16,5	3,2	0,5	5,5	30	111	1,7	Lichk
FG-010094	7,9	24	14	1	62	270	540	9,7	
FG-010095	24,5	34	41	4,3	140	32	1 600	209	Kadjaran
FG-010096	8,3	43	300	30	87	510	8 400	64,8	Tey
FG-010097	12,7	44	180	13	74	300	1 100	12,1	Fioletovo
FG-010098	14,5	120	294	147	56	125	55 000	14,7	Akhtala
FG-010099	9,5	53	139	3 260	123	282	3 900	9,4	
FG-010100	11,7	23	19	2,2	203	290	69	13,5	Hankadzor
FG-010101	8,8	33	21	1,5	143	430	340	15,4	
FG-010102	26,9	22	15	7,5	152	37	1 350	16,6	Kapan
FG-010103	8,4	42	8,4	8,5	18	57	4 800	79,8	
FG-010104	4,7	44	6,5	540	23	52	1 540	11,8	
FG-010105	11,9	38	159	31	73	42	14 300	10	Frolova Balka
FG-010106	16,2	37	32	1,6	163	770	1 700	18,9	Alaverdi
FG-010108	15,3	55	16	0,3	500	1620	73	40	
FG-010109	9,9	28	26	2,2	96	34	850	10,4	Agvi
FG-010110	14,1	34	28	1,7	149	750	1 400	18,6	
FG-010111	3,7	46	174	3	55	51	153	2,4	Spasakar
FG-010112	5,4	34	68	1,7	156	460	430	13,5	
FG-010113	4,8	37	340	5	135	44	101	3,2	
FG-010114	6,8	37	490	7,5	140	41	128	4,4	Shamlug
FG-010115	7,2	54	62	2,8	75	65	78	1,1	
FG-010116	7,3	46	28	1,6	48	57	110	1,4	
FG-010117	3,6	26	116	4	34	63	450	2,2	Sisamadan
FG-010118	3,3	26	128	4,9	27	89	330	2,5	

Tab. 4. Trace element concentrations of copper ores, determined by instrumental neutron activation analysis, in ppm.

Some characteristics of the major copper and polymetallic ore deposits in Armenia are given in *Table 3*, the compositions of some ore specimens as determined by NAA in *table 4.*

Figures 2 and 3 show a correlation of the As/Sb ratio vs. As and Ni vs. Ag in the analysed ores and artefacts. The observed variation of trace element concentrations in the artefacts (As, Sb, Ni, Co, Se, Au, Ag) allow the identification of some significant geochemical characteristics of the analysed artefacts. As can be observed in *Figure 2*, the majority of analysed copper artefacts and the crucible samples are characterised by high As/Sb ratios (As/Sb = 10–1280). Low As/Sb ratios (As/Sb < 10) are only observed in two daggers from Dimac, an axe head from Gyumri and a bronze ingot from Agarak. In general, As/Sb ratios and As concentrations are much lower in the analysed ores *(Fig. 2)*.

Because As becomes extremely volatile at the temperatures of copper smelting, it is very difficult to produce copper metal with more than 3–4% As. It is important to note that all analysed samples with extremely high As contents (above 7% and up to 20%) are partly oxidized. This high concentration of arsenic can possibly be explained by zoning and inhomogeneity produced by disintegration of a Cu–As solid solution due to corrosion and the resulting enrichment of the surface of the artefacts. However, it is noteworthy that in general high arsenic concentrations are typical for decorative objects rather than for tools and weapons *(Fig. 4)*. The concentrations of As in non-corroded, clean metal shavings range up to 6.5–6.8% (an axe head and adze from the hoard near Yerevan, Jrashen), but all other non-corroded samples have less then 5% arsenic.

The relative enrichment of arsenic over antimony is one of the problems related to these artefacts.

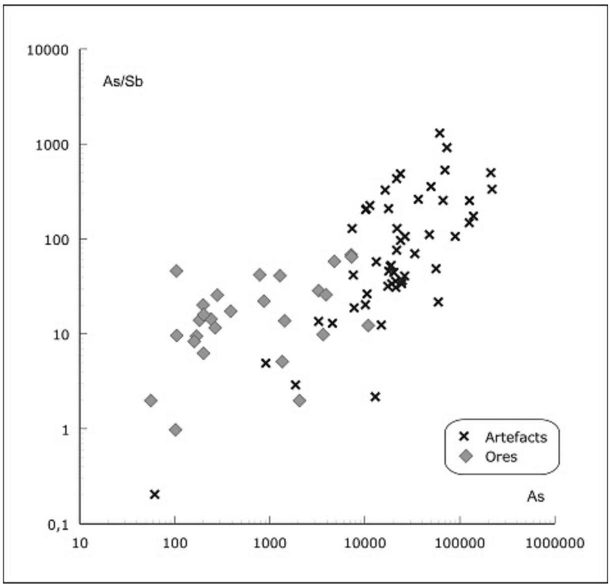

Fig. 2. Plot of As versus As/Sb ratio for Armenian copper ores and copper-based artefacts. Enrichment of arsenic over the antimony in the artefacts relatively to ores can be observed. Concentrations were recalculated to a total of 100% including copper.

This problem comes from the assumption that As and Sb are usually associated in the ores and smelting should produce copper that is rich in arsenic and also in antimony with ratios of As/Sb ranging from 10 to 50, as is typical for the copper ores. But there are some interesting observations concerning the distribution of As and Sb in Armenian ores:

1. The presence of high arsenic enargite-tennantite formations in some late stage ore bodies in deposits of Armenia (Hankadsor, Sisamadan, Hankvan, Sotk, Kapan, Alaverdi, Fioletovo, Aghvi and others).[11] Also, sometimes arsenopyrite occurs together with pyrite and chalcopyrite without any appreciable antimony minerals in association. These mineral associations are characterised by a dominance of arsenic over antimony.

2. Malachite and azurite ores that can be smelted directly without roasting are usually assumed to be the main sources for copper smelting in the Early Bronze Age. In fact, it is interesting to note that sometimes in oxidation zones arsenic is also present in the form of bright green or blue coloured minerals, such as skorodite, olivenite, erythrite, cuproadamite, adamite, annabergite and others. Obviously, these minerals may have been easily confused with green and blue malachite-azurite copper ores in the Bronze Age and smelted together. This was first suggested by R. Tylecote.[12] Contrary to the above-mentioned minerals, antimony minerals in the oxidation zone (such as senarmonite, valentinite, servantite, stibiconite etc.[13]) do not have bright colours, but are whitish-grey, grey, or grey to yellow in colour.

