Investigating Archaeological Material from Burials of the Aristocracy of the Xiongnu People (Noin-Ula, Mongolia) By Means of SRXRF, XAFS, and Micro-SRXRF

V. A. Trunova[a, e], V. V. Zvereva[a], N. V. Polosmak[b], D. I. Kochubey[c], V. V. Kriventsov[c], K. E. Kuper[d], Ya. V. Rakshun[d], and D. S. Sorokoletov[d]

[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
[b] *Institute of Archaeology and Ethnography, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
[c] *Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
[d] *Budker Institute of Nuclear Physics, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
[e] *Novosibirsk State University, Novosibirsk, 630090 Russia*
e-mail: valna-t@mail.ru

Abstract—A study of unique archaeological organic material from the burials of the aristocracy of the Xiongnu people (Noin-Ula, Nothern Mongolia) is performed by means of X-ray fluorescent analysis with synchrotron radiation (SRXRF), micro-SRXRF, X-ray absorption (XAFS), scanning electron microscopy, and high-resolution X-ray computed tomography.

INTRODUCTION

In 2006 and 2009, a joint Russian–Mongolian expedition studied burials of the aristocracy of the Xiongnu, a nomadic people who populated the territory of Central Asia in the past.

The excavation site was located in the Noin-Ula mountains of northern Mongolia. The grave fields were at a height of 1500 meters in the Sutszukte river valley. All tumuli were dated to between the first century BC and the first century AD. Thorough studies were completed at three tumuli of the Xiongnu aristocracy (no. 11, 20, and 31). All of these tumuli had been almost completely robbed soon after their construction, so the bodies of the people buried there were missing, along with many valuable items. Nevertheless, a considerable number of metal items (iron, bronze, copper, silver, and gold-plated objects) were found. The depths of the burials were 6 meters (tumulus no. 11), 13 meters (tumulus no. 31) and 18 meters (tumulus no. 20) (1).

These burials are unique primarily in the diversity of excavated organic material: locks and plaits of hair, bone and tooth enamel fragments, plant residue, and textile fragments (Polosmak, 2009). The hair found in the tumuli obviously did not belong to the individuals buried there, as one tumulus might contain up to 40 different plait of hair [2]. But all of the hair discovered in the tumuli belonged to contemporaries of the individuals buried there and are a unique source of information. Analysis of hair as the most abundant material available could shed light on aspects of the culture and lifestyle of the Xiongnu people and their interaction with the environment.

DIAGENESIS OF THE ORGANIC OBJECTS

Hair

Hair is one of the biological tissues most resistant to decomposition [3]. Keratin, the protein of hair, can retain its structure [3–6] for even thousands of years [7]. However, certain changes can occur *post mortem*, including heavy metal contamination and different taphonomic processes.

Hair can absorb and accumulate metal ions of both endogenous (from inner sources, via the hair roots) and exogenous (from external sources in the environment) origin. It is known that the preservation of materials such as skin, hair, and textiles in burial sites is often linked to the presence of metal cations when metal items are located in the immediate proximity [3, 8].

Hair's capacity for absorption results in the accumulation of cations from the environment. For example, studies by I.M. Kempson et al. [9] found high contents of copper in hair (up to 3000 µg/g) after placing it in river water, even though the content of copper in both the water and the hair was only several µg/g.

Possible changes in the elemental composition of hair can result from leaching-out, ion exchange and/or the sedimentation of inorganic compounds [9, 10–13].

There have been many studies of the elemental composition of hair, but such studies of ancient hair are very rare, due to the relatively small amounts of it found among archaeological material. Researchers are most often interested in the reasons behind the abnormally high content of certain chemical elements in hair [3, 14, 15].

A variety of methods are used in studies, including those involving X-rays: X-ray fluorescent analysis [8, 9, 15, 16], X-ray diffraction [3, 15, 17, 18], and X-ray absorption spectroscopy (XANES and EXAFS) [3]. The latter two are very seldom encountered in the literature, due probably to the complexity of organic material and the consequent difficulty of interpreting oscillations in the gathered spectra.

Bones and Tooth Enamel

Unlike the diagenesis of hair, that of bones is well-understood [19]. Bone tissue is 30% organic matter [20]. It is known that collagen, the protein of bone tissue, can persist long after the burial [21–23].

Tooth enamel is even less susceptible to degradation than bone tissue, though it is not completely immune from the diagenetic process [20, 24–26]. The content of organic matter in enamel is 1% [27–29]. The extracellular organic matrix contains several proteins, many of which are specific only to enamel [28, 30, 31].

The samples of tooth crowns found in tumulus no. 20 had degraded dentin, and only the tooth enamel remained.

DEGRADING OF COPPER AND BRONZE ITEMS IN THE BURIAL ENVIRONMENT

Relative to normal levels, an abnormally high content of copper (up to 1.6% by weight) was found in all of the studied samples of hair, tooth enamel, and textile fragments [32–34]. The high levels of iron in the samples can evidently be explained by the effect of the burials' immediate environment: clay with high concentrations of the element's oxides.

Numerous items of metalwork were found at the burial sites, including bronze and copper items. At one time, the barrows probably contained substantial amounts of such items, but they were either looted or destroyed. The hair in the burials was in the immediate proximity of these objects.

The soils in the region are heavy with clay; in addition, the burials' were often flooded with ground water as a result of their location in the river valley. All finds were thus discovered in wet clay [1], which can serve as an environment for the transport of metal cations (the pH of the burial environment was close to neutral).

