



# ICP-MS and ICP-OES Studies of Gold from a Late Sarmatian Burial

Mark E. Hall

*Archaeological Research Facility, 2251 College Building, University of California Berkeley, Berkeley, CA 94720, U.S.A.*

Steven P. Brimmer and Fu-He Li

*Microanalytical Laboratory, Department of Chemistry, University of California Berkeley, Berkeley, CA 94720, U.S.A.*

Leonid Yablonsky

*Institute of Archaeology, Russian Academy of Sciences, Dm. Ulianova, 19 Moscow 117306 Russia*

*(Received 4 March 1997, revised manuscript accepted 16 August 1997)*

The chemical composition of 17 gold foil artefacts from a Late Sarmatian burial were determined by inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-optical emission spectrometry (ICP-OES). The Au, Ag and Cu contents were determined by ICP-OES and the As, Bi, Co, Fe, Ni, Pb, Pt, Sb, Sn and Zn contents were measured by ICP-MS. The gold ranged in fineness from 921 fine to 998 fine. Copper was clearly an addition in four of the samples, but it is uncertain if the copper in the other 13 samples was intentionally added or part of the original gold alloy. Hierarchical cluster analysis of the trace element compositions suggests that the gold used in these artefacts came from three different “sources” or workshops. The high platinum content of one of the source groups suggests that the gold possibly came from the southern Urals. © 1998 Academic Press Limited

**Keywords:** INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY, INDUCTIVELY COUPLED PLASMA-OPTICAL EMISSION SPECTROMETRY, LATE SARMATIAN, POKROVKA, FINENESS, HIERARCHICAL CLUSTER ANALYSIS, DISCRIMINANT ANALYSIS, URAL MOUNTAINS.

## Introduction

While the goldwork of the nomadic peoples, such as the Saka, Sarmatians and Scythians, has been the subject of several stylistic studies (Artamonov, 1969; Sarianidi, 1985, 1989; Piotrovsky, Galanina & Grach, 1987; Pugachenkova & Rempel, 1991; Gossel-Raeck, 1993) there have been only a few analytical studies of this material. The only published analyses of nomadic goldwork comes from a series of Early Iron Age burials in central Kazakhstan (Kuznetsova & Teplovodskaya, 1994: 98–105), the Saka burial in kurgan 5 at ChilkTin, Kazakhstan (Chernikov, 1965: 176) and from the “Yueh-chih/Yuezhi” burials at Tillya-Tepe, Afghanistan (Sarianidi, 1989: 237, 238).

The aim of this paper is to present the results of the chemical analyses of 17 gold artefacts using inductively

coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-optical emission spectrometry (ICP-OES). All the samples in this study came from a Late Sarmatian period burial located in southern Russia.

These metal analyses can be used to identify the technology available to a given culture for alloying metals. When numerous metal analyses are combined with stylistic studies, the alloying patterns and trace element data can be used to discover local or regional workshops. Finally, in some cases, the trace element concentrations have been used to determine the provenance of some of the raw materials.

## Description of the Samples

The Sarmatians were a group of nomadic peoples living on the Eurasian steppes during the second half of the 1st millennium BC and into the early centuries AD

Correspondence to: M. E. Hall. Present address: Kokogaku Bu, Rekihaku, 117 Jonai-machi, Sakura-shi, Chiba 285, Japan.



Figure 1. Photograph of some of the gold foil artefacts from Pokrovka cemetery 2, kurgan 9, burial 1. The scale is subdivided into centimeters. (Photograph courtesy of Jeannine Davis-Kimball.)

(Sulimerski, 1970; Raev, 1986; Melyukova, 1990: 110–117; Barbarunova, 1995; Moshkova, 1995). Originally, living to the east of the Black Sea Scythians, the Sarmatians expanded westwards across the Don during the 3rd century BC and formed the polities known to the Classical world as the Alans, Aorsi, Iazyges and Roxolani. The Sarmatian polities controlled the southern Eurasian steppes between the Volga and the Danube rivers until being conquered by the Goths and Huns in the 3rd and 4th centuries AD.

The gold artefacts in this study were excavated in 1994 from burial 1, kurgan 9, in cemetery 2 at Pokrovka, Russia. Pokrovka is a Sarmatian cemetery situated in the southern Ural steppes along the banks of the Ilek river on the Russian-Kazakh border and has been the scene of annual excavations since 1991 (Yablonsky, 1993, 1994, 1995; Davis-Kimball, 1995; Davis-Kimball & Yablonsky, 1996). Most of the burials at Pokrovka are dated to the Early Sarmatian period (c. 400–200 BC), but this particular one is dated to the Late Sarmatian period (c. 2nd to 4th century AD) on a stylistic basis (Davis-Kimball & Yablonsky, 1996: 7–8). Bark from the timbers forming the tomb was radiocarbon-dated to  $1890 \pm 60$  BP (Beta 93786); this radiocarbon determination calibrates to AD 1–320 in the  $2\sigma$  range.

The kurgan had been robbed in antiquity, but the looters left behind a series of gold foil artefacts. These artefacts consist of small rectangular boxes, buttons, fish-shaped ornaments, orb-shaped objects believed to be belt or harness decorations, crushed, unrecognizable masses of gold foil (Figure 1), and a fairly large square box with a tamga sign (Davis-Kimball & Yablonsky, 1996: Plate 10). The artefacts were made by pressing sheet gold around a wooden form. In all these pieces, there was no evidence of filigree or granulation.