3. The presence of native arsenic in some deposits (in the Sevan-Amasian ore province, Amasia and Sotk). Native arsenic is relatively rare, but in spite of this it looks like metal, and the possibility that it was known and used in prehistoric times cannot be excluded.

An interesting geochemical feature of some of the analysed artefacts is their low Ag/Au ratios. All samples from Shengavit, except for FG-011837, are characterised by such low Ag/Au ratios (with Ag/Au less than or close to 1) as well as a spiral ring from Mokhrablur, (FG-010088), a pin from Bazum (FG-011847), one dagger from Dimac (FG-011875), a spearhead from Gyumri (FG-011838), an axe head from Jrashen (FG-011848) and seven artefacts from Berqaber (FG-011848, FG-011857, FG-011891, FG-011892, FG-011871, FG-011852, FG-011874). It is important to note that for all other artefacts from Berqaber the Ag/Au ratio is not very high (Ag/Au ratio within 1.4–4.1). All other analysed artefacts exhibit relatively high Ag/Au ratios (1.4–29). In Armenian copper ores the Ag/Au ratio usually varies from 2 to 30, except for some gold-rich ore bodies at Hanka-

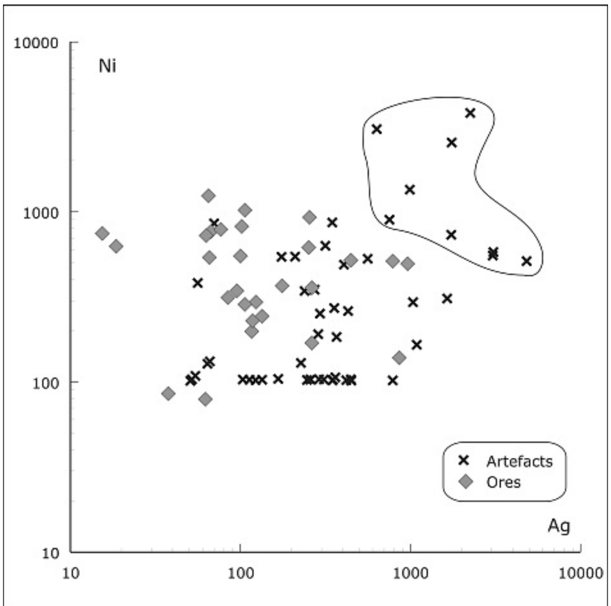

Fig. 3. Plot of Ag versus Ni for Armenian copper ores and copper-based artefacts. Some artefacts from Talin, Shirak and Harich exhibit high concentrations of nickel and silver. Concentrations were recalculated to a total of 100% including copper. The group of artefacts with relatively high concentrations of Ni and Ag is outlined.

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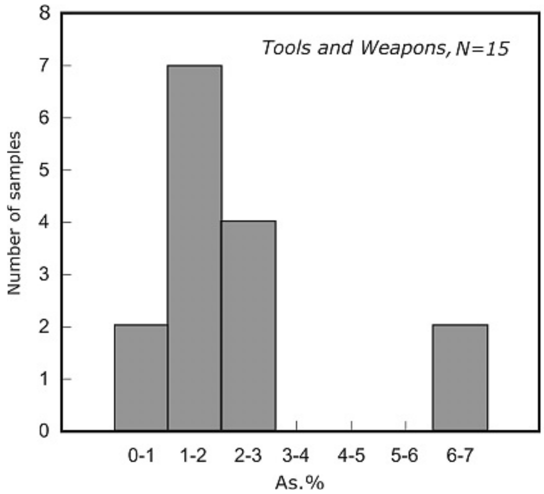
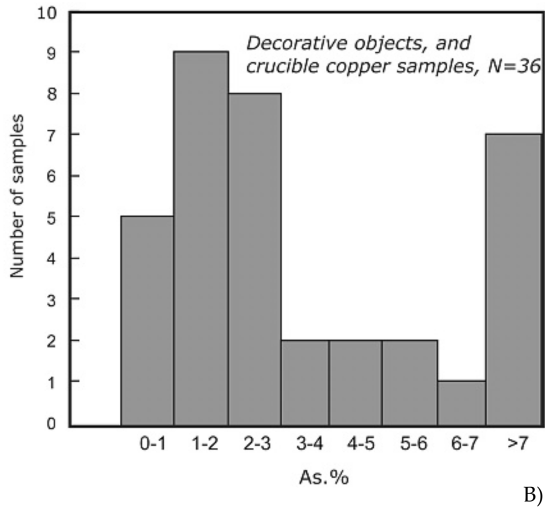
[11] Редкие и благородные элементы 1972.

[12] Tylecote 1976.

[13] Минералы рудных формаций Армянской ССР 1986.



A)



B)

Fig. 4. Statistical distribution of arsenic concentrations in EBA artefacts. A – Tools and weapons (15 samples), B- Decorative objects and crucible copper samples from crucibles (36 samples).

van, Fioletovo, Hankadzor, Alaverdi and Shamlug with Ag/Au less or close to one.[14]

Artefacts with concentrations above 500 ppm Ni and above 140 ppm Co can be clustered into a high Ni and Co group (*Tab. 2*). Relatively high nickel and cobalt concentrations were determined in two artefacts from Talin (FG-010085, FG-010086), three axes from Gyumri (FG-010081, FG-010082, FG-010081), a dagger from Dimac (FG-011836) and three samples from Harich (FG-020481, FG-020482, FG-020483). The limiting values of 500 ppm Ni and 140 ppm Co were selected as an indicator of relatively high or low Ni and Co contents, because the concentrations in other analysed artefacts are much lower: Also, Armenian copper ores are generally relatively poor in nickel and cobalt. Accordingly, they do not contain Ni and Co minerals, except for some polymetallic deposits related to small granite bodies and hosted within the regional ophiolitic belt (such as the Sotk gold – polymetallic deposit).[15] It is important to note that the concentration of nickel in artefacts may also depend upon the smelting temperature,[16] and that copper that is rich or poor in nickel could have been smelted from the same ore. It is noteworthy that artefacts rich in nickel from Talin and three axes from Gyumri also exhibit high silver contents *(Fig. 3)*. Artefacts with similar characteristics are known from the Nahal Mishmar hoard,[17]Arslantepe[18] and other regions. Except for artefacts rich in Ni and Ag from Talin, the axes from Gyumri and two artefacts from Harich, generally a good match of Ni and Ag concentrations in ores and artefacts can be observed in all other artefacts *(Fig. 3)*. Two samples from Shengavit (one artefact and one copper sample from a crucible) are also characterised by high Ni contents. But due to the oxidised state of these samples and their high iron contents, it is possible that high Ni content cannot be definitely assumed to be a geochemical signature of these samples.