Since the 1970s, several authors have attempted to shed light on the mechanisms behind the long-term corrosion of objects made of bronze and copper alloys [35]. There are several types of chemical compounds that are likely to form under these conditions: nantokite CuCl under a layer of cuprite Cu_2O [37, 38]; cupric oxide CuO [39]; covellite CuS (when there is an excess of sulfide in the environment) [36, 40, 41]; malachite $Cu_2(CO_3)(OH)_2$ [36, 38, 42]; and atacamite $Cu_2Cl(OH)_3$ [36, 38].

Copper

Copper is an essential chemical element. It is usually present in biological systems as a divalent cation [43]: normally, copper is bound to proteins or other organic compounds; free copper(II) ions are not to be found [44]. The metal is involved in the synthesis of collagen and elastin [45, 46].

Copper plays an important role in the formation and growth of hair and fur [47–49], and in hair pigmentation, via its involvement in the synthesis of melanin [50]. Copper is coordinated by such ligands as amines and thiolates, and by ionized peptides and carboxylates. It is known that hair contains both carboxyl and amine groups (up to 16% nitrogen), and is 11–18% S-containing amino acids (cysteine and methionine) [51].

Normal copper content in hair ranges from 1 to 100 μg/g, while acute copper poisoning can result in concentrations as high as 1200–1300 μg/g [52, 53].

It is known that the Xiongnu used copper and bronze items for household needs, including cooking [54, 55], so there could well have been an endogenous effect on the copper content in a person's hair during his or her lifetime.

One of the main aims of our study was thus to determine sources of elevated concentrations of copper in hair (and other objects of organic origin) and decide whether they were endogenous or exogenous.

EXPERIMENTAL

SRXRF

All measurements were done on the experimental SRXRF analysis station of the VEPP-3 electron–positron storage ring at the Budker Institute of Nuclear Physics, Siberian Branch, Russian Academy of Sciences. The VEPP-3 parameters are $E_{ex} = 2$ GeV, $B = 2$ T, and $I_e = 100$ mA.

Measurements were done in the open air. The SRXRF analysis station is equipped with a monochromator which is a Si (111) channel-cut monocrystal. The maximum beam size is 2×5 mm^2; the energy of excitation is 8–42keV. The elements detected range from K to U. The energy resolution of the semiconductor Si (Li) detector is 145 eV at 5.9 keV.

The following finds of organic origin were examined: from tumulus no. 20, nine locks of human hair (sample nos. 4–12) and two samples of tooth enamel; from tumulus no. 31, two locks of hair (sample nos. 3

and 13), a fragment of woolen cloth, a fragment of human bone, two local samples of clay, and two samples of millet grains; from tumulus no. 11, one fragment of human bone. An analysis was also performed for several human bone fragments from burials of Xiongnu commoners (barrow nos. 1, 36, 64, 70, 71, and 77).

Sample Processing

Hair samples were washed several times in deionized water, then placed in ethanol for two minutes and washed again in deionized water to remove any surface contaminants. The samples were then dried at a temperature of 45°C, after which they were ground in an agate mortar for 20 min; 20 mg of the dry powder was pressed into tablets 8 mm in diameter using a hydraulic press (mass per unit area is 0.04 g/cm^2). The tablets were placed between two layers of mylar and mounted in a fluoroplastic ring.

Samples of clay and woolen cloth were also prepared following the same procedure.

Additional preprocessing that included mechanical surface cleaning, abrading, washing in distilled water, and a sodium acetate buffer was used for the bone and tooth tissue samples [56].

Concentrations of the chemical elements in the samples were calculated using external standards. The internationally certified reference materials were three standard human hair samples, NCS ZC 81002b Human Hair (China), NCS DC 73347 Human Hair (China), and NIES 5 Human Hair (Japan); beef liver standard NIST 1577 Bovine Liver (United States) was also used to assay the concentrations of copper, large quantities of which were contained in the hair samples [57]. Clay samples were assayed against standard reference samples 381-93 BIL-1 Lake Baikal Sediment (Russia), NIES 2 Pond Sediment (Japan), and the standard soil sample IAEA Soil 7.

The samples of tooth enamel and bones were assayed using IRMM BCR 032 Phosphorite (United States), a sedimentary rock containing mostly phosphate minerals of the apatite group (the main mineral component of teeth and bones).

High Resolution X-ray Computed Tomography

High-resolution X-ray computed tomography was used to visualize inhomogeneities such as pores and inclusions in the archaeological samples of hair on the micrometer scale. This technique was applied on the Microscopy and Microtomography Station of the VEPP-3 electron-positron storage ring at the Budker Institute of Nuclear Physics' Siberian Center for Synchrotron and Terahertz Radiation.

Scanning Electron Microscopy (SEM)

A Hitachi Type II S-3400N scanning electron microscope was used to study the morphology and distribution of chemical elements in the hair samples (in cross section).

X-ray Absorption Spectroscopy (XANES and EXAFS)

XANES and EXAFS spectra (transmission and fluorescent) of the Cu K-edge for our samples were obtained on the VEPP-3 EXAFS Spectroscopy Station. A channel-cut Si (111) monocrystal was used as a monochromator. All EXAFS and XANES spectra were registered with steps of ~1.5 eV and ~0.3 eV, respectively.

All of the EXAFS spectra were processed according to the standard procedure in [58, 59]. Curve fitting for calculations of the interatomic distances and coordination numbers was performed using the EXCURV92 software [60] for $k^2\chi(k)$ in the wavenumber interval of 3.0−12.0 Å^{-1} after prelimiary Fourier filtration, using known X-ray results for bulk samples.

Micro-SRXRF

Micro-SRXRF analysis [61] was applied on the VEPP-3 SRXRF Elemental Analysis Station in confocal geometry, allowing us to scan a hair both along its length and in cross section without destroying this unique archaeological material.