Samples, approximately  $2 \times 5$  mm, were taken from 17 of these artefacts. In order not to damage the artefacts from an aesthetic perspective, all samples were taken from an interior edge.

## Methodology

### *Equipment and reagents*

All ICP-MS experiments were performed on a Perkin-Elmer Sciex Elan 5000A spectrometer equipped with a quadrupole mass separator and a channel electron multiplier. Typical operating conditions are listed in Appendix Table A1. A platinum sampler and skimmer cones were used throughout. The sample introduction system was equipped with a CETAC Technologies Model U-5000 AT ultrasonic nebulizer and a peristaltic pump.

All ICP-OES analyses were performed on a Perkin-Elmer PLASMA 40 sequential spectrometer. Optical emission from the plasma was viewed laterally 1.2 cm above the load coil and focused onto the entrance slit of the monochromator and detected with a photomultiplier. Appendix Table A2 contains the operating conditions.

Optima grade, ultra-pure hydrochloric and nitric acids were used for sample preparation. ASTM Grade II deionized water was used in the dilutions.

All statistical tests were done using SPSS for Windows 3.1, Version 6.01.

### *Procedure*

The elements analysed in this study were: antimony (Sb), arsenic (As), bismuth (Bi), cobalt (Co), copper (Cu), gold (Au), iron (Fe), lead (Pb), nickel (Ni), platinum (Pt), silver (Ag), tin (Sn) and zinc (Zn)\*. Copper and silver are the major metallic impurities in native gold and most gold ores (Boyle, 1979: 16; Yannopoulos, 1991: 1, 2; Raub, 1995: 245). In alluvial deposits, gold can be associated with cassiterite, iron hydroxides and the platinum group elements (PGEs), such as platinum, iridium (Ir) and osmium (Os) (Meeks & Tite, 1980; Taylor, 1980: 9; Tylecote, 1987: 79, 82–83). Gold ores in reef or lode deposits are often associated with quartzite and other metallic minerals such as arsenopyrite, chalcopyrite, galena, sphalerite, tellurides and tetrahedrite (Schwartz, 1944; Warren & Thompson, 1944; Boyle, 1979: 16–51; Ramdohr, 1980: 324, 327; Shikazono & Shimizu, 1988; Meinert, 1989; Lehrberger, 1995; Morteani, 1995: 100–102, 106–111).

The gold foil samples were ultrasonically cleaned in distilled, deionized water, dried in air, and weighed on a ultra-micro balance. The samples were dissolved in a heated solution of 3 ml concentrated hydrochloric acid and 1 ml of concentrated nitric acid. For ICP-OES analysis, the resultant solutions were diluted to 50 ml with deionized water and introduced directly into the ICP with a pneumatic nebulizer. For ICP-MS analysis, however, an additional 3 ml of concentrated nitric acid was added after dissolution and then the solutions

\*The choice of these elements was also confirmed by electron probe microbeam analysis. Samples A–E were examined and the only detectable trace element was iron. See Hall & Yablonsky (1997).

Table 1. Major and minor element concentrations of the gold foil artefacts from the Late Sarmatian burial at cemetery 2, kurgan 9, burial 1 at Pokrovka, Russia

Sample	Item	Au	Ag	Cu
P02:K09:B01:a	Fragment	92.0	3.41	2.48
P02:K09:B01:b	Fish	84.7	5.62	2.11
P02:K09:B01:c	Fragment	90.6	6.48	2.19
P02:K09:B01:d	Box	88.0	7.51	3.92
P02:K09:B01:e	Fragment	84.7	7.09	4.50
P02:K09:B01:f	Fragment	93.7	1.26	2.15
P02:K09:B01:g	Orb	90.7	3.05	2.64
P02:K09:B01:h	Fish	90.0	5.87	2.19
P02:K09:B01:i	Box	92.0	0.20	4.28
P02:K09:B01:j	Box	92.3	5.65	1.95
P02:K09:B01:k	Fragment	94.1	2.53	2.15
P02:K09:B01:l	Box	91.2	0.56	2.60
P02:K09:B01:m	Fish	92.1	1.59	2.14
P02:K09:B01:n	Fish	84.0	6.20	2.18
P02:K09:B01:o	Fish	92.4	3.36	2.57
P02:K09:B01:p	Box-tamga	88.0	6.24	2.12
P02:K09:B01:q	Button	84.5	1.78	5.94

All values are in wt. %. The gold and silver contents were obtained using an ICP-OES, while the copper content was obtained using an ICP-MS. The operating conditions are described in the text and the Appendix.

were vaporized to approximately 1 ml to drive off the hydrochloric acid. After vaporization, the solutions were diluted to 10 ml, 25 ml, or 50 ml respectively with deionized water based on the sample mass. The ICP-MS analyses were performed by introducing the sample solutions into the plasma with an ultrasonic nebulizer. Gallium, rhodium and tungsten were introduced as internal standards with the sample solutions to monitor and correct for instrumental drift.

The analytical procedure was validated using fine gold reference material FAU 10 from the Royal Canadian Mint. The relative standard deviation, a measure of the precision, ranges from 1.60% for bismuth to a low of 0.29% for platinum (see Appendix

Table A2). The accuracy ranges from 0.3% for copper to 5.9% for platinum (see Appendix Table A3).

