Ancient metallurgy in the Caucasus during the Chalcolithic and Early Bronze Age: recent results from excavations in Western Azerbaijan

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Abstract

Recent excavations of kurgans at Soyuq Bulaq in the western part of Azerbaijan, made by an Azerbaijanian-French team, have re-opened the question of the beginnings of metallurgy in the Caucasus during the Late Chalcolithic. In two kurgans, one of which was particularly rich, several metal artefacts (beads, rings, dagger, awl) – of arsenical copper, gold and auriferous silver – have been discovered. A joint analytical program done in the laboratories of Bochum and Baku has shown the existence of sophisticated techniques of manufacture as well as the use of an uncommon alloy – auriferous silver. Although the origin of the ores is not yet known, the composition of the objects nevertheless suggests either the intentional use of specific ores or the elaboration of characteristic alloys. Finally, these discoveries and their studies stress the importance of metal in the chalcolithic cultures of the Caucasus, a material that could have played a great role in the intensification of exchanges with Mesopotamia during the Late Chalcolithic period.

Introduction

In 2006, several kurgans from a cemetery located in Azerbaijan on the left bank of the Kura River, at Soyuq Bulaq (Agstafa district, Figs. 15 & 16), were excavated by an Azerbaijanian-French team co-directed by T. Akhundov and B. Lyonnet with the financial support of the Ministère des Affaires Etrangères of France, CNRS and a private sponsor (for a detailed report on these excavations, see Lyonnet et al. in press). The mentioned kurgans date to the Late Chalcolithic period, in the first half of the 4th millennium. In two of them (kurgan n°1 and n°4), several metal artefacts have been found and show an already high technical level in metallurgy while this period is still considered as representing the beginnings of metallurgy in the southern part of the Caucasus (or Transcaucasia)

Development

Description of kurgans 1 and 4.

From the outside, kurgan n°1 (diameter: 15 m) consists of a central rectangular enclosure, made of large river pebbles, surrounded by a ring made of the same kind of pebbles. It only slightly emerges from the actual surface of an old terrace of the Kura River. The rectangular enclosure covered a pit dug into the terrace (depth: 1.5 m), which was surrounded by a wall made of six rows of mud-bricks in the lower part. Different parts of one skeleton were found at various levels of the tomb, suggesting that the corpse had been lying on an intermediate level resting on the bricks. Neither skeleton nor bones were found *in situ* in the lower part of the grave, only a dagger made of a copper alloy (Fig. 1) and a stone scepter with an equine head were situated along the south-eastern wall. Within the sieved soil of the intermediate level, 164 beads were discovered: 65 in white paste – probably fired steatite – (20 ring-shaped, 45 tubular), 25 in an unknown brownish stone, 17 in cornelian (6 ring-shaped, 11 biconical), 1 biconical in lapis-lazuli, 33 in silver (10 barrel-like, 12 ring-shaped, 3 tubular, 8 biconical ; Fig. 2), and 23 in gold (16 biconical, 6 flat rings, 1 crimp, Fig. 3). Little ceramic material was associated with the grave. According to Bertille Lyonnet's studies, some equals "mesopotamian" ware while some other corresponds to the local Sioni culture. All ceramics date to the Late Chalcolithic 2-3 period (3800-3600 BC). In addition to the main grave, an adjacent smaller one has been found under the

Fig. 1: Dagger coming from the kurgan 1.

Fig. 2: Silver beads found in the kurgan 1.

Fig. 3: Gold beads found in the kurgan 1.

Fig. 4: Silver rings found in the kurgan 4.

Fig. 5: Awl found in the kurgan 4.

external ring and consists of a small pit (1.20 m × 1 m) totally filled by very large river pebbles. It did not contain skeleton, but 89 flat ring beads made of shell and one of an unknown black stone.

Kurgan n°4 was already partially destroyed on the outside (no external ring and only one part of the enclosure was visible). The chamber (depth: 1.2 m), was also surrounded by a wall made of five rows of bricks in its lower part. No complete skeleton was found in this grave, only very few bones. The grave contained a small pot and potsherds of different vases, all typical of the Late Chalcolithic, as well as three rings made of a silver alloy (Fig. 4) and one awl of a copper alloy (Fig. 5).

Analyses of the metal artefacts coming from kurgans 1 and 4

The analytical program

A joint analytical program has been engaged both by Aziza Gasanova, head of the archaeometallurgical laboratory of the Institute of Archaeology and Ethnology in Bakou and by Antoine Courcier, working under the direction of A. Hauptmann in the laboratory of the Bergbau Museum in Bochum. Except for the gold beads that have been investigated only in Bakou and some other beads which were too small to be divided, the metal artefacts have been analyzed by XRF and EDS in Bakou and in Bochum. Ten silver beads have been studied in the two laboratories, using typologically similar examples in each lab.

The analytical protocol at the laboratory of Bochum

In Bochum, EDS analyses have been performed with a SEM Jeol JSM-6400 (20 KeV; 2000-5000 counts). The samples have been fixed in resin for examination. This preparation has later been polished in order to study the interior of the sample. Finally, it has been covered with a carbon layer in order to avoid the phenomenon of accumulation of electrons. Some metallographies have also been conducted: the samples have been polished again and the sections of the artefacts have been observed through an optical microscope (Zeiss Axiophot) with different magnifications (12.5×, 25×, 50×, 100×, 200× and 500×). At first, the samples have been studied without etching. Then, in order to distinguish clearly the structure, the polished metal surface was treated with selected chemical agents. For the copper artefacts the etching solution was kaliumdisulfate ($K_2S_2O_7$); for silver, it consisted of a combination of cyanide potassium (KCN) and ammonium persulfate ($(NH_4)_2S_2O_8$). The time of etching has been comprised between 30 seconds and one minute.

The analytical protocol at the laboratory of Bakou

The analyses have been performed on ten samples with a spectrometer ISP-28. The oxidation of the artefacts has entailed a particular preparation. The arc reduced the metallic melting. In order to finish the evaporation completly, the oxide samples have been previously mixed with 80 % of C and 20 % $Ba(NO_3)_2$. 10 mg of this preparation have been placed – with a solution of polivinibutiral – in a carbon electrode crater. The alternative current of the arc is characterized by 15 A and 127 Volt. The spectrograph, through a lens optical system and an intermediate diaphragm, detects the evaporation which goes on for two or three minutes. Photos of the spectrum for quantitative analysis have been carried out through a nine stage of reflection. A method of objective photometric interpolation by MF permits also to do quantitative analyses.

Some XRF analyses have also been used, in particular for the highest contents.

Results

Limits of the study

In general, the sections of the beads present a microstructure composed of concentric edges. As shown by the metallographic studies, the degree of oxidation is very important and characteristic for corroded objects coming from semi-arid environments (Rehren *et al.* 1996: 4). Intrusive elements (principally Br and Cl), coming from the soil, have contaminated the edges of the artefacts, and occasionally even the core. This is explained by probable electrochemical exchanges between the artefacts and the soil (Mr. L. Robbiola, Laboratoire de Métallurgie Structurale de l'Ecole Nationale Supérieure de Chimie de Paris, personal communication): the areas of Agstafa and Qazakh are distinguished by a geological stratum of the paleogen ocean (Tethys) and marginal seas, and bromide and chloride correspond to salts stemming from the evaporation of these waters (Hedges 1976: 5; Mr. Khachatur Meliksetian, PhD student in the Institute of Geological Sciences, Armenian National Academy of Sciences, personal communication). To this chlorite-bromide patina some intergrowth of carbonate sinter in the metal is added. Beyond the process of corrosion, a depletion of silver has been noticed: Ag has been removed from its original position to form the patina. In consequence, the decrease of this element has increased the amount of gold and copper. According to a previous study of Ag-Au-Cu (Rehren et al. 1996), we can assume that gold and copper do not move and that they are still present in a percentage close to their original concentration. Unfortunately, this means that our results must be considered with caution since it is not possible to give the exact original composition of our objects.

The silver beads

Our investigations in Bochum have distinguished three types of composition for these beads (Tab. 1, 2 & 3): silver with little traces of copper, silver-gold-copper alloys, and silver-gold alloys. The alloys can be either natural or anthropogenic.