The spatial resolution of the X-ray confocal microscope was on the order of 10 μm. The method was used to describe the distribution of copper in the cross section of a hair from tumulus no. 20. The hair sample was placed in slots cut in a Teflon carrier ring, stretched, and fixed in position. The energy of excitation was 19 keV. The thickness of this particular hair sample was on the order of 100 μm; the scanning step was 5 μm; and the time of spectrum accumulation at each point was 150 s.

RESULTS AND DISCUSSION
SRXRF

All results obtained via SRXRF are presented in Table 1 (the limits of detection for Cr, Ni, Se, Rb and Hg were 0.70, 0.40, 0.20, 0.09 and 0.25 μg/g, respectively). All samples of human hair found in the barrows of the aristocracy display extremely high levels of copper (up to 1.6% by weight) with low contents of zinc, relative to the results for modern man. The normal copper content in the hair of people today falls in the interval of 1.06 to 146 μg /g [32−34]. Elevated copper levels were also found in the samples of woolen cloth and tooth enamel from the burials of the aristocracy, while the content of copper in the clay did not exceed normal levels.

Table 1. Content of chemical elements in samples of organic origin from burials of the Xiongnu aristocracy, µg/g

Samples	K	Ca	Cr	Mn	Fe	Ni	Cu	Zn	Se	Br	Rb	Sr	Hg	Pb
Normal content [32–34]							1.06–146	53–280						
Human hair no. 10, tumulus 20	480	2700	<DL	15	3100	35	**16000**	**85**	<DL	4.3	4.3	10	<DL	32
Human hair no. 8, tumulus 20	370	2100	<DL	9.2	2000	33	**12000**	**61**	<DL	4.4	1.5	6.8	18	540
Human hair no. 5, tumulus 20	580	2700	<DL	16	2500	32	**4300**	**46**	0.20	3.2	4.1	9.6	9	110
Human hair no. 12, tumulus 20	140	2100	3.3	15	780	5.3	**1000**	**15**	<DL	3.2	<DL	10	56	33
Human hair no. 9, tumulus 20	720	4100	4.9	17	2000	20	**9400**	**84**	0.26	4.3	2.5	10	6	8
Human hair no. 7, tumulus 20	320	2500	7.3	22	1600	16	**5800**	**47**	0.28	2.5	2.9	11	9	7
Human hair no. 6, tumulus 20	410	2000	5.1	19	1400	16	**1000**	**34**	0.38	2.2	3.5	9.7	4	13
Human hair no. 4, tumulus 20	220	4300	1.6	6.4	1200	11	**6800**	**44**	0.30	2.6	1.5	15	<DL	13
Human hair no. 3, tumulus 31	500	3700	<DL	290	17000	150	**11000**	**97**	<DL	7.8	<DL	37	5000	150
Human hair no. 13, tumulus 31	400	2600	14	140	2600	5.7	**6000**	**140**	0.39	3.6	<DL	14	4	15
S_r, %, relative standard deviation	18	15	21	8	6	19	11	6	14	12	17	18	21	19
Normal content [64]							6.0–16	450–700						
Tooth enamel no. 1, tumulus 20	600	440000	8	100	3400	<DL	**710**	**700**	<DL	1.0	<DL	190	<DL	60
Tooth enamel no. 2, tumulus 20	230	170000	6	28	1800	2.9	**170**	**360**	1.3	1.5	<DL	82	<DL	42
S_r, %	20	27	22	14	10	15	10	8	16	14		16		22
Normal content [62, 63]							2.0–400	104–837						
Human bone no. 1, tumulus 31	700	350000	90	5800	54000	<DL	**3.2**	**110**	12	2.6	3.4	800	<DL	8
Human bone no. 2, tumulus 11	330	200000	1.9	1100	1600	13	**20**	**680**	<DL	7.3	2.6	600	<DL	4.1
S_r, %	21	27	19	14	13	16	9	9	16	16	15	15		20
Millet grain no. 1, tumulus 31	4600	15000	7.2	170	15000	11	**51**	**45**	1.4	3.6	31	70	<DL	50
Millet grain no. 2, tumulus 31	8000	4700	4.5	110	12000	9	**45**	**24**	1.7	3.4	40	44	<DL	45
S_r, %	18	16	19	10	12	18	6	6	14	10	14	15		20
Woolen cloth no. 14, tumulus 31		2500	6	70	6900	28	**390**	**66**	0.49	1.4	0.11	14	34	16
S_r, %		15%	20%	12%	10%	18%	6%	7%	16%	16%	17%	16%	20%	22%
Lake clay no. 1, tumulus 31		4100	<DL	330	33000	<DL	**28**	**100**	<DL	<DL	90	140	0.6	28
Clay no. 1, tumulus 31		2000	<DL	350	43000	<DL	**75**	**220**	<DL	<DL	110	120	<DL	32
S_r, %		20		15	16		12	10	14		16	16	20	19

Table 2. Results from washing with nonionic detergent and EDTA (hair samples 3 and 8)

	S	K	Ca	Mn	Fe	Cu	Zn
Thickness of hair = 85−110 μm							
Human hair no. 3, barrow no. 31	47000	250	1000	73	5300	5600	43
Human hair no. 3 after washing with Triton X-100 and EDTA	46800	95	950	35	4500	2800	39
Thickness of hair, 65−80 μm							
Human hair no. 8, barrow no. 20	39000	200	2100	8.3	2200	12000	43
Human hair no. 8 after washing with Triton X-100 and EDTA	36000	90	500	1.2	750	6300	23
Sr %, relative standard deviation	30	18	16	20	14	16	10

The normal Bronze Age levels of copper in bones [62, 63] and tooth enamel [64] are also presented in Table 1.