A major concern was the use of platinum sampler and skimmer cones in the platinum analysis using ICP-MS. It was found that the platinum signals in the method blanks were insignificant. The platinum signal intensities obtained from the artefact solutions were at least 200 times higher than the method blanks.

## Results

### Major and minor elements

Table 1 lists the weight percentages of the major and minor elements found in the 17 samples. The gold content ranges from 84.0–94.1%, the silver content from 0.20–7.51% and the copper content from 1.95–5.94%.

### Trace elements

Iron has the highest concentration of all the trace elements found in these artefacts (see Table 2). The iron content ranges from a minimum of 259 ppm to a maximum of 937 ppm. For the other trace elements, only lead, platinum, tin and zinc are found at levels higher than 10 ppm. The lead content averages 30 ppm and ranges from 7.7 to 149.0 ppm. The majority of the samples have a platinum concentration between 17 ppm and 125 ppm, but the button contains 250 ppm of platinum. The tin content ranges from 19.6 ppm to 82.6 ppm. The zinc content ranges from 8.57 to 52.1 ppm.

The remainder of the elements sought were found at levels below 10 ppm. Six out of 17 artefacts had an arsenic level below the detection limit of the ICP-MS.

Table 2. Concentration of the trace elements found in the 17 gold foil samples

Sample	As	Bi	Co	Fe	Ni	Pb	Pt	Sb	Sn	Zn
P02:K09:B01:a	<0.1	0.93	0.35	543	5.33	7.70	27.6	1.51	20.4	8.57
P02:K09:B01:b	<0.1	0.23	0.30	501	5.02	9.50	53.1	0.49	49.5	11.6
P02:K09:B01:c	<0.1	0.51	0.34	577	5.60	20.3	61.0	1.00	42.8	12.2
P02:K09:B01:d	1.89	0.57	0.37	377	8.12	11.6	66.1	3.54	42.0	14.3
P02:K09:B01:e	2.35	2.25	0.60	755	12.1	33.7	137	13.9	82.6	32.0
P02:K09:B01:f	<0.1	0.60	0.60	556	4.98	20.8	49.0	0.97	35.3	11.9
P02:K09:B01:g	0.88	1.62	0.67	309	6.34	22.5	28.3	2.23	32.4	16.2
P02:K09:B01:h	1.12	0.86	0.44	634	5.49	27.5	61.7	1.45	43.4	14.2
P02:K09:B01:i	1.51	0.58	0.44	340	7.30	13.8	62.9	4.05	54.0	14.6
P02:K09:B01:j	<0.1	0.28	1.42	659	4.46	10.6	49.7	1.60	19.6	8.75
P02:K09:B01:k	0.10	0.46	0.47	697	4.98	14.4	53.8	1.01	32.8	12.2
P02:K09:B01:l	0.98	1.86	0.57	469	6.77	41.0	17.0	17.1	43.4	14.5
P02:K09:B01:m	0.99	1.48	0.70	570	4.76	29.3	63.3	2.64	66.0	15.7
P02:K09:B01:n	0.50	0.45	0.69	584	4.61	19.6	64.6	0.88	28.5	10.0
P02:K09:B01:o	1.98	1.39	1.62	937	6.91	39.0	33.1	2.28	48.6	23.3
P02:K09:B01:p	<0.1	0.47	0.61	776	4.92	149	49.9	3.45	48.8	16.9
P02:K09:B01:q	3.74	2.91	0.31	259	7.00	39.5	238	5.59	31.7	52.1

All values listed are in parts per million (ppm). All values were determined by ICP-MS as detailed in the text and the Appendix.

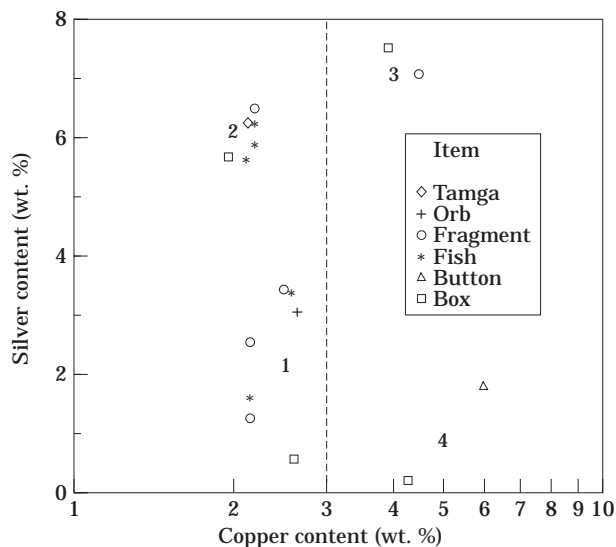


Figure 2. Plot of the silver content versus the logarithm of the copper content. Generally, gold alloys with more than 3% copper are considered to be intentional, human-made alloys. Between 1% and 3% copper, it is uncertain if the gold alloy was intentional or natural. The dotted line marks the 3% copper concentration. The number by each set of points indicates the major alloy group referred to in the text.

## Discussion

The fineness of the gold ranges from 921 to 998<sup>†</sup>. Assuming that these artefacts were not intentionally alloyed with silver or intentionally de-silvered, the fineness values indicate that the gold did not come from an epithermal, plutonic or volcanogenic deposit (Fisher, 1945a, b; Boyle, 1979: 197–207; Antweiler & Campbell, 1982; Morrison, Rose & Jaireth, 1991). The average fineness for these types of deposits ranges from 450 to 900. The gold could have originated in an archaean, placer, porphyritic or slate belt deposit (Boyle, 1979: 197–207; Morrison, Rose & Jaireth, 1991).