High Se concentrations of more than 100 ppm were observed only in artefacts FG-011838 (Gyumri), FG-011888, FG-011849 (Shengavit), FG-011891, FG-011892, FG-011843, FG-011852, FG-011873 (Berqaber) and FG-020482, FG-020484 (Harich). Concentrations of selenium in Armenian ores are quite variable, and it is unlikely that this element can be helpful for defining the provenance of copper artefacts in this case.

It is also noteworthy, that relatively high concentrations of zinc (2000 ppm) were detected only in the chance finds from Jrashen (near the Yerevan hoard).

One of the analysed artefacts, a spiral ring from Harich, sample FG-020479, turned out to consist of a Cu–As–Pb alloy. Lead is often associated with copper ores and is a frequent trace element in copper-based artefacts. But this artefact contains 4.3% lead, so that it may have been added intentionally. Alloying with lead is rare in the Early Bronze Age, but it is known in some artefacts in the Aegean and other regions of Mediterranean.[19] However, Aegean copper-lead alloys do not exhibit high contents of arsenic, whereas the spiral ring from Harich contains 13% arsenic and, thus, is a very unusual and interesting type of copper alloy.

14 Редкие и благородные элементы 1972.
15 Meliksetian et al. 2003.
16 Budd et al. 1992; Pernicka 1999.
17 Tadmor et al. 1995.
18 Hauptmann et. al. 2002.
19 Pernicka et. al. 1990.

Alloying with tin is only observed in a spiral ring from Talin, FG-010086, (11% tin) and in a small ingot from Agarak (3%), sample FG-020486. Notable concentrations of tin (0.6%, 0.71% and 1.35%) are also observed in an axe from Gyumri and two spearheads from Talin, samples FG-010081, FG-010084 and FG-010085 respectively. The situation with these artefacts is not clear, but it is more likely that they are also the result of alloying, because high concentrations of tin are not typical for Armenian copper and polymetallic ores and the southern Caucasia altogether. Maximal concentrations of 0.45% tin were reported in clean concentrates of tennantite–tetrahedrite (*fahlerz*) ores from the small Mecdsor deposit. In the Mecdsor deposit tin is usually present as isomorphic impurity in ore minerals, except for rare grains of microscopically visible cassiterite or stannite.[20] Obviously, Mecdsor could not be identified as a source of tin during the Bronze Age.

Isotope abundance ratios of the analysed artefacts and ores

With the introduction of lead isotope analysis (LIA), Pb isotope geochemistry became an important method to relate copper artefacts to their parent ore sources.[21] The main advantage of using LIA is that the lead isotope composition, being an important geochemical characteristic of ore deposit, remains unchanged during metallurgical processes. Pb isotope abundance ratios of the analysed artefacts and ores are given in *Tables 5 and 6* respectively.

Before we begin to compare the lead isotope composition of artefacts and ores, we consider it necessary to discuss here in brief some geological settings of the Armenian copper ores and the geological interpretation of the lead isotope data.

The territory of Armenia is formed by a complex mosaic of different geological blocks combined by Alpine geodynamics. Tectonic structure and magmatic activity are related to the collision of the Afro-Arabian and Eurasian plates. Special geological mineralogical, metallogenic and geochemical research in Armenia as summarized in "Geology of the Armenian SSR"[22] and in other sources[23] has outlined three metallogenic provinces: Pambak-Zangezour, Alaverdi-Kapan and Sevan-Amasian. Major copper deposits are related to the first two provinces *(Fig. 1* and *Tab. 3)*.

The Alaverdi-Kapan ore province is related to the Mesozoic Lesser Caucasus palaeo-island arc, and is associated with intensive island-arc type magmatic activity. The largest deposits in this province are of the volcanogenic massive sulphide type. The copper and polymetallic deposits of the Alavedri-Kapan zone can be divided into two groups by their geological formation ages: Late Jurassic-Early Cretaceous (Alaverdi, Kapan, Shamlug, Akhtala and others) and Middle-Late Eocene (Aghvi, Spasakar, Hankadsor, Sisamadan and others).

The Pambak-Zangezour metallogenic province is related to the south Armenian block (a northern fragment of the Iranian block), involved in Alpine tectonic and magmatic processes. The basement of this geological zone, outcropping in central Armenia (Tsakhkuniatc metamorphic complex) is of Gondwanaland type and is dated to the Late Proterozoic. Intensive Palaeogene and Oligocene-Miocene magmatism in the Pambak-Zangezour zone is related to the continental collision geodynamics. The majority of copper deposits in this zone are of the Cu and Cu–Mo porphyry type (Kadjaran, Agarak, Dastakert, Hankavan and others). The largest Cu and Cu-Mo porphyry deposits in south Armenia are dated to the Late Oligocene-Neogene. These deposits are genetically related to the young porphyry granite-granodiorite intrusive magmatism of the large polyphase Meghri pluton and are usually hosted in monzonites.

The third metallogenic province, Sevan-Amasian, is related to the regional ophiolitic belt, which represents remains of the ocean-type core of the Tethys palaeo-ocean formed with ocean-type basic and ultrabasic plutonic and volcanic rocks and specific associations of sediment rocks. This province is placed between the Pambak-Zangezour and Alaverdi-Kapan provinces and contains two separate segments along with outcrops of the regional ophiolitic belt. Some hydrothermal polymetallic and gold-bearing ores are related to this province (Amasia, Sotk). These deposits are associated with small Late Oligocene-Miocene granite bodies, synchronous to continental collision in the region. Some chromite ores associated with ophiolite ultrabasic rocks are also known. This province does not contain major copper ore deposits, but some arsenic ores. Some occurrences of nickel minerals in small polymetallic ores are noteworthy from an archaeometallurgical viewpoint.

It is obvious that such a complex geological structure in the small territory of Armenia with different blocks representing fragments of island arcs, continental plates and oceanic core will affect the lead isotope signature of regional ores.

The Pb isotope ratios of the analysed ores on the both 'uranogenic' and 'thorogenic' diagrams (see *Figs. 5 and 6* respectively) are generally related to

[20] Минералы рудных формаций Армянской ССР 1986.