The amounts (all the results in this paper are in wt.%) of Ag, Au and Cu are:

1 - silver-with little traces of copper -: 29.8-49.3 % Ag; 0.41-2 % Cu (Tab. 1).
2 - silver-gold-copper -: 9.6-59.2 % Ag; 0.5-29.7 % Au; 0.7-4 % Cu. In some cases, gold and copper are associated in small particles which can reach 45-60 % Au and 5-5.5 % Cu (Tab. 2)
3 - silver-gold: 21-52.7 % Ag; 9.5-27.9 % Au (Tab. 3).

These three types of alloys are not homogenous: the amount of elements fluctuate according to the regions analyzed. The oxidation principles are probably the main reasons for this heterogeneity. It can be considered that these compositions arise from insufficient metallurgical processes; an incomplete smelting of argentiferous ores or inadequate homogenous treatments could induce heterogeneities.

Tab. 1: Results of analyses of the silver beads which the compound is characterized by silver-with little traces of copper.

Lab.	Artef.	Composition (weight %)														
		O	Mg	Si	S	Cl	Ca	Cu	Ag	Br	Au	Sn	Pb	Zn	Sb	Fe
Bm	bead 1	13,70	0,28	3,28	0,67	6,57	13,52	n.d	40,22	21,58	n.d	n.d	n.d	n.d	n.d	n.d
Bm	bead 1	7,47	0,25	2,47	0,17	6,81	8,29	n.d	49,25	25,29	n.d	n.d	n.d	n.d	n.d	n.d
Bm	bead 1	11,08	0,33	1,32	0,39	5,71	18,25	n.d	39,38	23,53	n.d	n.d	n.d	n.d	n.d	n.d
Bm	bead 1	7,39	n.d	2,44	n.d	7,04	8,30	0,41	49,09	25,34	n.d	n.d	n.d	n.d	n.d	n.d
Bm	bead 3	17,30	n.d	1,02	0,76	4,23	33,23	2	29,81	11,65	n.d	n.d	n.d	n.d	n.d	n.d
Bm	bead 3	15,88	n.d	2,21	0,82	5,33	26,41	n.d	34,15	15,21	n.d	n.d	n.d	n.d	n.d	n.d
Bu	bead 3	n.d	n.d	n.d	n.d	n.d	n.d	1,57	35,14	n.d	0,034	0,02	0,2	0,2	0,02	0,05

Tab. 2: Results of analyses of the silver beads which the compound is characterized by an alloy silver-gold-copper.

Lab.	Artef.	Composition (weight %)								
		O	Si	S	Cl	Ca	Cu	Ag	Br	Au
Bm	bead 2	8,75	1,93	n.d	7,59	5,86	n.d	46,01	24,01	5,86
Bm	bead 2	5,63	1,99	n.d	7,81	1,99	n.d	51,41	25,79	5,38
Bm	bead 2	5,52	0,66	n.d	7,7	1,78	n.d	46,38	16,59	21,36
Bm	bead 2	2,17	2,55	n.d	2,05	0,27	5,5	19,17	8,26	60,04
Bm	bead 2	0,72	0,34	n.d	6,75	n.d	0,6	56,03	30,52	n.d
Bm	bead 2	0,18	0,31	n.d	6,54	n.d	0,04	57,23	30,76	n.d
Bm	bead 2	3,08	1,35	n.d	8,26	n.d	2,77	50,24	15,96	18,34
Bm	bead 2	18,91	1,78	n.d	1,27	33,77	5,31	9,56	0,74	28,66
Bm	bead 2	8,27	1,48	n.d	6,88	10,11	0,87	43,27	22,4	6,71
Bm	bead 2	10,91	1,89	n.d	8,6	n.d	2,74	46,4	14,75	14,71
Bu	bead 2	n.d	n.d	n.d		n.d	5,32	50,02	n.d	41,03
Bm	bead 6	15,54	1,67	0,89	5,86	24,07	n.d	34,51	15,08	2,37
Bm	bead 6	5,55	1,36	0,5	10,11	1,08	n.d	57,44	23,5	0,47
Bm	bead 6	20,19	0,74	0,98	2,98	31,49	1,58	22,61	4,13	15,31
Bm	bead 6	21,69	1,71	n.d	2,19	36,25	3,96	17,66	n.d	15,51
Bm	bead 6	2,73	1,87	0,35	8,65	0,16	n.d	58,06	28,17	n.d
Bm	bead 6	18,69	1,85	n.d	2,26	31,27	3,77	21,53	5,36	15,26
Bm	bead 6	16,33	1,41	n.d	3,35	30,48	2,7	29,51	8,95	10,88
Bm	bead 6	2,56	1,5	0,12	9,42	0,24	n.d	59,21	26,95	n.d
Bu	bead 6	n.d	n.d	n.d	n.d	n.d	1,58	34,72	n.d	6,95

Tab. 3: Results of analyses of the silver beads which the compound is characterized by an alloy silver-gold.

Lab.	Artef.	Composition (weight %)													
		O	Mg	Si	Cl	Ca	Cu	Ag	Br	Au	Sn	Pb	Zn	Sb	Fe
Bm	bead 4	4,23	n.d	1,6	7,26	4,45	n.d	48,24	20,21	14	n.d	n.d	n.d	n.d	n.d
Bm	bead 4	3,22	n.d	0,75	6,17	2,02	n.d	48	11,16	27,89	n.d	n.d	n.d	n.d	n.d
Bm	bead 4	4,63	n.d	1,33	7,72	4,55	n.d	52,67	16,99	11,68	n.d	n.d	n.d	n.d	n.d
Bm	bead 4	8,27	0,3	2,51	6,5	6,38	n.d	42,94	15,62	17,29	n.d	n.d	n.d	n.d	n.d
Bm	bead 4	4,2	n.d	0,75	6,91	4,08	n.d	45,37	15,45	9,51	n.d	n.d	n.d	n.d	n.d
Bm	bead 5	19,18	7,23	13,61	5,8	2,73	n.d	32,78	18,12	n.d	n.d	n.d	n.d	n.d	n.d
Bm	bead 5	20,83	8,32	16,18	5,59	1,78	n.d	30,94	16,35	n.d	n.d	n.d	n.d	n.d	n.d
Bm	bead 5	21,93	n.d	n.d	n.d	36,33	n.d	21	n.d	21,04	n.d	n.d	n.d	n.d	n.d
Bu	bead 5	n.d	n.d	n.d	n.d	n.d	0,72	30,45	n.d	8,12	0,02	0,05	0,2	0,2	0,15

Fig. 6: Section of the bead n°2 with SEM observations.

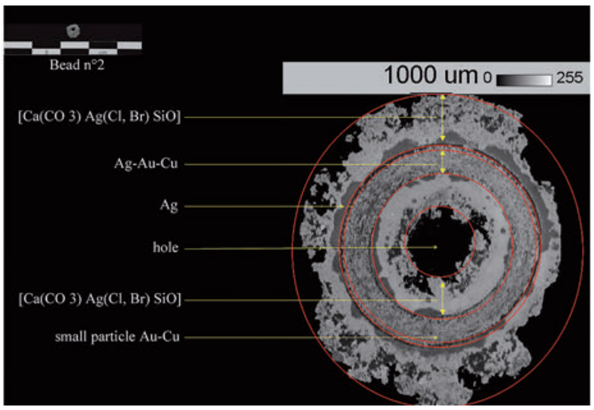
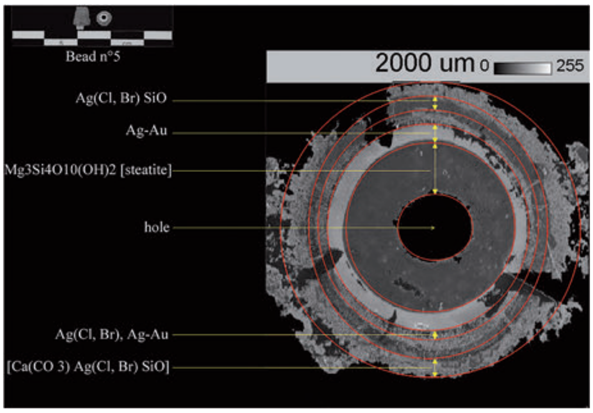


Fig. 7: Section of the bead n°5 with SEM observations.