Utilizing both archaeological and geological data on gold, it has been proposed that gold alloys containing more than 3% copper are intentional human-made alloys, while alloys with less than 1% copper are naturally occurring (Hartmann, 1970, 1982; Tylecote, 1987: 74; Raub, 1995: 245). Alloys with 1–3% copper could be natural or human made (Tylecote, 1987: 74; Pingel, 1995: 389, 390).

With the above in mind, a plot of the silver content versus the logarithm of the copper content indicates that four different gold alloys were used to make the artefacts found at Pokrovka (Figure 2). The first alloy type comprises seven artefacts that have a silver content between 0.5% and 4% and a copper content between 2% and 3%. The second alloy type, evidenced by six artefacts, has a silver content between 5% and 7% and contains between 1.5% and 2.5% copper. It is

<sup>†</sup>Fineness is calculated here as  $(Au \times 1000)/(Au + Ag)$ .

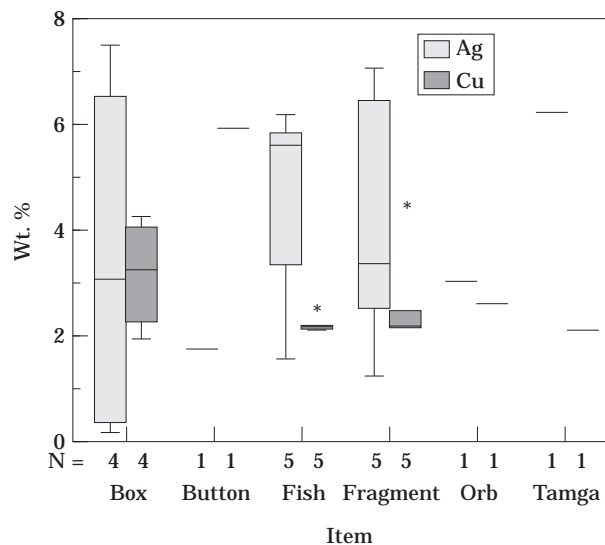


Figure 3. Range of copper and silver contents in a given type of gold foil artefact. The shaded regions mark the 68% confidence interval, while the bars mark the 95% confidence interval. The heavy black bars are the mean values.

Table 3. Pearson correlation coefficients between copper and select trace elements

	Cu	Bi	Ni	Pt	Zn
Cu	1.00	0.66	0.70	0.81	0.81
Bi		1.00	0.56	0.61	0.61
Ni			1.00	0.41	0.53
Pt				1.00	0.89
Zn					1.00

Values above 0.6 are considered significant.

uncertain whether these two alloys are natural or human made. The other two alloy types are considered to be human made since they contain more than 3% copper. The third alloy type contains more than 6% silver, while the fourth alloy type has a silver content ranging from 0.20% to 2%.

Figure 3 shows the range of values of the minor elements for a given artefact type. The silver values vary by more than 1 weight percent for all the artefact types. While there is some variation in the range of values for the copper contents, the copper content of the fish-shaped artefacts is quite constrained. The average copper content for the fish-shaped artefacts is 2.23% with a standard deviation of 0.18%. The narrow range of copper values for this artefact class suggests that the fish-shaped artefacts were made from the same source of gold or from the same melt.

Since copper was added to at least some of the gold alloys, there is a high probability that it brought other trace elements with it. Table 3 lists the Pearson correlation coefficients for copper and the trace elements. Arsenic is excluded from the table since it was not detected in six of the samples. The strong positive

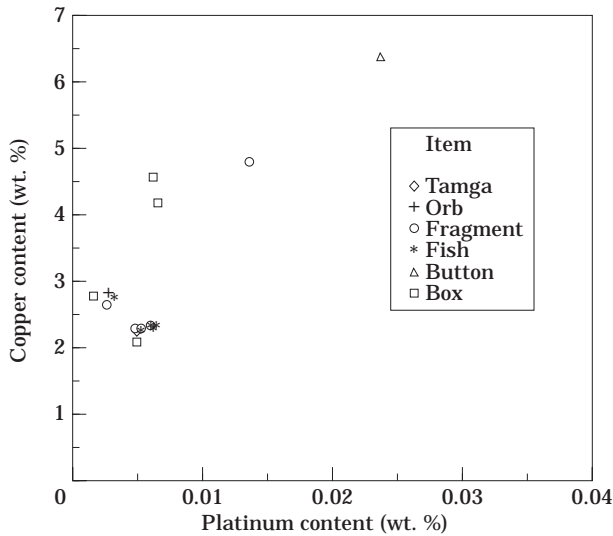


Figure 4. Plot of the copper versus platinum content.

correlation coefficients between the bismuth, copper, nickel and zinc contents suggests that these trace elements entered the gold with the copper. In the case of the platinum, the strong positive correlations are due to two outliers in the data set (Figure 4); it is quite unusual for copper or copper ores to contain over 100 ppm platinum.