[21] Gale / Stos-Gale 1982.

[22] Геология Армянской ССР 1967.

[23] Карапетян 1982; Минералы рудных формаций Армянской ССР 1986.

Sample	Site	Composition	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$
FG-010084	Talin	Cu, As,Sn	2,08738	0,84750	38,4923	15,6284	18,4405
FG-010085		Cu, As (Sn)	2,08648	0,84516	38,6292	15,6474	18,5131
FG-010086		Cu, Sn (Ni)	2,10720	0,86213	38,3201	15,6787	18,1854
FG-020479	Harich	Cu, As,Pb	2,07173	0,83482	38,7216	15,6035	18,6908
FG-020480		Cu, As	2,08726	0,84853	38,4196	15,6191	18,4069
FG-020481		Cu (As, Ni)	2,08701	0,84540	38,6477	15,6545	18,5184
FG-020482		Cu, As	2,05619	0,82551	39,0105	15,6616	18,9718
FG-020484		Cu, As	2,07488	0,83427	39,0087	15,6846	18,8004
FG-010088	Mokhrablur	Cu, As	2,08463	0,84554	38,5275	15,6267	18,4814
FG-010089	Chkalovka	Cu	2,05608	0,82725	38,9461	15,6698	18,9418
FG-020485	Agarak	Cu, As	2,08478	0,84570	38,5642	15,6438	18,4988
FG-020486		Cu, As	2,06989	0,83638	38,8302	15,6895	18,7595
FG-020487		Cu, Sn	2,08327	0,84451	38,6230	15,6591	18,5396
FG-011848	Jrashen	Cu, As	2,09236	0,85390	38,2521	15,6102	18,2816
FG-011876		Cu, As	2,07962	0,84057	38,6711	15,6295	18,5940
FG-011846	Bazum	Cu	2,09043	0,84836	38,5290	15,6367	18,4307
FG-011847		Cu, As	2,05941	0,83340	38,7471	15,6779	18,8131
FG-011836	Dimac	Cu	2,07966	0,84010	38,6618	15,6175	18,5895
FG-011875		Cu, As	2,07807	0,84275	38,5542	15,6334	18,5521
FG-010081	Gyumri	Cu (Sn, Ni)	2,11813	0,87190	37,8514	15,5811	17,8702
FG-010082		Cu, As	2,09819	0,85717	38,2290	15,6173	18,2202
FG-010083		Cu, As	2,11051	0,86646	38,0563	15,6241	18,0324
FG-011838		Cu, As	2,05578	0,82725	38,9570	15,6764	18,9494
FG-011834	Shengavit	Cu, As	2,07947	0,84585	38,3553	15,6011	18,4437
FG-011835		Cu, As	2,07365	0,83790	38,6818	15,6306	18,6543
FG-011837		Cu, As	2,07818	0,84130	38,6284	15,6374	18,5868
FG-011849		Cu, As	2,07667	0,83966	38,6717	15,6365	18,6223
FG-011887		Cu, As	2,08030	0,84480	38,4931	15,6318	18,5036
FG-011888		Cu, As	2,07788	0,84299	38,6131	15,6677	18,5837
FG-011889		Cu, As	2,07714	0,84238	38,8384	15,7506	18,6976
FG-011889		Cu, As	2,08112	0,84375	38,5908	15,6456	18,5433
FG-020498		Cu	2,08509	0,84603	38,5286	15,6322	18,4782
FG-011840	Berqaber (Choghas)	Cu, As	2,07451	0,83764	38,7344	15,6393	18,6710
FG-011841		Cu, As	2,08204	0,84218	38,6539	15,6347	18,5646
FG-011842		Cu, As	2,08551	0,84554	38,5675	15,6362	18,4919
FG-011853		Cu	2,08536	0,84558	38,5627	15,6363	18,4924
FG-011854		Cu, As	2,09228	0,85013	38,5028	15,6447	18,4027
FG-011855		Cu, As	2,09199	0,84975	38,5551	15,6715	18,4302
FG-011857		Cu	2,10127	0,86095	38,2221	15,6607	18,1900
FG-011871		Cu, As	2,08223	0,84171	38,6651	15,6299	18,5688
FG-011873		Cu, As	2,08570	0,84566	38,5529	15,6319	18,4846
FG-011874		Cu, As	2,08880	0,84699	38,6839	15,6861	18,5196
FG-011891		Cu (As)	2,09245	0,84977	38,3951	15,5930	18,3495
FG-011843		Cu, As	2,08383	0,84374	38,6514	15,6497	18,5466
FG-011844		Cu, As	2,08499	0,84505	38,5784	15,6359	18,5030
FG-011850		Cu, As	2,07707	0,84163	38,7052	15,6838	18,6351
FG-011852		Cu, As	2,08605	0,84578	38,6064	15,6528	18,5069
FG-011872		Cu, As	2,08637	0,84610	38,6427	15,6713	18,5214
FG-011892		Cu, As	2,08106	0,84114	38,6342	15,6147	18,5632
FG-011893		Cu, As	2,08097	0,84138	38,7286	15,6585	18,6098

Tab. 5. Lead isotope abundance ratios of analysed artefacts measured with MC-ICP-MS.