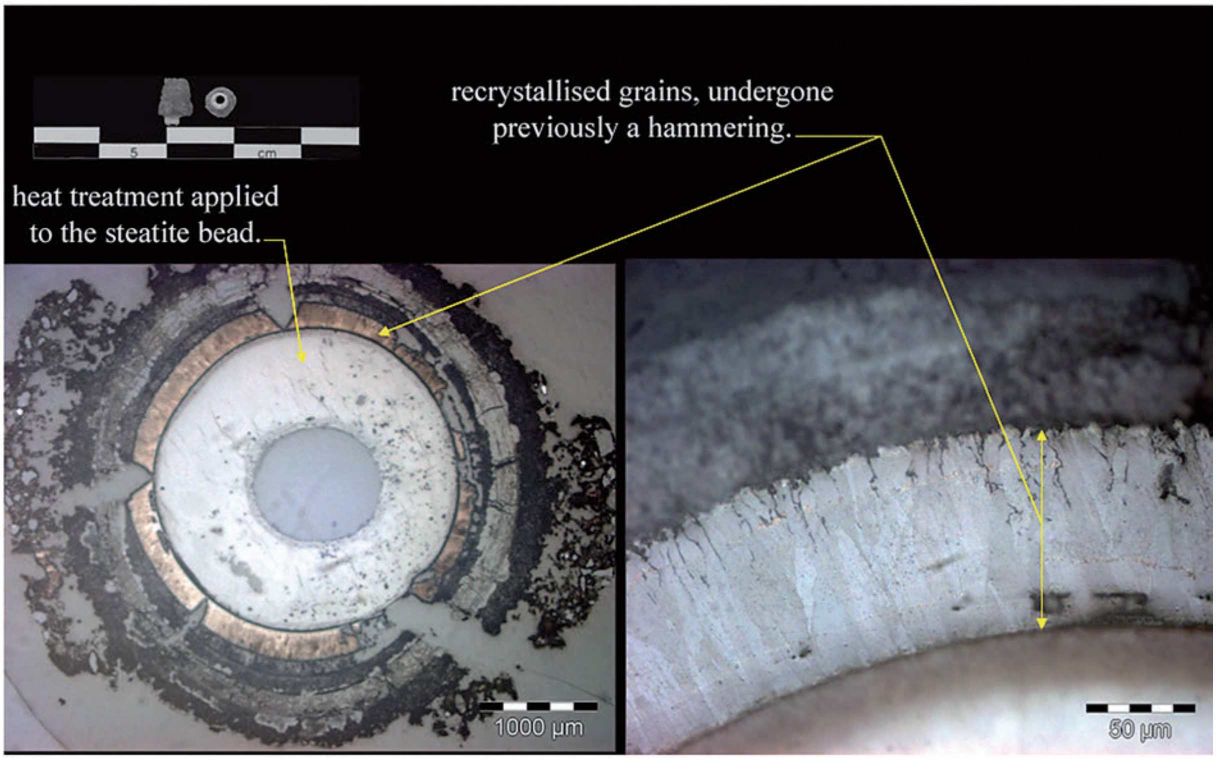


Fig. 8: Microstructure of the bead n°2, etched sample, magnifications 50× and 100 ×.

Lastly, natural dis-alloying could lead to an enrichment of the alloying elements on the surface. These three causes could be cumulative.

A mapping of one of these beads plainly illustrates this heterogeneity. Two fronts of corrosion – corresponding to two edges – have been observed: one around the hole and the other on the external edge (Figs. 6 & 7). These two zones are rich in calcite, silicate, bromide and chloride. These corrosion products are associated only with Ag. The middle ring consists of an association of Ag with small particles of Au-Cu, and the lacunas square corresponds to porosities. In the external part, some stripes of Ag could be identified. It seems that these are raised by the corrosion.

Up to now, it is difficult to distinguish the structures coming from the oxide process from those coming from the manufacturing techniques. All the sections of the beads consist of concentric circles (Figs. 6 & 7).

In four beads, the microstructure has been partly preserved (Figs. 8, 9, 10 & 11). It seems that several metal sheets were rolled successively around a core. Before applying a new sheet, the previous one was probably hammered. Indeed, a stage of cold hammering can be observed in a ring in the middle part of the section of the beads. The grains are equiaxed – parallel to the curve – deformed and stretched; generally, they are lenticular or acircular. If the thin white line is not a result of oxidation, it could indicate the external edge of the bead. According to EDS analysis, the white line consists of pure silver. So, we could assume that the final step of manufacture consisted in a coating with a sheet of pure silver. One of the beads, which includes a fired steatite bead, is different: the microstructure of the ring close to the stone shows the heat treatment applied to the steatite bead. So, we can suppose that, in a first stage, a metal sheet was rolled around an unfired steatite bead, and that, in a second one, the bead was heated. We ignore the other steps of the manufacture because the oxidation has definitively destroyed the structures. It is possible that the other sheet of metal was rolled by hammering and a final cladding.

The gold bead

One of the gold beads was investigated by XRF in Baku.

Analysis shows: 86.05 % Au, 1.9 % Ag, and 6.32 % Cu. According to the content of gold and the homogeneity, we can suppose that native gold was used.

The rings

Two rings, studied in Bochum, are made in a silver-gold-copper alloy (Tab. 4). The contents of the main elements are:

Ring 1: 51.6-88 % Ag; 4.2-9.5 % Au; 1.9- 2.7 % Cu.

Ring 2: 17.9-42.8 % Ag; 0.5-21.7 % Au; 0.6-5.2 % Cu.

For practical reasons, one of the rings (n°2) has been analyzed only on its surface; in the future, we would like to make a LIA analysis on this artefact. In order