Since the platinum and remaining trace elements were part of the gold, they can be seen as reflecting the “source” from which the gold artefacts came. The term

“source” is used here to mean not only the geographic provenience of the gold, but also to include the mixing of scrap and/or raw materials from a variety of geographic regions. Furthermore, aside from the PGEs, the trace element concentrations could also reflect the melting, alloying and refining practices of the craft workers since antimony, arsenic, bismuth, lead and zinc can all volatilize from molten gold-silver alloys at temperatures above 1000°C in an oxidizing atmosphere (Taylor, 1980: 14; Raub, 1995: 251–253).

The antimony, cobalt, lead, platinum and tin contents were treated by hierarchical cluster analysis to see if the artefacts came from the same source. Arsenic is not included in the cluster analysis since it was not detected in six of the 17 artefacts. Iron is also excluded since it is a component of common gangue minerals and does not reflect the geographic provenience of the gold (Antweiler & Campbell, 1977: 19, 1982: 38). The concentration data was not transformed in any manner since scaling and log normalizing can distort or hide clusters present in the original data (Milligan, 1996: 352). Furthermore, it must be remembered that most clustering algorithms do not assume normally distributed data (Milligan, 1996: 347).

The dendrogram in Figure 5 was obtained using the Wards method algorithm and the squared Euclidean distance to evaluate the similarities of the trace element data. Visually there appear to be 3 major clusters.

The validity of these clusters can be verified using stepwise discriminant analysis (Shennan, 1988: 229). The test was done with the five trace elements (Sb, Co, Pb, Pt, Sn) with the goal of maximizing the

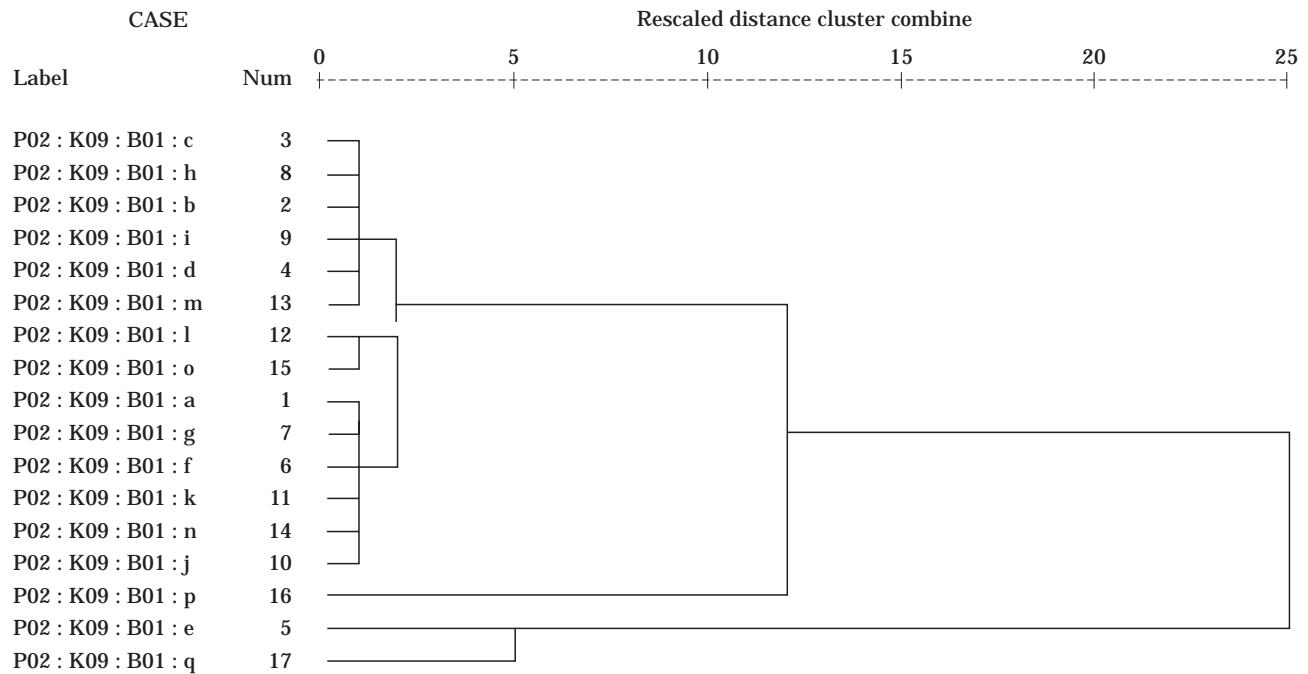


Figure 5. Dendrogram based on the Wards method algorithm and the squared Euclidean distance to evaluate the similarities between the antimony, cobalt, lead, platinum and tin contents of each artefact. Visually, there appear to be three distinct groups.

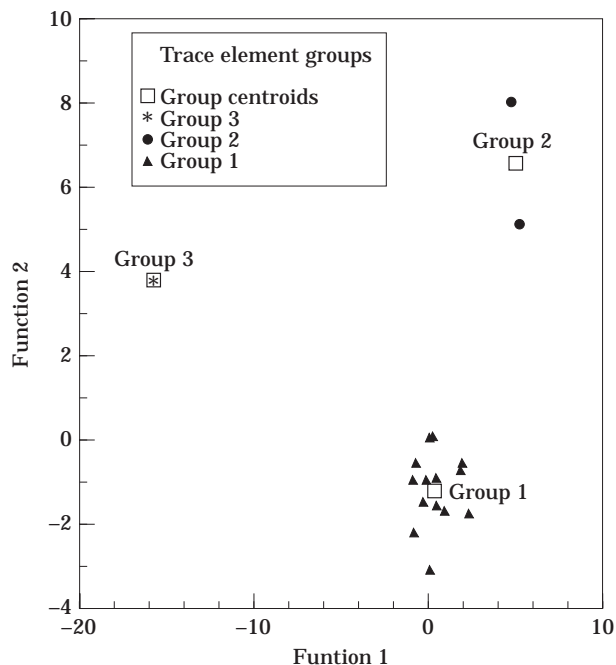


Figure 6. Plot of the first two canonical discriminant functions of the trace element groups obtained by stepwise discriminant analysis. Note the separation between groups. Similar results are obtained when the *F* to enter and *F* to remove are raised and lowered, and all the trace elements are entered together.