Sample	Deposit	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$
FG-010091	Agarak	2,09654	0,85272	38,3421	15,5951	18,2883
FG-020518		2,08845	0,85020	38,3921	15,6338	18,3831
FG-010094	Lichk	2,07482	0,83858	38,6202	15,6106	18,6160
FG-010095	Kadjaran	2,07182	0,83652	38,6561	15,6062	18,6574
FG-020523		2,04992	0,82141	38,8923	15,5841	18,9726
FG-020516		2,07958	0,83898	38,6562	15,5951	18,5881
FG-020517		2,05457	0,82337	38,9410	15,6031	18,9511
FG-020519	Tey	2,07801	0,83763	38,6677	15,5870	18,6080
FG-010096		2,07716	0,83705	38,7136	15,6002	18,6372
FG-020706	Dastakert	2,10014	0,86103	38,0189	15,5867	18,1022
FG-020525	Hankavan	2,07714	0,83716	38,6964	15,5958	18,6283
FG-010100	Hankadsor	2,07427	0,83789	38,7822	15,6657	18,6971
FG-010101		2,09380	0,85230	38,4042	15,6332	18,3415
FG-020525		2,05654	0,82729	38,8037	15,6104	18,8624
FG-020521		2,10920	0,86960	37,8489	15,6048	17,9486
FG-010105	Frolova Balka	2,08063	0,84276	38,5509	15,6153	18,5291
FG-020522		2,07763	0,83940	38,6113	15,6007	18,5848
FG-010097	Fioletovo	2,07715	0,84038	38,5790	15,6080	18,5718
FG-020514		2,06022	0,82761	38,8352	15,5997	18,8511
FG-020515		2,08156	0,84005	38,6909	15,6135	18,5866
FG-020704		2,05632	0,82483	38,8638	15,5884	18,8992
FG-020524	Sotk	2,07429	0,83664	38,6335	15,5820	18,6243
FG-010110	Aghvi	2,08144	0,84326	38,5648	15,6236	18,5275
FG-010109		2,08124	0,84323	38,5540	15,6207	18,5247
FG-020707		2,09135	0,84751	38,5663	15,6280	18,4397
FG-020708		2,06917	0,83395	38,8930	15,6768	18,7970
FG-010108	Alaverdi	2,07744	0,84432	38,7240	15,7385	18,6414
FG-010106		2,08247	0,84414	38,5843	15,6407	18,5276
FG-020512		2,09700	0,85869	38,1571	15,6230	18,1929
FG-020709		2,05487	0,82354	38,8888	15,5865	18,9262
FG-020513	Shamlug	2,08200	0,84339	38,5705	15,6243	18,5256
FG-020526		2,07889	0,84306	38,4680	15,6006	18,5047
FG-010114		2,08017	0,84310	38,5452	15,6229	18,5325
FG-010098	Akhtala	2,07230	0,83704	38,6327	15,6048	18,6413
FG-010099		2,07166	0,83661	38,6206	15,5966	18,6425
FG-010102	Kapan	2,07263	0,83742	38,6118	15,6005	18,6289
FG-010103		2,05068	0,82145	39,0090	15,6260	19,0226
FG-010104		2,04803	0,81935	39,0399	15,6183	19,0605
FG-020520	Sisamadan	2,08146	0,84002	38,6836	15,6114	18,5846
FG-020705		2,09601	0,85355	38,3673	15,6244	18,3060
FG-010112	Spasakar	2,07811	0,83769	38,6922	15,5958	18,6177

Tab. 6. Lead isotope abundance ratios of analysed ores measured with MC-ICP-MS.

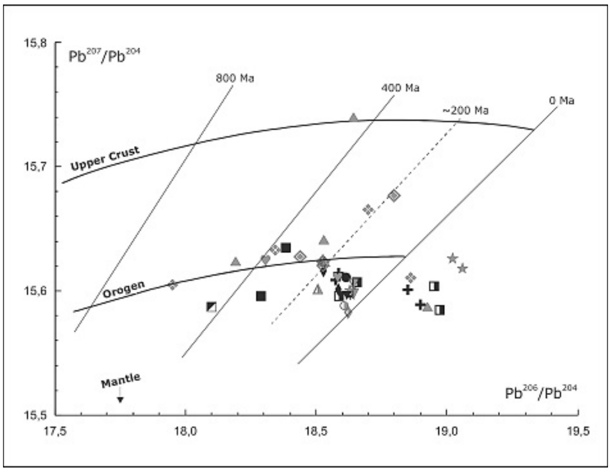


Fig. 5. Diagram of $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ in the analysed ores. Evolutional growth curves and age estimation lines are taken from (Doe / Zartman, 1979). The dotted line represents an approximate age of 200 Ma. Symbols are as in Figure 6.

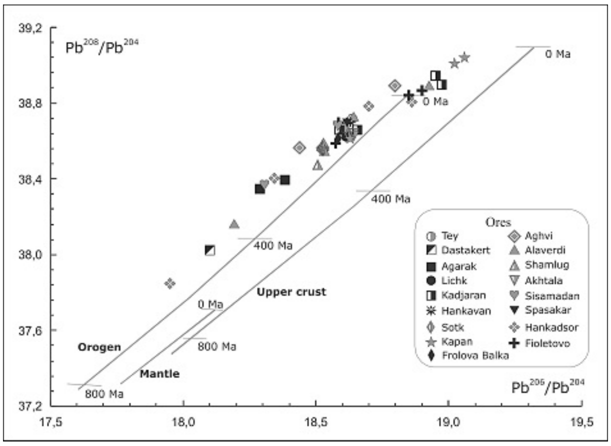


Fig. 6. Diagram of $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ in analysed ores. Evolutional growth curves and age estimation lines are taken from (Doe / Zartman, 1979).

the lead isotope evolution "orogen" curve as defined by Doe and Zartman.[24] Such an isotope composition is usually interpreted as a mixture of lead from mantle and upper crust sources during "orogeny" (subduction and collision geodynamics). Only one sample from Alaverdi is clearly located on the upper crust evolution curve *(Fig. 5)*. Data points of the analysed ores are located on the both sides of the "orogen" curve *(Fig. 5)*, evidently indicating the predominance of lead derived from the mantle or upper crustal sources.

Some samples from Kadjaran, Kapan, Hankadsor and Alaverdi and Fioletovo exhibit negative single-stage growth model ages in both "uranogenic" *(Fig. 5)* and "thorogenic" *(Fig. 6)* diagrams. It is suggested that lead in these samples can be interpreted as representing a radiogenic isotope composition. Such a composition can arise due to the presence of Th and U in the ores or in ore-bearing rocks of substrata. Radioactive decay of ^{238}U, ^{235}U and ^{232}Th produce ^{206}Pb, ^{207}Pb and ^{208}Pb lead isotopes respectively. Furthermore, an excessive admixture of these isotopes affects the lead isotope signature of ores, making the lead anomalously "younger".

Although the oldest copper deposits in Armenia are of Late Jurassic–Early Cretaceous age (~154–122 Ma), some samples from Late Jurassic–Early Cretaceous Alaverdi and Shamlug, Middle-Late Eocene Hankadsor, Aghvi, Sisamadan and even Late Oligocene-Neogene Agarak and Dastakert deposits show ages older than ~200 Ma *(Figs. 5; 6)*. And for three samples from Alaverdi, Hankadsor and Agarak the age estimate based upon the Pb isotope ratios is even older than ~400 Ma. It is suggested that ore-bearing solutions of some mineralization stages of the above-mentioned deposits re-mobilized the lead from the geologically older rocks and that the lead isotope fingerprints of these ores inherit the specific lead isotope signature of substrata.