Additional washing was used to distinguish exogenous and endogenous influences for hair samples with high copper contents. We chose a procedure that used nonionic detergent (Triton X-100) with further ethylene diamine tetraacetate treatment (EDTA), since this removes exogenous copper from hair samples most efficiently [65, 66]. As can be seen from Table 2, more than half the copper content is washed out of the hair samples, indicating the exogenous origin of the element's accumulation in the hair.

High Resolution X-ray Computed Tomography

The results from high resolution X-ray computed tomography are shown in Fig. 1 as a 3D image and a plain projection of a hair stem (from tumulus no. 20). It can be seen that the hair sample was hollow along its full length. A similar situation was observed in [15] in studying the hair of a mummy: the inner structure of the hair was missing. The inner structure (medulla) of hair consists mostly of the lipid fraction that is least resistant to microbiological and chemical actions [3, 13, 67, 68] and is especially subject to biodegradation. Unlike the lipid component, hair keratin can last for even thousands of years [4–6], so we may assume here that we were seeing only the keratin carcass of the hair.

Scanning Electron Microscopy (SEM)

Figure 2 shows our SEM results for a human hair sample from tumulus no. 20. Data is presented only for the elements with the highest concentrations. It can be seen that sulfur is distributed uniformly (we know that hair contains S-containing amino acids, cysteine and methionine). Aluminum and silicon were deposited on the hair surface as a result of it being buried in clay, as has also been noted by other researchers [9, 15].

Copper is distributed uniform over the cross section of hair, allowing us to assume it had an exogenous source (in the external environment).

Little is known regarding the reactivity of Cu with respect to hair keratin fibers. It has been reported that Cu^{2+} ions are bound mostly to the carboxylic groups of keratin and lipids.

XANES

The XANES and EXAFS spectra of the *K*-edge of copper for the hair and tooth enamel samples are shown in Figs. 3 and 4, respectively.
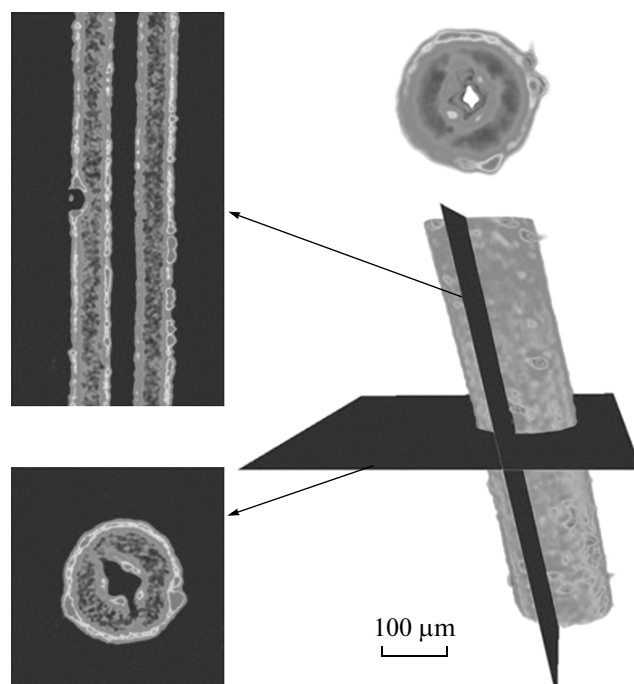