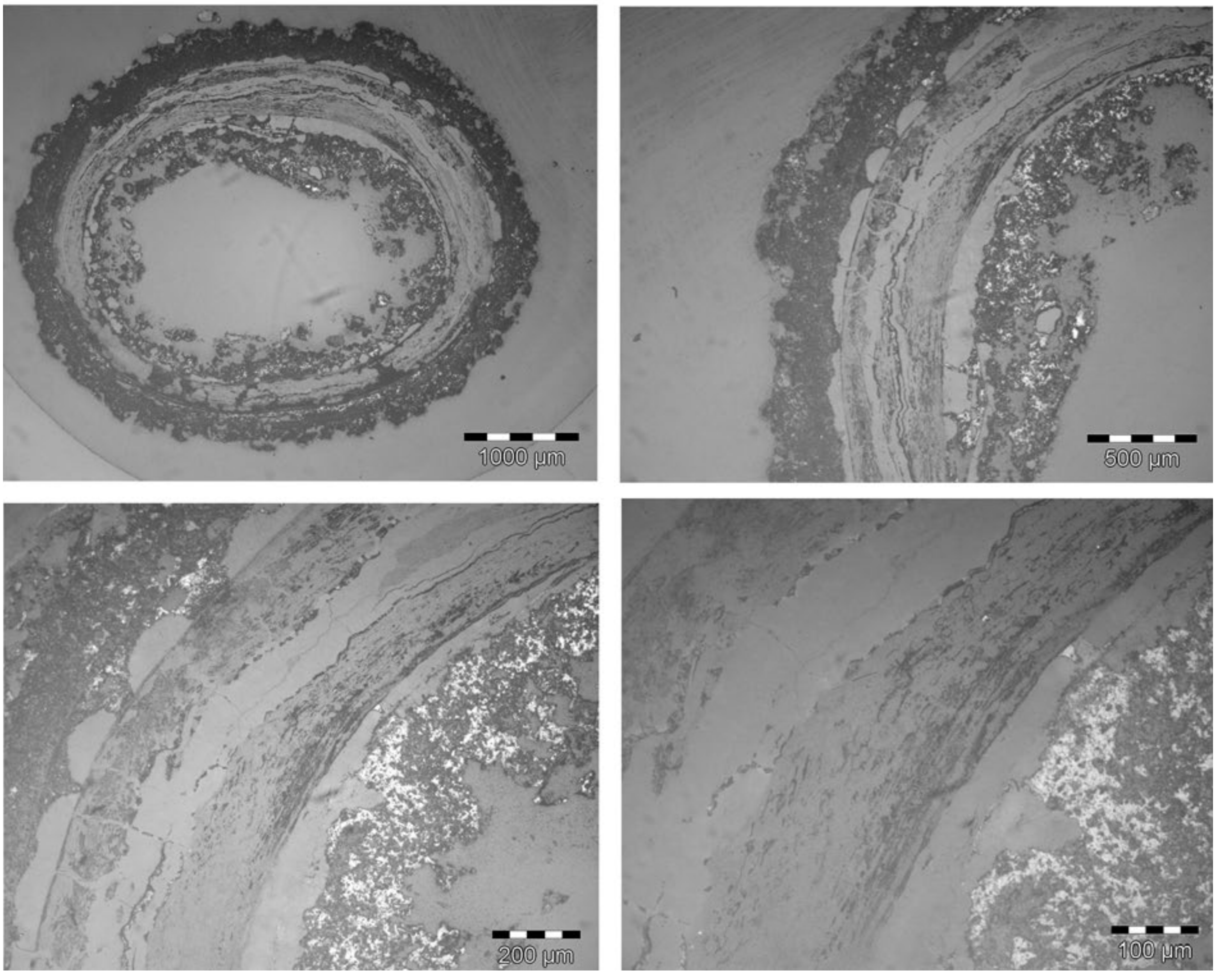
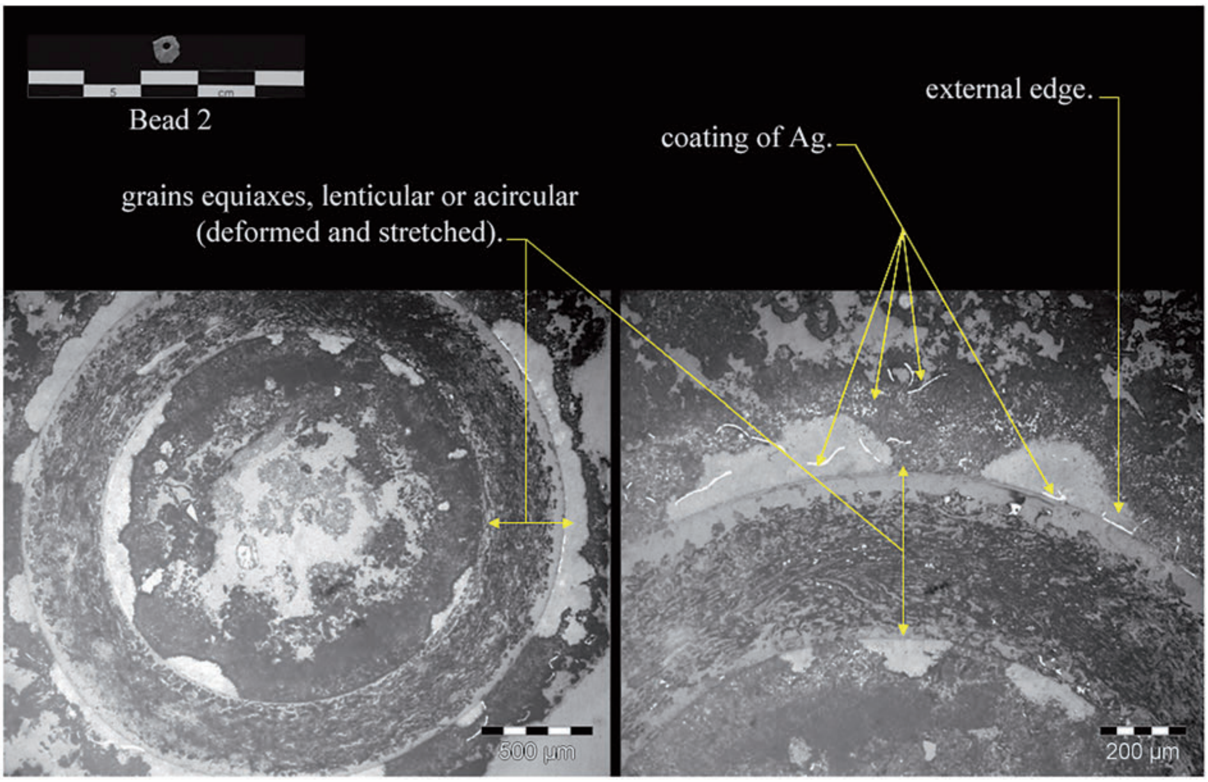


Fig. 9: Microstructure of the bead n°3, etched sample, magnifications 25×, 50× and 100x.

Fig. 10: Microstructure of the bead n°5, etched sample, magnifications 50× and 100×.



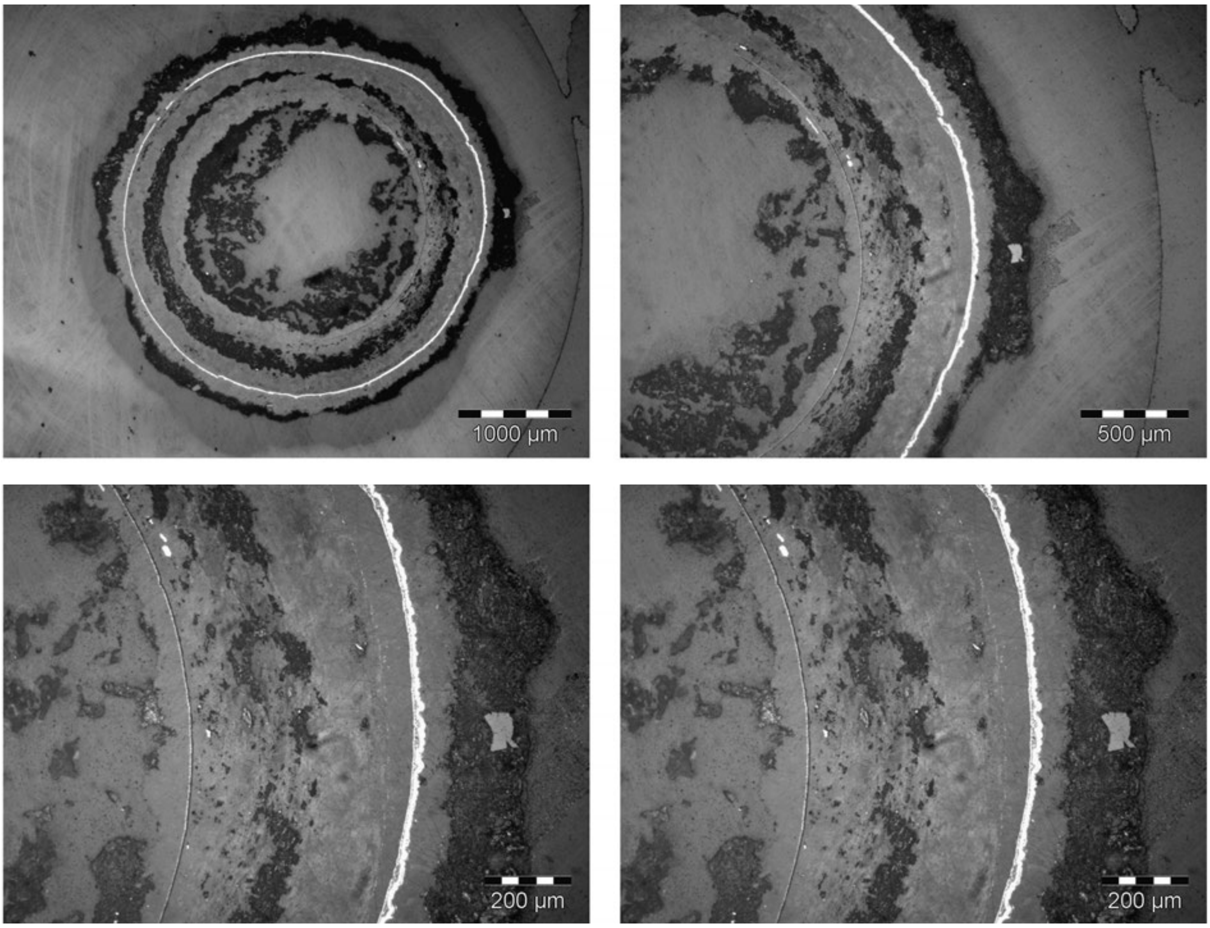


Fig 11: Microstructure of the bead n°6, etched sample, magnifications 25×, 50×, 100× and 200×.

to do so, we could not fix it with resin to analyze the heart of the ring. Because the protocols are different, it is difficult to compare the results of the two rings. It seems that their degree of oxidation is less important than it is on the beads (Fig. 12). Therefore, the amounts of elements measured by EDS rather equate to the original material of the rings than to the original material of the beads.