Thus, the lead isotope abundance ratios of the analysed Armenian ores show wide variations. Armenian ores can be divided into three groups based on their Pb isotopy: "radiogenic" lead, "old" lead and "ordinary" lead group. The "ordinary" lead group represents a lead isotope composition between 0 Ma and ~200 Ma, while "radiogenic" lead – younger than 0 Ma and the "old" group unite the samples, showing Pb isotope composition older than ~200 Ma *(Figs. 5; 6)*. Such a division of ores, based upon their Pb isotopy, is relative and does not characterise ore deposits or metallogenic provinces, because samples from the investigated ore deposits can be found in all these groups (for example Hankadsor). It is suggested that such a grouping of lead isotope data of the ores can be helpful for further interpretations and correlations between ores and artefacts.

As shown above, lead isotope inhomogeneity can be found not only within metallogenic zones and age groups, but even within a single ore deposit like Hankadsor, Alaverdi, Kadjaran and others. Of course, such a situation makes the interpretation of lead isotope data of artefacts and their comparison with ores quite complicated. But it is noteworthy that wide variations of Pb isotope ratios are typical also for the analysed artefacts. Furthermore, some obvious relation between isotope compositions of some ores and artefacts can be found *(Fig. 7)*.

The three groups of isotope abundance ratios outlined above are separated as compositional fields on the $^{208}Pb/^{206}Pb$ vs. $^{207}Pb/^{206}Pb$ *(Fig. 8)*. The "old" lead isotope compositional field of the Arme-

[24] Doe / Zartman 1979.

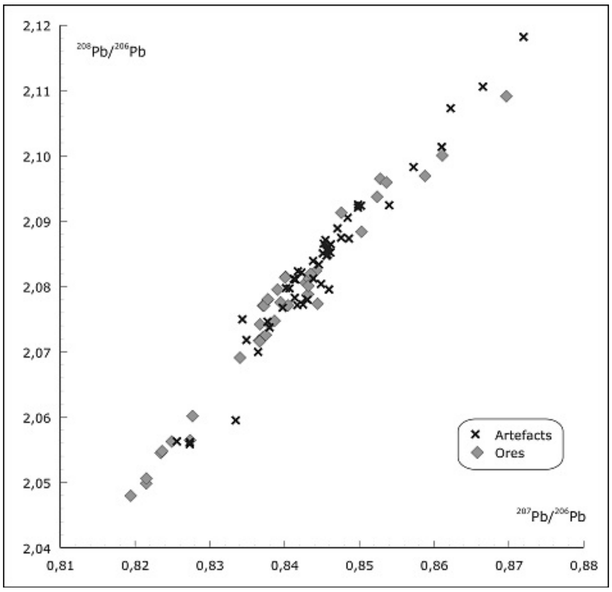


Fig. 7. Diagram of $^{207}Pb/^{206}Pb$ vs. $^{208}Pb/^{206}Pb$ showing a general correlation of the analyzed ores and EBA artefacts.

nian ores defines more precisely than the one outlined earlier.[25] This diagram also shows the isotope composition fields of ores from Turkey, Oman as well as Feinan in southern Jordan. These compositional fields are used for comparison and are taken from papers containing some summarized isotope data of the above-mentioned ores.[26] As is obvious

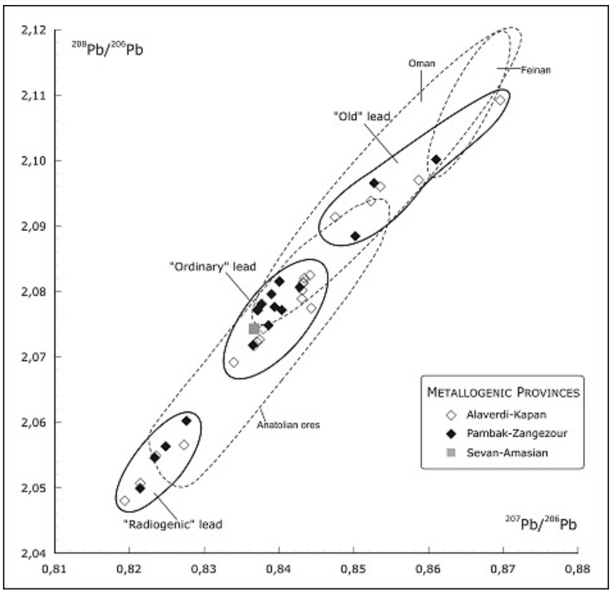


Fig. 8. Diagram of $^{207}Pb/^{206}Pb$ vs. $^{208}Pb/^{206}Pb$ in the analysed ores. The lead isotope fields of Armenian ores are grouped as follows: 1. "radiogenic" lead group, 2. "ordinary" lead group, 3. "old" lead group. The dotted lines outline the lead isotope compositional fields from ores of from Anatolia, Oman and the Feinan deposit, Jordan.

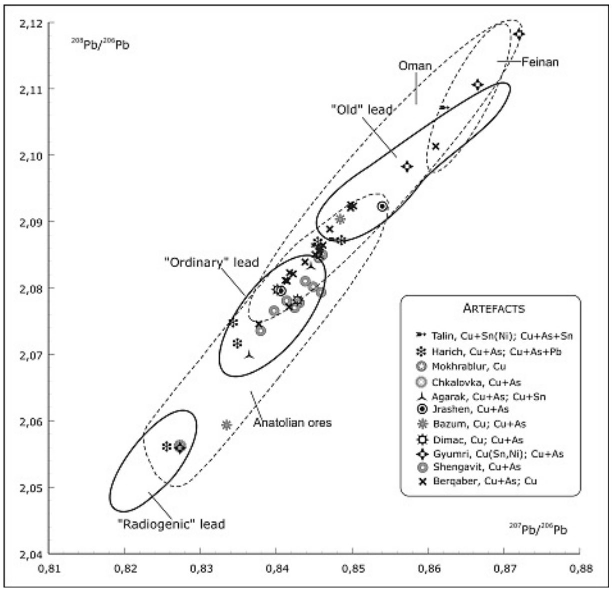


Fig. 9. Diagram of $^{207}Pb/^{206}Pb$ vs. $^{208}Pb/^{206}Pb$ in analysed artefacts together with isotope fields of Armenian ores: 1. "radiogenic" lead group, 2. "ordinary" lead group, 3. "old" lead group. The dotted lines outline the lead isotope fileds of ores from Anatolia, Oman and the Feinan deposit, Jordan.

from these diagrams, most of the Armenian ores are within the isotope compositional field of Anatolian ores. But Armenian ores show a wider variation of lead isotope compositions, as the "Anatolian" field does not cover the "radiogenic" and "old" lead fields completely. Sources in Jordan and Oman exhibit generally "higher" $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios than Armenian and Anatolian ones, although part of the data points of the ores from Armenian "ordinary" lead group match the lower part of the Oman ore field. Data points of the "old" lead group of Armenian ores fit into the lead isotope compositional field of Oman and Feinan ores.