Fig. 1. Human hair from the burial of Xiongnu aristocracy (tumulus no. 20). Results from high-resolution X-ray computed tomography.
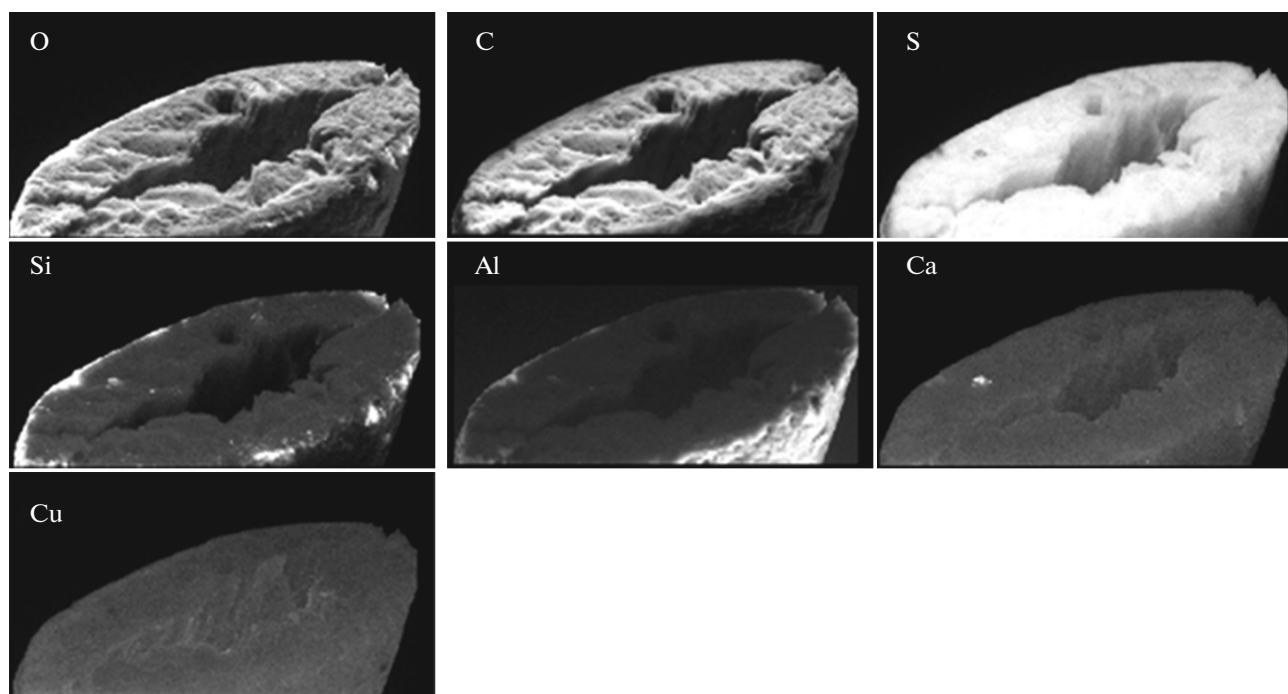
Fig. 2. Distribution of chemical elements in the cross section of a hair sample from the burial of Xiongnu aristocracy (tumulus no. 20). SEM results.
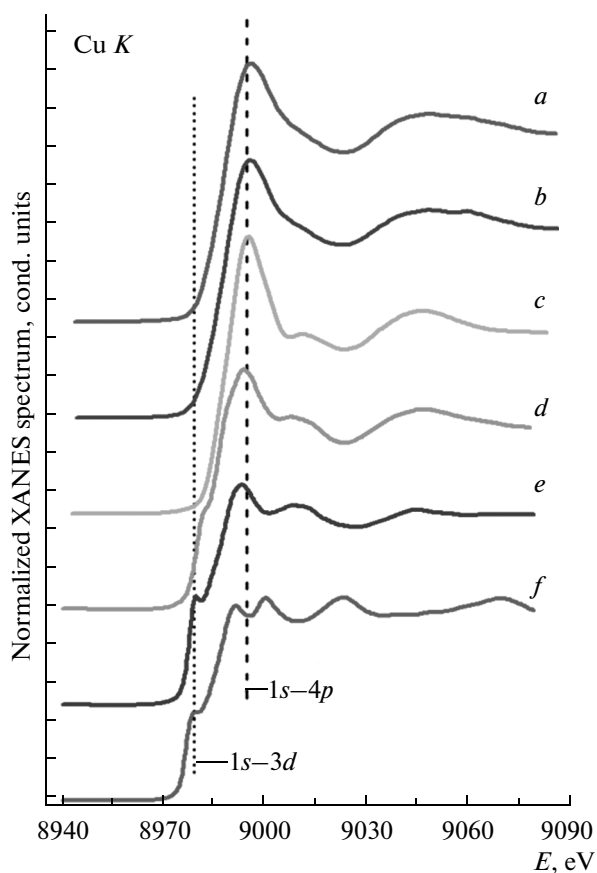

Fig. 3. XANES spectra: (*a*) human hair from tumulus no. 20; (*b*) tooth enamel from tumulus no. 20; (*c*) Cu−FeO$_x$ · (H$_2$O)$_y$ catalyst (mixed oxide system), distorted octahedron; (*d*), (*e*), (*f*) standard samples of CuO, Cu$_2$O, and Cu, respectively.

Figure 3 shows normalized XANES results (Cu K-edge) for (*a*) samples of hair and (*b*) tooth enamel from the burial of Xiongnu aristocracy (tumulus no. 20), along with standards of (*f*) copper foil, (*d*, *e*) copper oxides, and (*c*) a model Cu−FeO$_x$ · (H$_2$O)$_y$ catalyst.

A detailed comparative analysis of our XANES spectra and data from the literature (for inorganic and metal-organic copper compounds) allows us to suggest that the XANES spectra of the hair and tooth enamel are almost identical; minor differences are observed in the locations and forms of peaks. The local copper surroundings were obviously identical for these samples. No signs were found of either metallic copper or its oxides (the Cu$_2$O and/or CuO phases).

Both XANES spectra of our samples have the most in common with the spectrum obtained for Cu−FeO$_x$ · (H$_2$O)$_y$ catalyst (a mixed oxide system) [69]. It was established earlier that the copper in such catalysts is in the Cu^{2+} charge state and a distorted octahedral coordination (4 + 2). Such coordination is characteristic of both inorganic mixed oxides and hydroxide copper nanosystems (nonstoichiometric systems or mixed phases) and metal−organic copper complexes (with such ligands as oxygen and/or nitrogen).

The copper in our samples of hair and tooth enamel was probably in the Cu^{2+} charge state and surrounded by ligands of light atoms (O/N) in distorted octahedral geometry (4 + 2).
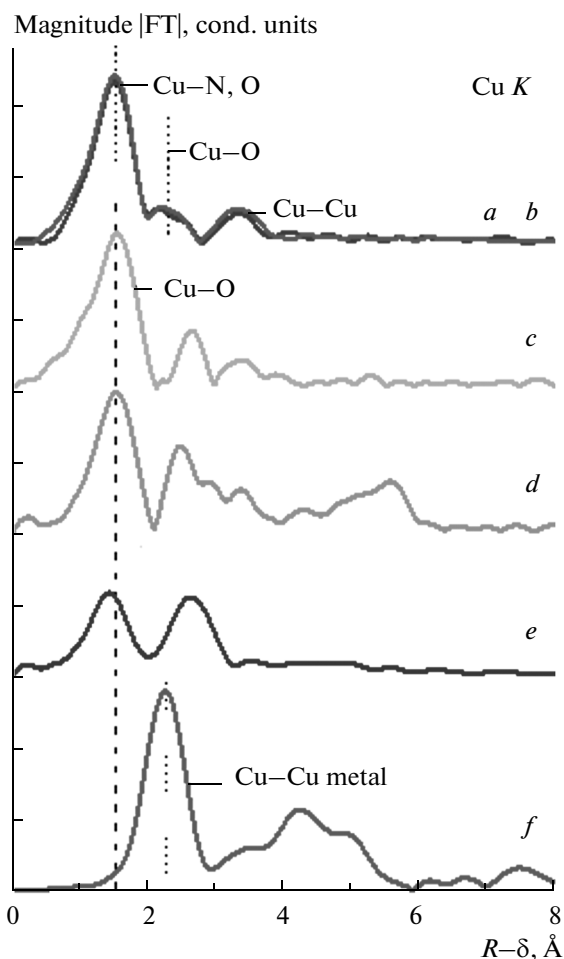
Fig. 4. Radial distribution function showing the immediate environment of copper atoms in the following samples: (*a*) human hair from tumulus no. 20; (*b*) tooth enamel from tumulus no. 20; (*c*) Cu−FeO$_x$ · (H$_2$O)$_y$ catalyst (mixed oxide system), distorted octahedron; (*d*), (*e*), (*f*) standard samples of CuO, Cu$_2$O, and Cu, respectively.