Mahalanobis distance between groups. The prior probabilities between groups was assumed to be equal, the probability of *F* to enter equals 0.5, and the probability of *F* to remove was 1.0. Figure 6 is a plot of the first two discriminant functions. These first two discriminant functions describe 99% of the variation and 100% of the cases are correctly grouped. Similar results were obtained when *F* to enter and *F* to remove was raised and lowered, the variables were entered all at the same time, and all the trace elements were used as variables.

The cluster analysis and discriminant analysis implies that there were three distinct sources that produced the gold artefacts found in the Late Sarmatian burial at Pokrovka. Source 1 contains 14 members (samples a, b, c, d, f, g, h, i, j, k, l, m, n, o), while source 2 consists of two members (samples e and q), and sample p is the sole member of source 3. Table 4 lists the diagnostic features of each group.

Since the craftsmen in Late Antiquity did not have the technology to remove the PGEs found in gold totally, the concentration of these elements can give some insights into where the gold could have originated (Meeks & Tite, 1980: 267, 268; Tylecote, 1987: 82, 83; Williams & Ogden, 1994: 15). Both the alluvial and magmatic sulphide gold deposits of the Ural Mountains contain platinum in excess of 100 ppm (Petrovskaia, 1973: 92–93; Razin, 1977: 121–122), while the various alluvial and reef deposits in Kazakhstan, the Transbaikalia and Uzbekistan contain less than 100 ppm platinum (Petrovskaia, 1973: 92–93; Borodaevskaya & Rozhkov, 1977: 3–81; Berger *et al.*, 1994). It is quite possible that the artefacts comprising source 2 were manufactured from gold from the Ural Mountains. For the other two groups, it is uncertain whether the trace element concentrations are reflecting distinctive ore bodies, the recycling of scrap or the mixing of raw materials from various regions.

There is no direct correspondence between the major alloy groups and the trace element groups. The only noticeable pattern is that both items in source 2 had copper added to them, but their silver content varied widely. This lack of correspondence between the two types of groups could be due to: (1) the recycling of gold from various geographic sources; (2) variation in the silver content of the original ore; and (3) the removal of silver from the gold.

## Conclusions

The gold foil artefacts from the Late Sarmatian burial at Pokrovka were made from four different gold alloys. Two of the alloy groups contain more than 3% copper and were intentional, human-made alloys. The other two alloy groups, containing between 1.5 to 2.8% copper, could be naturally occurring alloys or human-made alloys.

Based on the trace element data, the gold used in the artefacts came from 3 different sources. The gold from source 2, containing over 100 ppm platinum, could have originated in the alluvial or reef deposits of the Ural mountains. The geographical provenience of the other two trace element groups is unknown.

Archaeologists and art historians have traditionally seen the Altai as being the source of the gold used by

Table 4. Chemical characteristics of the trace element groups

Group ("Source")	Co (ppm)	Pb (ppm)	Pt (ppm)	Sb (ppm)	Sn (ppm)
1	0.61 ± 0.36	20.5 ± 10.5	49.3 ± 16.3	2.91 ± 4.21	39.9 ± 12.8
2	0.45 ± 0.20	36.6 ± 4.10	187 ± 71.4	9.74 ± 5.87	57.2 ± 36.0
3	0.61	149	49.9	3.45	48.8

The mean value and first standard deviation are reported for each group. The primary elements determining group membership are platinum and lead.

the Central Asian nomads (Mayor, 1994). The results here suggest, at least for the Sarmatians, that they utilized several different sources of gold. With more ICP studies of nomadic goldwork, archaeometallurgists should be able to define the various sources that were used by the Saka, Sarmatians and Scythians.

## Acknowledgements

The authors would like to thank Dr Jeannine Davis-Kimball of the Kazakh-American Research Foundation and Dr Steve Shackley of the Phoebe Hearst Museum of Anthropology for their insightful comments. Funding for this project was provided by the UNESCO/Hirayama Silk Road Fellowship programme.