Figure 9 shows the lead isotope abundance ratios $^{208}Pb/^{206}Pb$ vs. $^{207}Pb/^{206}Pb$ of the artefacts combined with the compositional fields of ores outlined on *Figure 8*. Separate symbols are used for artefacts from different sites. Pb isotope ratios of the majority of the analysed artefacts are within or close to the "ordinary" lead compositional field of the Armenian ores. Data points of some artefacts from Harich, Gyumri and Chkalovka are within or close to the "radiogenic" lead compositional field. Some artefacts from Berqaber, Bazum, Harich, Talin, Gyumri and Jrashen plot into the "old lead" compositional field.

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25 Meliksetian et al. 2003.

26 Pernicka et al. 1990; Schreiner et al. 2003.

The lead isotope abundance ratios of the artefacts and crucible copper from Shengavit, daggers from Dimac, a dagger and a pin from Agarak, an adze from Jrashen, a ring from Mokhrablur and eleven samples from Berqaber plot within a rather narrow range. Within or close to this range are isotope compositions of the next four artefacts from Berqaber, the bracelet from Basum, the pin and a dagger from Harich and the axe head from Jrashen. The lead isotope abundance ratios of the majority of the analysed samples from the Shamlug, Alaverdi, Aghvi, Frolova Balka, Fioletovo, Hankadsor, Sisamadam, Spasakar and Hankavan copper deposits (north Armenian ores) are close to the isotope composition of the above-mentioned artefacts. Geographically, north Armenian ores are not far (60–120 km) from the archaeological sites of the Ararat valley (Shengavit, Jrashen, Agarak, Mokhrablur). The Shirak plateau (Harich) is much closer, and the Dimac, Basum and Berqaber are located within the immediate area of north Armenian group of copper ores. Obviously Shamlug, Alaverdi, Aghvi, Frolova Balka, Fioletovo, Hankadsor, Sisamadam, Spasakar and Hankavan were possible sources of copper for these Bronze Age settlements. It is notable that the lead isotope abundance ratios of the artefacts from Berqaber show wide variations *(Fig. 9)*. Possibly, this is a result of the Pb isotope heterogeneity of the ores used, mixing of different ore sources or intensive metal recycling. Yet, it is noteworthy that the trace element composition of all artefacts from Berqaber is more or less homogeneous (*Tab. 2*). Most probably the first assumption is true, and the metal was produced from a chemically homogenous, but isotopically heterogeneous copper deposit. There are several copper deposits inhomogeneous in their Pb isotope composition and geographically close to Berqaber; Alaverdi, Hankadsor, Agvi and others can be supposed as possible sources of copper for this settlement, but more analytical data are needed to confirm this assumption.

A similar situation, namely roughly identical trace element compositions but diverse lead isotope ratios, is typical of some analysed chance finds. This holds true, for example, for the artefacts from Bazum as well as for finds from Jrashen (near the Yerevan hoard).

Four artefacts (a spearhead from Gyumri, a bracelet from Chkalovka, a pin from Bazum and an awl from Harich) are characterised by low ^{208}Pb/^{206}Pb and ^{207}Pb/^{206} Pb isotope abundance ratios. Similar ratios are typical of some ore samples from the Kapan, Kadjaran, Fioletovo, Hankadsor and Alaverdi deposits. Most probably, the lead isotope ratios of these ores are affected with admixture of radiogenic ^{206}Pb, as different samples from these same deposits show also much higher ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb values. The fact that the isotope abundance ratios of Hankadsor and Fioletovo deposits are closer to these artefacts indicates that these ores could represent the possible sources of metal for these artefacts located within "radiogenic" lead compositional field.

The isotope composition of the single object made of tin bronze (11% Sn) from Talin (FG-010086) shows rather high ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb isotope ratios and low ^{206}Pb/^{204}Pb. If one assumes that a Cu+Sn alloy with 11% of tin is a result of alloying, i.e. the mixing of metal from two separate sources of copper ore and tin ore, it is obvious that the lead isotope abundance ratios were also affected by mixing. It is usually assumed that in such a mixture of copper and tin the lead isotope ratios are largely determined by the copper and not the tin. The reason is that cassiterite, the most likely mineral used for the production of tin, usually contains very low concentrations of lead. On the other hand, a few ppm of lead are quite common in smelted copper. This together with the fact that tin comprises only between 5 and 15% in most ancient bronzes leads to the conclusion that the lead isotope ratios in bronze are an indicator of the provenance of the copper, rather than that of tin. If this holds true, then this bronze object must have been imported from another region. Using diagrams of the evolution of lead isotope compositions with isochrones[27] for the bronze ring from Talin with lead isotope abundance ratios ^{208}Pb/^{204}Pb (38,3201), ^{207}Pb/^{204}Pb (15,6787) and ^{206}Pb/^{204}Pb (18,1854), we can estimate that the model age of the lead in this artefact is more than 400 Ma. Therefore, we must look for geologically old host rocks with copper or tin ores or for ores with anomalous, "old" Pb isotope signatures. Similar lead isotope fingerprints for most of third millennium B.C. tin bronzes have been reported for Troy[28] and other sites in Aegean.[29] Recently, similar lead isotope ratios of early tin bronzes were reported from the Persian Gulf[30] and from Velikent, Dagestan.[31] It is noteworthy that the isotope ratios ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb of the two spearheads from Talin (FG-010084, FG-010085 respectively) with Sn concentrations of 0.71 and 1.35 respectively are somewhat higher than the majority of the analysed ores and artefacts, but lower than the ones of the tin bronze ring from Talin (FG-010086). It is possible that the Pb isotope ratios in this artefact were affected by the mixing of imported "precious" tin bronze with local copper. Another sample with high tin content, a

27 Doe / Zartman 1979.

28 Pernicka et al. 1990.

29 Begemann et al. 1992; Pernicka et al. 1990; Stos-Gale et al. 1984.

30 Weeks 1999.

31 Kohl / Weeks 2002.

small bronze ingot from the Agarak settlement (3% tin), shows an isotope composition within the "ordinary" lead compositional field. But because of its high tin content the provenance of this sample also remains unknown.