Fig. 5. Cu distribution in the cross section of a hair sample (barrow no. 20) with a scanning step of 5 μm.

images). The distribution of copper was almost uniform (the light area covering a considerable part of the cross section), supporting our assumption of its exogenous origin [8, 70].

EXAFS

Figures 4*a*, 4*b* show the radial distribution functions for our samples. Three distinct peaks are visible: the first peak (at 1.2−2.0 Å) corresponds to Cu−O and Cu−N distances, while other two peaks with lower amplitudes (in the regions of ~2.0−2.8 Å and ~2.8−4.0 Å) can be attributed to the Cu−O distances (to the more distant vertices of the octahedron) and those of Cu−Cu, respectively.

All of the data from XANES and EXAFS agree with those in the literature for Cu complexes with amino acids, including the data on interatomic distances and types of coordination [35, 46].

Micro-SRXRF

Figure 5 shows the distribution of copper in a hair cross section obtained via micro-SRXRF (scanning step, 5 μm). The hair was hollow inside (as in the SEM
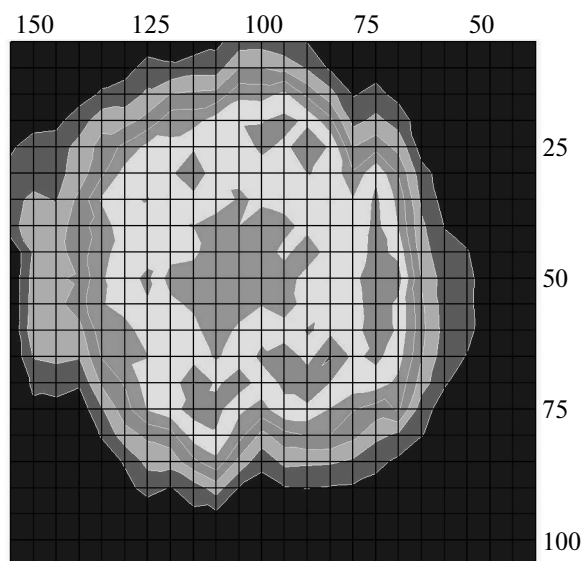
CONCLUSIONS

According to the SRXRF results, all hair samples from the burials of the aristocracy of the Xiongnu people display abnormally high copper contents.

Considering the pH of the surroundings and other conditions of the burials, our XAFS results, and the data from the literature, we may assume that the presence inorganic compounds like pure copper oxides (I and II), sulfides, sulfates, chlorides, phosphates, silicates, and hydrocarbonates (which might have been found) can be ruled out. In addition, the EXAFS results indicate that the first interatomic distance belongs to Cu−O and Cu−N; the second, to the Cu−O distance in a distorted octahedral geometry.

Even though such inorganic copper compounds as mixed oxide and hydroxide systems (nonstoichiometric or mixed different phases) cannot be completely ruled out, Cu is in this case probably coordinated by functional groups of amino acids. Our results fit well with models describing Cu complexes with amino acids, indicating the binding of Cu to such proteins as hair keratin or glycoproteins.

The copper content in the hair from the burials of the Xiongnu people considerably exceed that in normal human hair even for cases of acute copper poisoning. The homogeneity of the copper distribution for the hair cross section in the SEM and micro-SRXRF images testifies to a probable external source of its intake by the hair. The high copper concentrations in

the hair of the Xiongnu people can apparently be explained by the effects of the environment in the area of the burials, due to the proximity of copper and bronze items. An endogenous source of copper intake by the hair is in this case unlikely.

ACKNOWLEDGMENTS

REFERENCES

1. Polos'mak, N.V., *Nauka Iz Pervykh Ruk*, 2009, no. 2, pp. 82−91.

2. Rudenko, S.I., *Kul'tura khunnov i Noinulinskie kurgany* (Xiongnu Culture and Noinulinskie Barrows), Moscow: USSR Acad. Sci., 1962.

3. Bertrand, L., Doucet, J., Dumas, P., Simionovici, A., Tsoucaris, J., and Walter, P., *J. Synchrotron Rad.*, 2003, vol. 10, pp. 387−392.

4. Busson, B., *PhD Thesis*, Paris Univ., 1998.

5. Gillespie, J.M., *Science*, 1970, vol. 170, pp. 1100−1102.

6. Ryder, M.L., *Nature*, 1974, vol. 249, pp. 190−192.

7. Macko, S.A. and Engel, M.H., *New Sci. Mag.*, 1998, no. 2164, p. 34.

8. Bertrand, L., Vichi, A., Doucet, J., Walter, Ph., and Blanchard, Ph., *J. Archaeol. Sci.*, 2014, vol. 42, pp. 487−499.