## References

- Antweiler, J. C. & Campbell, W. L. (1977). Application of gold compositional analyses to mineral exploration in the United States. *Journal of Geochemical Exploration* **8**, 17–29.
- Antweiler, J. C. & Campbell, W. L. (1982). Gold in exploration geochemistry, In (A. A. Levinson, Ed.) *Precious Metals in the Northern Cordillera*. Rexdale, Ontario: Association of Exploration Geochemists, pp. 33–44.
- Artamonov, M. I. (1969). *Treasures from the Scythian Tombs*. London: Thames & Hudson.
- Barbarunova, A. (1995). Early Sarmatian Culture, In (J. Davis-Kimball, V. Bashilov & L. Yablonsky, Eds) *Nomads of Eurasia in the Early Iron Age*. Berkeley: Zinat Press, pp. 121–136.
- Berger, B. R., Drew, L. J., Goldfarb, R. & Snee, L. W. (1994). An epoch of gold riches: the Late Paleozoic in Uzbekistan, Central Asia. *Society of Economic Geologists Newsletter* **16**, 7–11.
- Borodaevskaya, M. B. & Rozhkov, I. S. (1977). Deposits of gold, In (V. I. Smirnov, Ed.) *Ore Deposits of the USSR, Volume 3*. London: Pitman Publishing, pp. 3–81.
- Chernikov, S. S. (1965). *Zagadke Zolotogo Kurgana*. Moscow: Nauka.
- Davis-Kimball, J. (1995). Excavations at Pokrovka, Russia, 1990–1994. *Old World Archaeology Newsletter* **18**, 12–17.
- Davis-Kimball, J. & Yablonsky, L. (1996). Excavations of Kurgans in the Southern Orenburg District, Russia: questions concerning the Northern Silk Route. *Silk Road Art and Archaeology* **4**, 1–16.
- Fisher, N. H. (1945a). The Fineness of gold, with special reference to the Morobe Goldfield, New Guinea. *Economic Geology* **40**, 449–495.
- Fisher, N. H. (1945b). The Fineness of gold, with special reference to the Morobe Goldfield, New Guinea, Part II. *Economic Geology* **40**, 537–563.
- Gossel-Raeck, B., Ed. (1993). *Gold der Skythen*. Hamburg: Karl Wachholtz Verlag.
- Hall, M. E. & Yablonsky, L. (1997). An EPMA study of some Late Sarmatian Gold Artefacts. *Bulletin of the Metals Museum*, forthcoming.
- Hartmann, A. (1970). *Prähistorische Goldfunde aus Europa. Studien zu den Anfängen der Metallurgie, Band 3*. Berlin: Gebr. Mann Verlag.
- Hartmann, A. (1982). *Prähistorische Goldfunde aus Europa II. Studien zu den Anfängen der Metallurgie, Band 5*. Berlin: Gebr. Mann Verlag.
- Kuznetsova, Z. F. & Teplovodskaya, T. M. (1994). *Drevniaia Metallurgiya I Goncharstvo Tsentralbnogo Kazakhstana*. Alma-Ata: Gylım.
- Lehrberger, G. (1995). The gold deposits of Europe: an overview of the possible metal sources for prehistoric gold objects. In (G. Morteani & J. P. Northover, Eds) *Prehistoric Gold in Europe*. NATO ASI Series E: Vol. 280. Dordrecht: Kluwer Academic Publishers, pp. 115–144.
- Mayor, A. (1994). Guardians of the gold. *Archaeology*, November/December, 53–59.
- Meeks, N. D. & Tite, M. S. (1980). The analysis of platinum-group element inclusions in gold antiquities. *Journal of Archaeological Science* **7**, 267–275.
- Meinert, L. D. (1989). Gold skarn deposits—geology and exploration criteria. In (R. R. Keays, W. R. H. Ramsay, D. J. Groves, Eds) *Geology of Gold Deposits: The Perspective in 1988*. Economic Geology Monograph 6. New Haven: Economic Geology Publishing Company, pp. 537–552.
- Melyukova, A. I. (1990). The Scythians and Sarmatians. In (D. Sinor, Ed.) *The Cambridge History of Early Inner Asia*. Cambridge: Cambridge University Press, pp. 97–117.
- Milligan, G. W. (1996). Clustering validation: results and implications for applied analyses. In (P. Arabie, L. J. Hubert & G. de Soete, Eds) *Clustering and Classification*. Singapore: World Scientific, pp. 341–377.
- Morrison, G. W., Rose, W. J. & Jaireth, S. (1991). Geological and geochemical controls on the silver content (fineness) of gold in gold-silver deposits. *Ore Geology Reviews* **6**, 333–364.
- Morteani, G. (1995). Mineral economics, mineralogy, geochemistry and structure of gold deposits: an overview. In (G. Morteani & J. P. Northover, Eds) *Prehistoric Gold in Europe*. NATO ASI Series E: Vol. 280. Dordrecht: Kluwer Academic Publishers, pp. 97–114.
- Moshkova, M. (1995). A brief review of the history of the Sauromatian and Sarmatian tribes. In (J. Davis-Kimball, V. Bashilov & L. Yablonsky, Eds) *Nomads of Eurasia in the Early Iron Age*. Berkeley: Zinat Press, pp. 85–90.
- Petrovskaya, N. V. (1973). *Samorodnoe Zoloto*. Moscow: Nauka.
- Pingel, V. (1995). Technical aspects of prehistoric gold objects on the basis of material analyses. In (G. Morteani & J. P. Northover, Eds) *Prehistoric Gold in Europe*. NATO ASI Series E: Vol. 280. Dordrecht: Kluwer Academic Publishers, pp. 385–398.
- Piotrovsky, B., Galanina, L. & Grach, N. (1987). *Scythian Art*. Oxford: Phaidon.
- Pugachenkova, G. A. & Rempel, L. I. (1991). Gold from Tilia-tepe. *Bulletin of the Asia Institute* **5**, 11–25.
- Raev, B. A. (1986). *Roman Imports in the Lower Don Basin*. BAR International Series 278. Oxford: British Archaeological Reports.
- Ramdohr, P. (1980). *The Ore Minerals and Their Intergrowths*. 2nd ed. Oxford: Pergamon Press.
- Raub, Ch. J. (1995). The metallurgy of gold and silver in prehistoric times. In (G. Morteani & J. P. Northover, Eds) *Prehistoric Gold in Europe*. NATO ASI Series E: Vol. 280. Dordrecht: Kluwer Academic Publishers, pp. 243–259.
- Razin, L. V. (1977). Deposits of platinum metals. In (V. I. Smirnov, Ed.) *Ore Deposits of the USSR, Volume 3*. London: Pitman Publishing, pp. 100–124.
- Sarianidi, V. (1985). *The Golden Hoard of Bactria*. New York: Harry N. Abrams.
- Sarianidi, V. (1989). *Khram I Nekropolb Tillyatepe*. Moscow: Nauka.
- Schwartz, G. M. (1944). Host minerals of native gold. *Economic Geology* **39**, 371–411.
- Shennan, S. (1988). *Quantifying Archaeology*. San Diego: Academic Press.
- Shikazono, N. & Masaaki Shimizu. (1988). *Electrum: Chemical Composition, Mode of Occurrence, and Depositional Environment*. Tokyo: University of Tokyo.
- Sulimski, T. (1970). *The Sarmatians*. New York: Praeger Publishers.
- Taylor, J. (1980). *Bronze Age Goldwork of the British Isles*. Cambridge: Cambridge University Press.
- Tylecote, R. F. (1987). *The Early History of Metallurgy in Europe*. London: Longman.
- Warren, T. (1944). Minor elements in gold. *Economic Geology* **39**, 457–471.
- Williams, D. & Ogden, J. (1994). *Greek Gold: Jewelry of the Classical World*. London: British Museum Press.