The metallographic studies of one of the rings (n°1) prove that a heat treatment has been applied after cold working; indeed, annealing twins could be observed in many grains (Fig. 13). The homogenization of this alloy (Ag-Au-Cu) would have required prolonged heating at a temperature high enough to overcome the miscibility, i.e. 650 °C., over a period of time long enough to allow a sufficient diffusion (Rehren et al. 1996: 5). It is difficult to estimate the nature of the cold treatment and the manufacturing process before the final annealing. We can suppose either the hammering of the edge of a cast blank with rectangular section, or the hammering of the two shorter sides of a rod until a circular section was obtained (Lechtman 1996: 40; Thornton et al. 2004: 49-50).

Tab. 4: Results of analyses of the silver rings.

lab.	Artef.	Composition (weight %)																
		O	**Al**	**Si**	**Cl**	**Ca**	**Cu**	**As**	**Ag**	**Br**	**Au**	**Sn**	**Pb**	**Zn**	**Sb**	**Ni**	**Co**	**Fe**
Bm	ring 1	1,85	1,13	2,61	0,99	2,04	2,66	n.d	83,19	n.d	5,54	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Bm	ring 1	n.d	0,9	3,52	0,57	n.d	2,69	n.d	87,85	n.d	4,49	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Bm	ring 1	10,14	n.d	2,84	3,87	13,71	2,06	0,13	51,86	10,62	4,77	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Bm	ring 1	0,87	n.d	3,38	0,7	0,18	2,53	n.d	87,96	0,23	4,15	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Bu	ring 1	n.d	n.d	n.d	n.d	n.d	1,9	0,03	51,57	n.d	9,5	0,02	0,03	0,05	0,2	0,01	0,02	0,12
Bm	ring 2	10,08	n.d	1,12	7,17	8,66	n.d	n.d	42,79	26,42	3,77	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Bm	ring 2	2,79	n.d	0,6	9,14	1,53	0,58	n.d	56,23	28,6	0,54	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Bm	ring 2	19,08	n.d	2,11	3,32	20,87	5,15	n.d	17,35	9,36	21,74	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Bu	ring 2	n.d	n.d	n.d	n.d	n.d	1,5	0,03	51,85	9,7	n.d	0,02	0,05	0,02	0,05	0,005	0,02	0,12

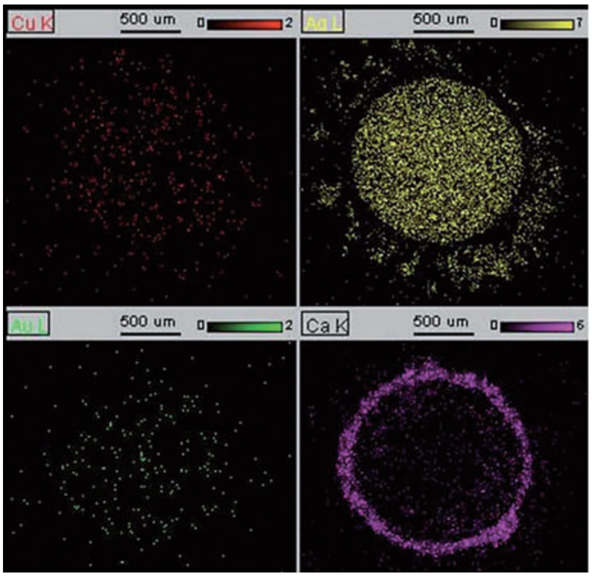


Fig. 12: Mapping of the ring n°1.

The awl

The awl is made of copper with an averaged low percentage of arsenic (0.8-6.8 % As, Tab. 5). Nickel has also been detected (0.8-6.4 % Ni). The metallographic studies after etching reveal small equiaxed, hexagonal and rhomboidal grains (Fig. 14). This isotropic structure is difficult to interpret. It is probably due to a homogenization process at high temperature leading to recrystallization. This process aims at coming back to stable conditions (new microstructure) after a cold working.

The dagger

The dagger is probably in arsenical copper (Tab. 6). Unfortunately, the sample analyzed in Bochum was limited to the corroded surface and was wrapped in a container that ruined part of it. EDS analyses made in Baku detected arsenic (1-2 % As). We were unable to perform a metallographic study of this artefact.

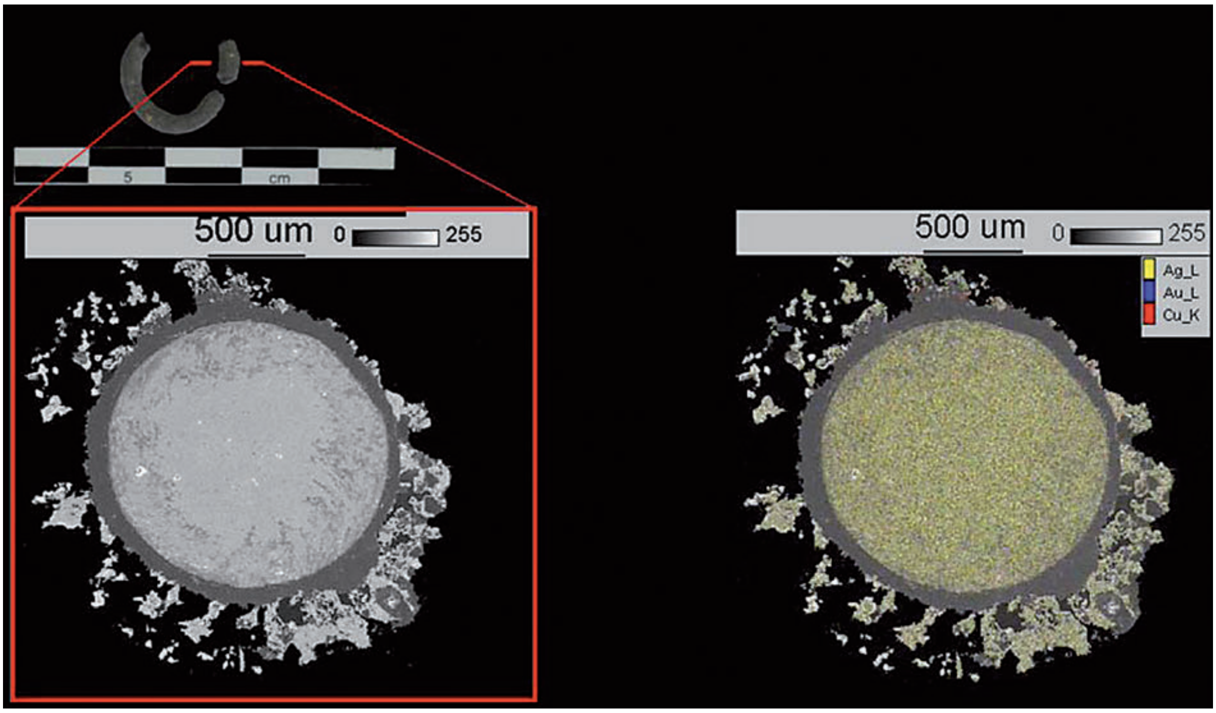


Fig. 13: Metallographies studies of the ring n°1, etched sample, magnifications 500x.