9. Kempson, I.M., Skinner, W.M., and Martin, R.R., *Archaeometry*, 2010, vol. 52, pp. 450−66.

10. Turner-Walker, G., *Conservator*, 1998, vol. 22, pp. 26−35.

11. Trueman, C.N., Benton, M.J., and Palmer, M.R., *Palaeogr., Palaeoclimatol., Palaeoecol.*, 2003, vol. 197, pp. 151−169.

12. Polacheck, I., *Proc. COST Action G8 Working Group Meeting*, Jerusalem, 2005, p. 265.

13. Wilson, A.S., Dixon, R.A., Edwards, H.G.M., Farwell, D.W., Janaway, R.C., Pollard, A.M., and Tobin, D.J., *Chungar, Revista de Antropologia Chilena*, 2001, vol. 33, pp. 293−296.

14. Martin, R.R., Biesinger, M.C., and Skinner, W.M., *Can. J. Anal. Sci. Spectrosc.*, 2001, vol. 46, pp. 108−110.

15. Mansilla, J., Bosch, P., Menéndez, M.T., Pijoan, C., Flores, C., López, M.C., Lima, E., and Leboreiro, I., *Cungar, Revista de Antropologia Chilena*, 2011, vol. 43, pp. 293−302.

16. Valkovic, V., *Human Hair*, vol. 1: *Fundamentals and Methods for Measurement of Elemental Composition*, Boca Raton: CRC Press, 1988.

17. Fraser, R.D.B., MacRae, T.P., Rogers, G.E., and Filshie, B.K., *J. Molec. Biol.*, 1963, vol. 7, pp. 90−94.

18. Fraser, R.D.B., MaCrae, T.P., Parry, D.A.D., and Suzuki, E., *Proc. Nat. Acad. Sci. USA*, 1986, vol. 83, pp. 1179−1183.

19. Ambrose, S.H., *J. Archaeol. Sci.*, 1990, vol. 17, pp. 431−451.

20. Kohn, M.J., Schoeninger, M.J., and Barker, W.W., *Geochim. Cosmochim. Acta*, 1999, vol. 63, pp. 2737−2747.

21. Armstrong, W.G., Halstead, L.B., Reed, F.B., and Wood, L., *Philos. Trans. Roy. Soc. London B*, 1983, vol. 301, pp. 301−343.

22. Stafford, T.W., Jr., Brendel, K., and Duhamel, R.C., *Geochim. Cosmochim. Acta*, 1988, vol. 52, pp. 2257−2267.

23. Gillespie, R., Hedges, R.E.M., and Wand, J.O., *J. Archaeol. Sci.*, 1984, vol. 11, pp. 165−170.

24. Lee-Thorp, J.A. and Van der Merwe, N.J., *J. Archaeol. Sci.*, 1991, vol. 18, pp. 343−354.

25. Trueman, C.N. and Tuross, N., in *Phosphates: Geochemical, Geobiological, and Materials Importance, Reviews in Mineralogy and Geochemistry*, Kohn, M.J., Rakovan, J., and Hughes, J.M., Eds., Washington, Mineral. Soc. Amer., 2002, pp. 489−521.

26. Dauphin, Y. and Williams, C.T., *Comptes Rendus Palevol.*, 2004, vol. 3, pp. 583−590.

27. Hillson, S., *Teeth, Cambridge: Manuals in Archaeology*, Cambridge, Cambridge Univ. Press, 1986.

28. Wang, L., Tang, R., Bonstein, T., Orme, C.A., Bush, P.J., and Nancollas, G.H., *J. Phys. Chem.*, 2005, vol. 109, pp. 999−1005.

29. Pan, H., Tao, J., Yu, X., Fu, L., Zhang, J., Zeng, X., Xu, G., and Tang, R., *J. Phys. Chem.*, 2008, vol. 112, pp. 7162−7165.

30. Termine, J.D., Belcourt, A.B., Christner, P.J., Conn, K.M., and Nylen, M.U., *J. Biol. Chem.*, 1980, vol. 255, pp. 9760−9768.

31. Robinson, C., Kirkham, J., Brookes, S.J., Bonass, W.A., and Shore, R.C., *Int. J. Develop. Biol.*, 1995, vol. 39, pp. 145−152.

32. Altaf, W.J., Akanle, O.A., Admans, L.L., Beasley, D., Butler, C., and Spyrou, N.M., *J. Radioanal. Nuclear Chem.*, 2002, vol. 259, pp. 493−498.

33. Trojanowski, P., Trojanowski, J., Bokiniec, M., and Antonowicz, J., *Baltic Coastal Zone*, 2009, vol. 13, pp. 163−186.

34. Goss, H. and Green, M.M., *Sci., Rep. Lett.*, 1955, vol. 122, pp. 330−331.

35. Deschamps, P., Zerrouk, N., Nicolis, I., Martens, T., Curis, E., Charlot, M.-F., Girerd, J.J., Prangé, T., Bénazeth, S., Chaumeil, J.C., and Tomas, A., *Inorg. Chim. Acta*, 2003, vol. 353, pp. 22−34.

36. Quaranta, M. and Sandu, I., *Proc. 9th Int. Conf. on NDT of Art*, Jerusalem, 2008, pp. 1−8.

37. Bernard, M.C. and Joiret, S., *Electrochim. Acta*, 2009, vol. 54, pp. 5199−5205.

38. Pourbaix, M., *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Oxford, etc.: Cebelcor; Brussels: Pergamon Press, 1966.