- Yablonsky, L. (1993). *Kurgany Levoberezhnogo Iлека. Volume 1.* Moscow: In-t. Arkheologii RAN.
- Yablonsky, L. (1994). *Kurgany Levoberezhnogo Iлека. Volume 2.* Moscow: In-t. Arkheologii RAN.
- Yablonsky, L. (1995). *Kurgany Levoberezhnogo Iлека. Volume 3.* Moscow: In-t. Arkheologii RAN.
- Yannopoulos, J. C. (1991). *The Extractive Metallurgy of Gold.* New York: Van Nostrand Reinhold.

## Appendix 1

Table A1. Operating conditions for the ICP-MS

Forward power	1.25kW
Reflected power	<5 W
Plasma gas	14 L/min
Auxiliary gas	1.4 L/min
Nebulization gas	0.45 L/min
Nebulizer	Ultrasonic
Sampler	Platinum
Skimmer	Platinum
Dwell time	50 ms
Sweeps per reading	100
Resolution	Normal

Table A1a: Settings and operating configuration for the Perkin-Elmer Elan 5000A ICP mass spectrometer

Element	Mass-to-charge ratio (m/z)	Detection limit (ppm)	Relative standard deviation (%)
Fe	57	0.8	1.11
Co	59	0.0018	0.68
Ni	60	0.01	0.85
Cu	65	0.006	0.79
Zn	68	0.006	1.17
As	75	0.012	1.55
Ga*	69	0.002	
Sn	118	0.004	1.25
Sb	121	0.002	1.86
Rh*	103	0.0016	
Pt	195	0.004	0.29
Pb	208	0.002	1.42
Bi	209	0.001	1.60
W*	182	0.002	

The elements marked by an asterisk are internal standards. The detection limits are calculated by multiplying the manufacturer's detection limit for the machine by the dilution factor. The dilution for the method was 5 mg of sample in 10 ml of solution. The relative standard deviations for the 11 trace elements were obtained by analysing 50 ppb of standards via ICP-MS with internal standards being used. Five replicates were run.

Table A2. Operating conditions for the ICP-OES

Forward power	1.25 kW
Reflected power	<5 W
Plasma gas	16 L/min
Auxiliary gas	0.5 L/min
Nebulization gas	0.8 L/min
Nebulizer	Pneumatic
Viewing height	1.2 cm above the load coil of the ICP

Table A2a: Settings and operating conditions for the Perkin Elmer Plasma 40 ICP optical emission spectrometer

Element	Wavelength (nm)	Detection limit (ppm)	Relative standard deviation (%)
Au	(I) 267-595	120	0.55
Ag	(I) 328-068	30.0	0.53

The detection limits are calculated by multiplying the manufacturer's detection limit for the machine by the dilution factor of the samples. The average dilution was 2.5 mg of sample into 50 ml of solution. The relative standard deviation for Au and Ag were obtained by analysing a 10 ppm Au and 5 ppm Ag standard solution without internal standards being used. Five replicates were analysed in both cases.

Table A3. Analytical results of FAU 10

Element	Certified value for FAU 10 (ppm)	Experimental value (ppm)
Fe	90.4	88.5
Co	not reported	<0.1
Ni	14.6	14.5
Cu	9.8	9.8
Zn	20.9	20.3
As	29.4	28.3
Ag	49.7	49.6
Sn	49.7	47.7
Sb	not reported	<1
Pt	5.1	5.4
Pb	49.7	52.1
Bi	53.9	56.5

The operating conditions for the ICP-MS and ICP-OES are those described in Tables A1 and A2. The values reported in the experimental value column are an average of five runs.