Tab. 5: Results of analyses of the awl.

lab.	Composition (weight %)																
	O	**Al**	**Si**	**S**	**Cl**	**Ca**	**Cu**	**As**	**Br**	**Ni**	**Sn**	**Pb**	**Zn**	**Sb**	**Au**	**Bi**	**Co**	**Fe**
Bm	3,95	n.d	0,44	n.d	0,24	n.d	92,34	1,2	0,32	1,51	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Bm	4,07	0,52	0,53	0,14	0,75	n.d	91,87	0,72	n.d	1,39	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Bm	3,18	0,61	0,34	n.d	n.d	n.d	95,87	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Bm	4,20	0,54	0,44	n.d	2	n.d	90,01	2,83	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Bm	6,19	0,48	0,49	0,11	0,27	n.d	79,29	6,79	n.d	6,38	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Bm	4,14	0,35	0,26	n.d	2,89	0,26	88,94	2,36	n.d	0,79	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Bu	n.d	n.d	n.d	n.d	n.d	n.d	90,05	1,20	n.d	1,18	0,03	0,1	0,2	0,2	0,055	0,03	0,20	0,12

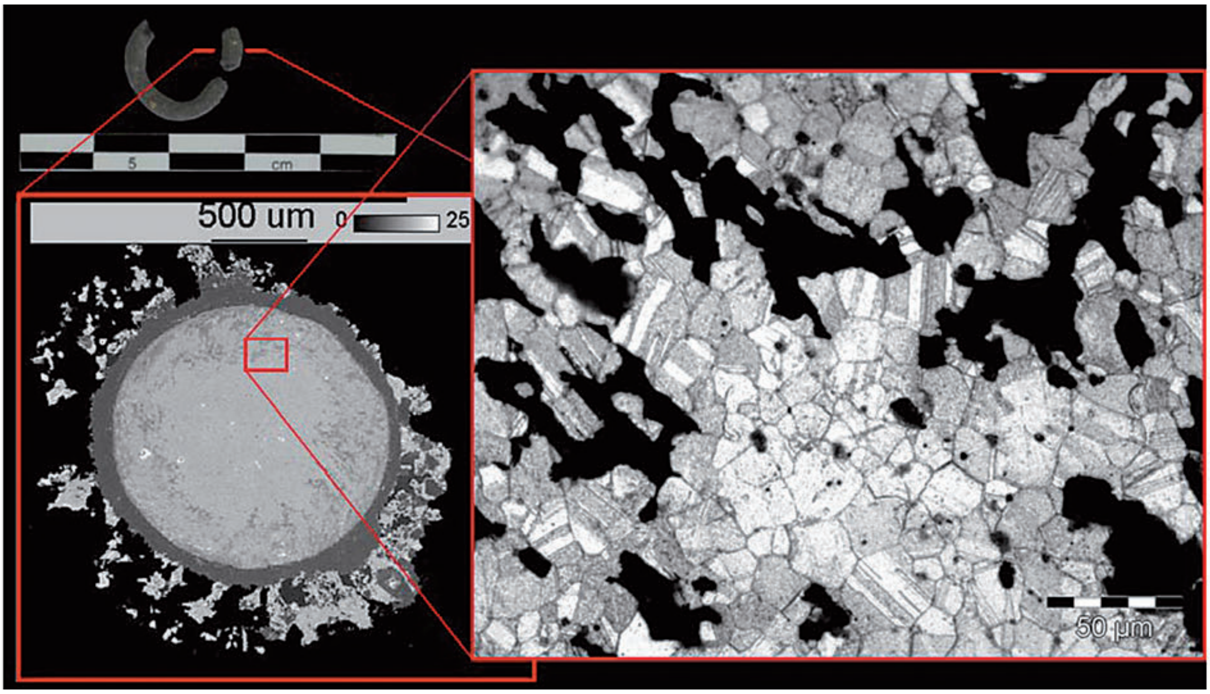


Fig. 14: Metallographies studies of the awl, etched sample, magnifications 500x.

The geological/metallogenical environment

The area where the cemetery of Soyuq Bulaq is located is characterized by a stratum dated to the Upper Cretaceous (upper Senonian, Danian stage) and Lower-Middle Quaternary era. The host-rocks are limestone, perlite, volcanic tuff, trass and bentonite (Economic and Social Commission for Asia and the Pacific 2000, map in annex).

Close to Soyuq Bulaq, ore deposits are not numerous. But, within 30-35 km as the crow flies, three ore-bearing regions are attested (Bolnisi-Madneuli in Georgia, Alaverdi in Armenia and Qazakh in Azerbaijan, Fig. 16). We can also mention the ore district of Kedabek-Dashkesan in Azerbaijan which is situated 55 km from Soyuq Bulaq.

The earliest studies did not identify nickel in copper ores (Selimkhanov 1970: 58); generally, this element seems to be associated with ophiolites in the Caucasus. A belt of ophiolites is well known (Sevan-Akara ophiolite belt) in the eastern part of Armenia (Sevan) and the middle part of Azerbaijan (region of Karabagh)(Knipper et al. 1986: 226; Gasanov 1979: 399-400). Some punctual formations of ophiolites could exist in the northern part of this belt. Nickel is clearly mineralized in polymetallic deposits - Analyses show 0.99 % NiO in chlorites foliage and 5 % NiO in shuhardites (type of chlorine $KNaCu_3O(SO_4)_3$). Nickel has been discovered in serpentines in the right bank of the rivers Alagchichay and Terter (Mustafayev 2005: 324-325; Efendiyev 1961: 239).

The origins of auriferous silver and arsenical copper

The question about the origins of auriferous silver has already been discussed in details in several previous studies (Prag 1978: 40-41; Gale et al. 1981a:

Tab. 6: Results of analyses of the dagger.

Sector	Artefact type	Composition (weight %)																
		O	Al	Si	Cl	Ca	Cu	As	Sn	Pb	Zn	Sb	Ag	Au	Bi	Ni	Co	Fe
K. 1	dagger	10,42	0,77	0,23	15,76	0,3	71,24	1,29	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
K. 1	dagger	15,78	0,53	0,13	22,67	0,22	62,67	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
K. 1	dagger	10,89	0,42	0,05	18,31	0,14	68,66	1,51	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
K. 1	dagger	11,67	0,61	17,52	n.d	0,19	68,59	1,42	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
K. 1	dagger	13,18	0,65	17,96	n.d	0,34	65,76	2,1	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
K. 1	dagger	n.d	n.d	n.d	n.d	n.d	70,21	1,17	0,37	0,05	0,21	0,25	0,005	0,05	0,03	0,01	0,3	0,2

Fig 15 : settlements mentioned in the text : 1- Soyuq-Bulaq, 2- Staromyshatovskaja, 3- Majkop, 4- Arslantepe, 5- Hacinebi, 6- Tell Brak, 7- Tepe Gawra, 8- Sé-Girdan, 9- Byblos, 10- Tell esh-Shuna, 11- Naqâda.

104-109; Gale et al. 1981b: 288-294; Rehren et al. 1996: 6-8). Two complex possibilities need to be considered: a geological source or an artificial origin (alloys or constant recycling).

We face a similar problem for arsenical copper. Indeed, one of the metallogenical characteristics of the cuprous ores in this area derives from the natural association of arsenic and copper.

We dispose of LIA analyses of two artefacts in silver-gold-copper alloy. Unfortunately, ICP-AES or LIA analyses cannot be done on the samples of arsenical copper analyzed in Bochum.