Three axes from Gyumri (chance finds in the Shirak area, FG-010081, FG-010082, FG-010083) are characterised by high $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ and low $^{206}Pb/^{204}Pb$ isotope ratios. The estimated age of the lead in these artefacts is between 400 and 800 Ma, which points to a Late Proterozoic–Early Palaeozoic ore source. Occurrences of copper of this age are unknown in Transcaucasia and, therefore, we conclude that the material for these axes was imported. Matching lead isotope signatures are found in copper ores of Oman as well as Feinan in Jordan. On the other hand, it is noteworthy that some Armenian ore samples (Agarak, Hankadsor, Alaverdi, Dastakert, Sisamadan, Aghvi) also exhibit relatively high $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ and low $^{206}Pb/^{204}Pb$ isotope ratios ("old lead" compositional field of Armenian ores). The Pb isotopy of these ores indicates a much older source of lead than the geological ages of the deposits. However, the distribution of ores with such a lead isotope signature is unknown, so that a possible relation of artefacts and ores within the "old" lead compositional field remains unidentified.

Conclusions

The chemical compositions of Armenian Early Bronze Age metal artefacts indicate, in general, that the metal is richer in arsenic relative to antimony in comparison with the analysed Armenian copper ores. We suppose that the copper with high arsenic concentrations could have been produced from mixed oxidised copper ores together with bright blue and green secondary arsenic minerals that can be confused with malachite and azurite. Alternatively, copper ores rich in enargite-tennantite and/or arsenopyrite-chalcopyrite from geologically young ore bodies of some Armenian copper deposits could have been used.

The lead isotope ratios in Armenian ores varies greatly, caused by the country's complex geological structure that is a combination of fragments and blocks of palaeo-island arc, continental plate and ocean core environments. According to their Pb isotopy, three groups of ores are defined: "radiogenic" "ordinary" and "old" lead groups. The "ordinary" lead group ranges within the Anatolian lead isotope field, generally matching the isotope composition of the ores of the Pontides. Parts of the "radiogenic" and "old" lead groups are outside the "Anatolian" field, signifying wider variations of Pb isotope composition in Armenian ores.

Lead isotope analyses of artefacts and ores suggest a significant probability that north Armenian copper ores and/or isotopically close ores of eastern Turkey could have been exploited for some of the analysed artefacts found in Early Bronze Age settlements in the Ararat valley, the Shirak plateau and northern Armenia. This conclusion is based upon isotope composition of artefacts matching the "ordinary" and "radiogenic" lead groups of Armenian ores as well as on their trace element composition, which generally fits with Armenian ores. These artefacts match the "ordinary", "radiogenic" and "Anatolian" compositional fields, and it can be assumed, in general, that they were produced from local copper ores.

On the contrary, some artefacts do not match Armenian and Anatolian ores isotopically and were most likely imported. The lead isotope characteristics of the tin bronze from Talin is comparable to most of the Early Bronze Age tin bronzes from the Aegean, the Levant, the Persian Gulf and Dagestan; the provenance of these tin-copper alloys remains unknown so far. Three axes from Gyumri also exhibit unusually high $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ and low $^{206}Pb/^{204}Pb$ isotope ratios, suggesting import of copper, possibly from sources further south with similar lead isotope fingerprints. Although the lead isotope characteristics of some of these artefacts are within or close to the "old" lead group of Armenian ores, these artefacts cannot be related to local ores, as it is not clear how widely distributed in Armenia ores with such a lead isotope signature actually are. Further, the trace element compositions of these artefacts are different from other Armenian artefacts and copper ores, especially regarding their high concentrations of nickel and silver.

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Summary

The geochemical and isotope characteristics of Armenian Early Bronze Age copper-based artefacts are discussed in this paper. Most of the analyzed artefacts belong to the Kura-Araxes culture (mid fourth millennium to the last quarter of the third millennium B.C.). The artefacts consist of arsenical and pure copper, but some copper-arsenic-tin, copper-arsenic-lead alloys and tin bronzes are also present.

A possible relationship of Early Bronze Age artefacts to Armenian and other copper ores in the south Caucasus region is also discussed. Lead isotope analyses of artefacts and ores suggest a significant probability that copper ores in northern Armenia may have supplied the metal of Early Bronze Age artefacts found in settlements in the Ararat valley, the Shirak plateau and northern Armenia. On the other hand, the geochemical and lead isotope fingerprints of the artefacts from Talin, Gyumri and some other areas obviously indicate that they originate from regions other than the southern Caucasus.

Among the analyzed Armenian Early Bronze Age artefacts some unusual Pb isotope compositions and high Ni and Ag concentrations were measured. Especially the rare early tin bronzes exhibit a Pb isotope pattern that is different from the most of the analyzed artefacts, but is similar to Early Bronze Age finds from other regions like Troy, the Aegean, the Persian Gulf region and Dagestan. These results obviously indicate an exchange of metal between the Caucasus, Anatolia and the Middle East.

Резюме

В статье приведен геохимический и изотопный анализ медесодержащих предметов материальной культуры раннего бронзового века Армении, большая часть которых относится к Куро-Аракской культуре (середина 4 – последняя четверть 3 тыс. до н. э.). В основном, эти предметы состоят либо из чистой меди, либо из меди с примесью мышьяка, однако, встречаются также и такие легирования как: медь – мышьяк – олово и медь - мышьяк – свинец, а также оловянистая бронза.
В статье локализуются месторождения меди, как на территории современной Армении, так и в других регионах Южного Кавказа, служивших источником сырья для предметов материальной культуры раннего бронзового века. Проведенный над ними изотопный анализ дал возможность установить, что металлические предметы с поселений Араратской долины, плато Шираки и северной Армении снабжались рудой с месторождений, расположенных на севере Армении, в то время как памятники находящиеся на территории современных талинского, гюмринского и некоторых других районов Армении снабжались рудой с месторождений вне границ Южного Кавказа.

При анализе предметов материальной культуры раннего бронзового века Армении были также выделены некоторые характерные особенности, такие как редкий состав изотопов свинца (Pb) и высокая концентрация изотопов никеля (Ni) и серебра (Ag). Изотопная структура свинца (Pb) у собенно редко встречающейся здесь оловянистой бронзы нетипична для Армении, известна, однако, с памятников, расположенных как на территории Дагестана, так и на побережье Эгейского моря, Трои и Персидского залива. Это свидетельствует о наличии торговых связей между Кавказом, Анатолией и Ближним Востоком.