39. Fu, Q., Jin, P., Ling, X., Zhang, Sh., Sun, W., and Xia, Y., *Int. J. Corrosion*, 2012, vol. 2012, pp. 1−6.

40. Xu, S., Wang, Q., Cheng, J.H., Meng, Q.H., and Jiao, Y., *Powder Technol.*, 2010, vol. 199, pp. 139−143.

41. Jin, P.J., Yao, Z.Q., Zhang, M.L., Li, Y.H., and Xing, H.P., *J. Raman Spectrosc.*, 2010, vol. 41, pp. 222−225.

42. McCann, L.I., Trentelman, K., Possley, T., and Golding, B., *J. Raman Spectrosc.*, 1999, vol. 30, pp. 121−132.

43. Uau, R., Olivares, M., and Gonzalez, M., *Am. J. Clin. Nutr.,* 1998, vol. 67, p. 952S−959S.

44. Copper and human health − a review, *Technical Note no. 34*, Copper Development Assoc., 1984,

45. Kałuŝa, J., Jeruszka, M., and Brzozowska, A., *Ann. Nat. Inst. Hygiene*, 2001, vol. 52, pp. 111−118.

46. Nicolis, I., Deschamps, P., Curis, E., Corriol, O., Acar, V., Zerrouk, N., Chaumeil, J.-C., Guyon, F., and Bénazeth, S., *J. Synchrotron Rad.*, 2001, vol. 8, pp. 984−986.

47. Robbins, C.R., *Chemical Composition of Different Hair Types, in Chemical and Physical Behavior of Human Hair*, Berlin, Heidelberg: Springer, 2012, pp. 105−176.

48. Pyo, H.K., Yoo, H.G., Won, C.H., Lee, S.H., Kang, Y.J., Eun, H.Ch., Cho, K.H., and Kim, K.H., *Arch. Pharm. Res.*, 2007, vol. 30, pp. 834−839.

49. Kempson, I., Skinner, W.M., and Kirkbride, K.P., *J. Toxicol. Environ. Health Part B: Crit. Rev.*, 2007, vol. 10, pp. 611−622.

50. Slominski, A., Wortsman, J., Plonka, P.M., Schallreuter, K.U., Paus, R., and Tobin, D.J., *J. Invest. Dermatol.*, 2005, vol. 124, pp. 13−21.

51. Hinners, T.A., Terrill, W.J., Kent, J.L., and Colucci, A.V., *Enrviron. Health Perspect.*, 1974, vol. 8, pp. 191−199.

52. Nogué, S., Sanz, P., Munne, P., and Gadea, E., *Bull. World Health Org.,* 2000, vol. 78, p. 4.

53. Spitalny, K., Brondum, J., Vogt, R., Sargent, H., and Kappel, S., *Pediatrics*, 1984, vol. 74, pp. 1103−1106.

54. Fielstroop, F.A., *Collected Articles of Anthropologic Group of Kazakhstan Expedition of USSR*, 1930, no. 12.

55. Eliade, M., *Asian Alchemistry*, Paidos, Barcelona, 1992.

56. Lambert, J.B., Weydert, J.M., Williams, S.R., and Buikstra, J.E., *J. Archaeol. Sci.*, 1990, vol. 17, pp. 453−468.

57. Trunova, V.A. and Zvereva, V.V., *J. Struct. Chem.*, 2008, vol. 49, pp. 211−216.

58. Kochubey, D.I., *EXAFS-Spectroscopy of Catalysts*, Novosibirsk: Nauka, 1992.

59. Klementev, K.V., *J. Phys. D Appl. Phys.*, 2001, vol. 34, pp. 209−217.

60. Binsted, N., Campbell, J.V., Gurman, S.J., and Stephenson, P.C., *EXCURV92 Program Code*, SERC Daresbury Lab., 1991.

61. Dar'in, F.A. and Rakshun, Ya.V., *Nauch. Vestn. Novosib. Gos. Tekhn. Univ.*, 2013, no. 2(51), pp. 119−120.

62. Grattan, J., Abu Karaki, L., Hine, D., Toland, H., Gilbertson, D., Al-Saad, Z., and Pyatt, B., *Mineral. Mag.*, 2005, vol. 69, pp. 653−666.

63. Güner, C., Aliyev, V., Atamtürk, D., Duyar, İ., and Söylemezoğlu, T., *Eurasian J. Anthropol.*, 2011, vol. 2, pp. 27−39.

64. Reitznerová, E., Amarasiriwardena, D., Kopčáková, V., and Barnes, R.M., *Fresenius J. Anal. Chem.*, 2000, vol. 367, pp. 748−754.

65. Buckley, R.A. and Dreosti, I.E., *Amer. J. Clin. Nutrition*, 1984, vol. 40, pp. 840−846.

66. McKenzie, J.M., *Amer. J. Clin. Nutrition*, 1978, vol. 31, pp. 470−476.

67. Wilson, A.S., Dodson, H.I., Janaway, R.C., Pollard, A.M., and Tobin, D.J., *British J. Dermatol.*, 2007, vol. 154, pp. 450−457.

68. Kenney, D., *Cosmet. Toiletries*, 1981, vol. 96, pp. 121−122.

69. Minukova, T.P., Hasin, A.A., Baronskaya, N.A., Plyasova, L.M., Kriventsov, V.V., Rozhko, E.S., Filonenko, G.A., and Yurjeva, T.M., *Kinet. Catal.*, 2012, vol. 53, pp. 527−533.

70. Bartkus, L., Amarasiriwardena, D., Arriaza, B., Bellis, D., and Yañez, J., *Microchem. J.,* 2011, vol. 98, pp. 267−274.

Translated by N. Bokareva