If we accept, on the one hand, the origin of auriferous silver to be geological/metallogenical, we can exclude the possibility of argentiferous lead ores, as EDS did not detect Pb in the artefacts. On the other

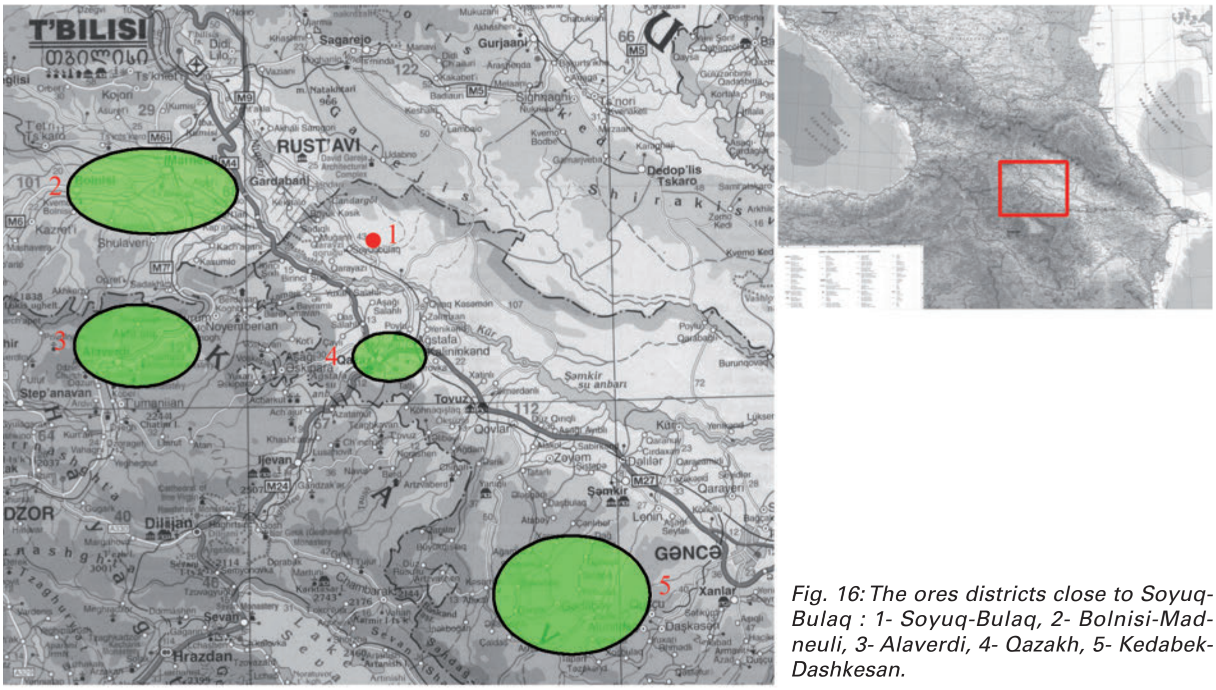


Fig. 16: The ores districts close to Soyuq-Bulaq : 1- Soyuq-Bulaq, 2- Bolnisi-Madneuli, 3- Alaverdi, 4- Qazakh, 5- Kedabek-Dashkesan.

hand, due to the composition of these objects: electrum (Au, Ag), liujinyinite (Ag_3AuS_2), a derivative of auricupride (Cu_3Au) like argentocuproauride ($Cu_3(Au, Ag)$), uytenbogaardtite ($AgAu_3S_2$), or an unnamed ore ($Ag_6AuCu_2S_5$), several auriferous or argentiferous ores could be considered. Such ores, or similar associations, are known in the district of Kedabek-Dashkeshan. Furthermore, Ag – argentit $(Ag)_2S$ - is mineralized in polymetallic and copper ores in the Kedabek district (Efendiyev 1961: 353-354). Native Silver has been identified in the tributaries of the Kura River (Baba-Zade et al. 2005: 467-479). In Agstafa district, a cuprous deposit is associated with an auriferous one and is found close to Ag occurrences. In Tovuz district, another Au deposit is well known (Mustafayev 2005: 239-245).

As for the other possibility, that is an artificial origin of the auriferous silver, we can argue that this alloy is known during the Chalcolithic and the Early Bronze age (Gale et al. 1981a: 114-115; Rehren *et al.* 1996: 7) in the Levant (Tell esh-Shuna – later EB I period, Byblos – 3800-3200 B.C.) (Graham et al. 1993: 17; Prag 1978: 36-37; in Byblos the graves where the auriferous silver artefacts coming from are: 4bis, 14, 19, 23, 29, 30, 35, 42, 77, 97, 115, 117, 119, 145, 147, 153, 163, 174, 196, 203, 210, 216, 222, 230, 236, 240, 247, 249, 272, 630, 631, 689, 889, 1020, 1081, 1106, 1191, 1266, 1314, 1424, 1546, 1546 bis, 1555, 1563, 1566, 1567, 1580, 1608, 1668, 1670, 1671, 1674, 1675) in Egypt (Naqâda – Predynastic period (Gale et al. 1981a: 111-113; Prag 1978: 36-37) and Mesopotamia (Tepe Gawra, tomb 109, level X) (Moorey 1994: 231). According to previous studies, the production of a deliberate ternary alloy is unfounded. Nevertheless, we cannot exclude that this alloy is the result of constant recycling (Gale et al. 1981a: 115; Rehren et al. 1996: 8).

The addition of small quantities of copper reduces the melting temperature of this alloy; according to the ternary system Ag-Au-Cu, the addition of 5 wt.% of Cu lowers the melting point of the alloy by 50 °C. To add the same ratios of gold induces the opposite effect. Furthermore, the addition of copper increases the strength of silver. The addition of gold modifies the colour of the alloy (Rehren *et al.* 1996: 8).

Actually, as far as the southern part of the Caucasus is concerned, we cannot solve the question of the origins of these alloys (Cu-As and Ag-Au-Cu). Indeed, it is not easy to compare the results of our analyses with the few studies of Chalcolithic/Early Bronze Age metal artefacts that were done a long time ago and that are difficult to make use of (Chernykh 1966: 35-50, 98-103; Kushnareva et al. 1970: 130-135; Selimkhanov 1960a: 91, 93, 96, 98, 100-101; Selimkhanov 1960b: 77; Selimkhanov 1962: 77-79; Selimkhanov 1966: 224, 230-231). Furthermore, very few metallurgical wastes have been found and no real metallurgical structure (furnace, "workshop") has yet been discovered in the Caucasus for these periods.

Conclusion

From a metallurgical point of view, kurgans 1 and 4 are particularly rich in metal. Our joint analytical program shows the high level reached by metallurgy, both on precious metals (gold and silver) and on copper alloys (arsenical copper) during the first half of the IVth millennium. Some of our results show the mastery of casting, of cold and heat treatments and sophisticated methods of jewellery. Although we still lack many data proving that this was a local metallurgy (lack of furnaces, of metallurgical tools and wastes, problems concerning the nature of the origin of the alloys), the existence in the vicinity of ore deposits containing all the elements found in the metal objects leads us to suppose such a possibility.

The artefacts of kurgans 1 and 4, especially the beads, show typological similaritieswith the "treasures" of Maikop and Staromyshatovskaja (Chernykh 1992: 67). Some typological parallels also exist with Tell Brak (Oates et al.1997: 287, 291; Emberling et al.2003: 32) where a cache (350 beads in carnelian, gold, silver, lapis lazuli and other stones) has been found in a tripartite building in TW 16, dated to the northern Middle Uruk (not later than 3500 B.C.). A pair of earings – probably made of a silver alloy (not yet analyzed) – has been found in an infant-tomb jar in a level dated to the Late Chalcolithic A (summed range 4250-3350/combined range 3780-3640 B.C.) at Hacinebi (Stein et al., 1997: 141-142). Other comparisons can be made with Sé Girdan, the date of which is still to be established precisely (Muscarella 2003: 130), where, in tumulus IV, have been found fragments of a silver vessel, a copper alloy dagger, two long silver rods, and many gold, stone and paste beads (Muscarella 1969: 20; Muscarella 1971: 11). Lastly, we can mention the metal objects of the "Royal" tomb at Arslantepe, though it dates later than Soyuq Bulaq (ca. 3000 B.C.). This grave contained gold objects (3 beads, 1 hair spiral), silver beads (3 large, 65 small) some of which are Ag-Cu alloys, and carnelian and limestone beads (Frangipane 2001: 108-109; Hauptmann et al. 2002: 46; Frangipane 2004: 140-142).

We hope to be able to conduct a metallurgical survey in the areas mentioned above with our colleagues of Azerbaijan in order to identify features of ancient metallurgy and to sample different local ores (cuprous, argentiferous and auriferous). We also hope to proceed with our joint analytical program (EDS, LIA, ICP-AES, XRD) in order to better understand the beginnings of metallurgy, particularly in the southern part of the Caucasus.

Acknowledgement

Antoine Courcier would like to express to Prof. A. Hauptmann his warmest acknowledgments for his generosity and very valuable scientific support during these analyses in the Bochum Laboratory

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Bibliography

Baba-Zade, V.M., Nadirov, A.A., Bagirov, G.S., Bektashi, S.A., Mamedov, M.M., Ramazanov, V.G., Musaev, Sh.D. & Akhundov, F.A. (2005): *Mineral'no-syr'evye resursy Azerbajdzhana (uslovija formirovanija, zakonomernosmi razmeshchenija nauchnye osnovy prognozirovanija),* Natsional'naja Akademija Nauk Azerbajdzhanskoj Respubliki, Ministerstvo ekologii i prirodnykh resursov Azerbajdzhanskoj Respubliki, Ministerstvo obrazovanija Azerbajdzhanskoj Respubliki. Ozan, Bakou.

Chernykh, E.N. (1966): *Istorija drevnejshej metallurgii Vostochnoj Evropy.* Academija Nauk SSSR, Moscou.

Chernykh, E.N. (1992): *Ancient Metallurgy in the USSR. The Early Metal Age*. Cambridge University Press, Cambridge.

Economic and Social Commission for Asia and the Pacific (2000): *Atlas of Mineral Resources on the ESCAP Region. Geology and Mineral Resources of Azerbaijan*. United Nations Press, New-York.

Efendiyev, G.H. (1961): Nikelenostnost' ul'traosnovnikh porod Azerbajdzhana, *Geologija Azerbaidzhana*, 4, 323-355.

Emberling, G.G. & McDonald, H. (2003): Excavations at Tell Brak 2001-2002: Preliminary report, *Iraq* 65, 1-75.

Frangipane, M. (2004): *Alle origini del potere, Arslantepe, la collina dei leoni*, catalogue de l'exposition, Rome 13 Octobre 2004 – 9 Janvier 2005. Electra Milan.

Frangipane, M., Di Norcera, G.M., Hauptmann, A., Morbidelli, P., Palmieri, A., Sadori, L., Schultz, M. & Schmidt-Schultz, T. (2001): New symbols of a new power in a "Royal" tomb from 3000 BC Arslantepe, Malatya (Turkey), *Paléorient*, 27-2, 105-139.

Gale, N.H. & Stos-Gale, Z.A. (1981a): Ancient Egyptian Silver, *Journal of Egyptian Achaeology* 67, 103-115.

Gale, N.H. & Stos-Gale, Z.A. (1981b): Sources of Galena, Lead and Silver in Predynastic Egypt, *Revue d'Archéométrie* 3, 285-295.

Gasanov, T. A. (1979): The age of Ophiolites and the Independence Nature of the Gabbro-Diabase Complex of the Sevan-Akeri Zone of the Lesser Caucasus, *Geotectonics* 5, 86-97.

Graham, P. & Baird, D. (1993): Preliminary report of the second (1992) season of excavations at Tell es-Shuna North, *Levant* 25, 13-37.

Hauptmann, A., Schmitt-Strecker, S., Begemann, F. & Palmieri, A. (20029. Chemical composition and lead isotopy of metal objects from the "Royal" tomb and other related finds at Arslantepe, Eastern Anatolia, *Paléorient* 28-2, 43-70.

Hedges, R.E.M. (1976): On the occurrence of bromine in corroded silver, *Studies in Conservation* 21, 4-46.

Kekelia, S., Kekelia, M. & Moon, C.J. (2001): *Arcview Metallogenic Map of the Caucasus*, *Project INTAS n°97-1416*. University of Leicester Press, Leicester.

Knipper, A., Ricou, L.E. & Dercourt, J. (1986): Ophiolites as indicators of the geodynamic evolution of the Tethyan ocean, *Tectonophysics* 123/1-4, 213-240.

Kushnareva, K.Kh. & Chubinishvili, T.N. (1970): *Drevnie kul'tury Juzhnogo Kavkaza*. Nauka, Leningrad.

Lechtman, H. (1977): Style in technology: some early thoughts. *In*: Lechtman, H. & Merrill, R.S. (eds.), *Material Culture: Styles, Organization, and Dynamics of the Technology*. West Publishing, St Paul, 3-20.

Lechtman, H. (1996): Cloth and metal: the culture of technology. *In*: Boone E.H. (ed.), *Andean Art at Dumbarton Oaks*. Dumbarton Oaks Research Library and Collection, Washington D.C., 33-43.

Lyonnet, B., Akhundov, T., Almamedov, K., Bouquet, L., Courcier, A., Jellilov, B., Huseynov, F., Loute, S., Makharadze, Z. & Reynard, S. (in press): Late Chalcolithic Kurgans in Transcaucasia. The cemetery of Soyuq Bulaq (Azerbaijan). *Mitteilungen aus Iran und Turan*

Moorey, P.R.S. (1994): *Ancient Mesopotamian Materials and Industries: the Archaeological Evidence*. Clarendon Press, Oxford.

Muscarella, O.W. (1969): The tumuli at Sé Girdan, a preliminary report, *Metropolitan Museum Journal* 2, 5-25.

Muscarella, O.W. (1971): The tumuli at Sé Girdan: second report, *Metropolitan Museum Journal* 4, 5-28.

Muscarella, O.W. (2003): The Chronology and Culture of Sé Girdan: Phase III. *Ancient Civilizations from Scythia to Siberia, an International Journal of Comparative Studies in History and Archaeology,* 17-131.

Mustafayev, G.V. (2005): Projavlenie nikel'a v porodakh ofiolitovoj formatsii Malogo Kavkaza, *Geologija Azerbaidzhana*, 239-250.

Oates, J. & Oates, D. (1997): An open gate: cities of the fourth millennium B.C. (Tell BraK 1997), *Cambridge archaeological Journal* 7-2, 287-307.

Prag, K. (1978): Silver in the Levant in the fourth millennium B.C. *In*: Moorey, R. & Parr, P. (eds.), *Archaeology in the Levant, Essays for Kathleen Kenyon*. Aris and Phillips LTD, Warminster, 36-45.

Rehren, T., Hess, K. & Philip, G. (1996): Auriferous silver in Western Asia: ore or alloy?, *The Journal of the Historical Metallurgy Society* 30-1, 1-10.

Selimkhanov, I.R. (1960a): Issledovanija metallicheskikh predmetov iz "eneoliticheskikh" pamjatnikov Azerbajdzhana i Severnogo Kavkaza, *Sovetskaja Arkheologija* 2, 89-102.

Selimkhanov, I.R. (1960b): Spektralanalytische Untersuchungen von Metallfunden des 3. und 2. Jahrtausends aus dem östlichen Trankaukasian-Azerbaidzhan, *Archaeologia Austriaca* 28, 71-79.

Selimkhanov, I.R. (1962): Spectral Analysis of Metal Articles from Archaeological Monuments in the Caucasus, *Proceedings of the Prehistoric Society* 28, 68-79.

Selimkhanov, I.R. (1966): Ergebnisse von spektralanalytischen Untersuchungen an Metallgegenständen des vierten und dritten Jahrtausends aus Transkaukasien, *Germania* 44, 221-231.

Selimkhanov, I.R. (1970): *Razgadanye sekrety drevnej bronzy*. Nauka, Moskva.

Selimkhanov, I.R. & TorosJan, R.M. (1969): Metallograficheskij analiz drevnejshikh metallov v Zakavkaze, *Sovetskaja Arkheologija* 3, 229-235.

Stein, G.S., Edens, C., Edens, J.P., Keith, K., McMahon, A. & Özbal, H. (1997): Excavations at Hacinebi, Turkey – 1996: preliminary report, *Anatolica* 23, 111-168.

Thornton, C.P. & Lamberg-Karlovsky, C.C. (2004): A new look at the prehistoric metallurgy of southern Iran, *Iran* 42, 47-59.

Nr. 15.1

Bochum 2008

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METALLA (Bochum)
erscheint in zwei Heften bzw. einem Doppelheft jährlich.

Bezugspreis € 25,- pro Jahr inkl. Porto und Verpackung, Bestellungen formlos an das Deutsche Bergbau-Museum Bochum
Am Bergbaumuseum 28
D-44791 Bochum

Impressum

Herausgeber:
Deutsches Bergbau-Museum Bochum
Museumsdirektor: Prof. Dr. Rainer Slotta

Schriftleiter:
Dr. rer. nat. Michael Prange

Layout/Titelgestaltung:
Dipl. Ing. Angelika Friedrich

Druck und Verarbeitung:
Meiling Druck, Haldensleben

ISSN 0947-6229