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DETERMINATION OF THE ORIGIN OF THE MEDIEVAL GLASS BRACELETS DISCOVERED IN DUBNA (MOSCOW REGION, RUSSIA), USING THE NEUTRON ACTIVATION ANALYSIS

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Дмитриева С. О. и др. E18-2016-88
Определение происхождения средневековых стеклянных браслетов, найденных в Дубне (Московская обл., Россия), с использованием нейтронного активационного анализа

Работа посвящена определению происхождения средневековых стеклянных браслетов посредством использования метода нейтронного активационного анализа (НАА). В процессе раскопок на месте древнерусских городов среди подобных археологических артефактов находят изделия как созданные в древнерусских мастерских, так и привезенные из Византии. Авторы статьи доказывают древнерусское происхождение стеклянных браслетов домонгольского периода, найденных на городище Дубна. Выводы авторов основаны на анализе данных о химическом составе избранной группы из 10 фрагментов браслетов, подвергнутых НАА на реакторе ИБР-2 (ЛНФ ОИЯИ).

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Препринт Объединенного института ядерных исследований. Дубна, 2016

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Determination of the Origin of the Medieval Glass Bracelets Discovered in Dubna (Moscow Region, Russia), Using the Neutron Activation Analysis

The work is dedicated to the determination of the origin of archaeological finds from medieval glass using the method of neutron activation analysis (NAA). Among such objects we can discover things not only produced in ancient Russian glassmaking workshops but also brought from Byzantium. The authors substantiate the ancient Russian origin of the medieval glass bracelets of pre-Mongol period, found on the ancient Dubna settlement. The conclusions are based on the data about the glass chemical composition obtained as a result of NAA of ten fragments of bracelets at the IBR-2 reactor, FLNP, JINR.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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In the work process, the first comprehensive study of glass bracelets of pre-Mongol period, found on the territory of ancient Russian settlement Dubna, was carried out. The Dubna fortress was founded in the first half of the XII century on the border of the Rostov-Suzdal principality and survived until Mongol invasion in 1238. Two types of archaeological objects of ancient Dubna can be distinguished: imported things, which came to Dubna from other countries, and objects created in Russia, as a rule, using Byzantine models (crosses-enkolpion, stamps-molybdoboyllon, trading seals). Glass bracelets are significant and not yet explored group of these finds. These are glass bracelets of pre-Mongol period, found during excavations of Dubna's horizon of XII–XIII centuries [1] (see Fig. 1).

The comparative-stylistic analysis of the external characteristics of the medieval glass bracelets allows only to determine approximately their origin. While the study of the glass chemical composition allows making valid conclusions about Byzantine or the ancient Russian origin, as well as making assumptions about the peculiarities of trading and social relations of Dubna's settlement.

Fig. 1. Glass bracelets from the exposition of the Museum of Archaeology and Local History of Dubna. The photos are provided by the Museum of Archaeology and Local History of Dubna

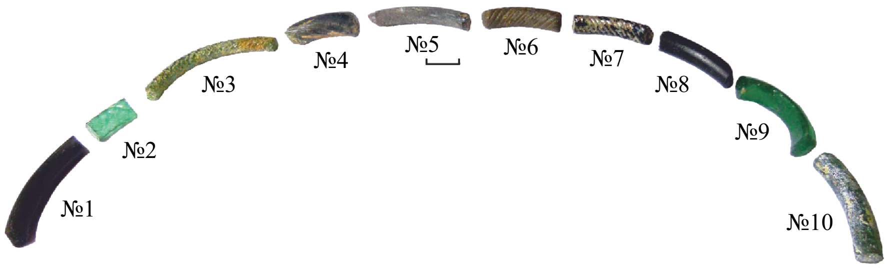

Fig. 2. The fragments of glass bracelets from the Dubna settlement

The “Nasledie” Moscow Regional Public Fund of Historical and Local Historical Researches and Humanitarian Initiatives provided a special group of ten pieces of bracelets to study the chemical composition of glass (see Fig. 2). The elemental composition was determined using the reactor neutron activation analysis. NAA is widely used in archaeology [2] and in the analysis of medieval glass [3]. As a result of the experiment, the data on the qualitative and quantitative composition of the elements in the investigated group were obtained.

The concentrations of these elements have been recalculated as oxides for comparison with data about the chemical composition of the Russian and Byzantine glass bracelets found in the cities of Vladimir-Suzdal Rus’ [4] (ancient Russian Dubna was located on the border of the Rostov-Suzdal principality), as well as Byzantine bracelets found in Romania [5].

As a result of the NAA, 45 elements were found: Na, Mg, Si, S, Cl, K, Ca, Sc, Ti, Cr, Mn, Fe, Ni, Co, Zn, Se, As, Br, Rb, Sr, Zr, Nb, Mo, Ag, In, Sb, Ba, Cs, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Yb, Hf, Ta, W, Au, Hg, Th, U. The elements with the most significant concentrations were selected to analysis: Na, Mg, Si, K, Ti, Mn, Fe, Ca [6].

Modern researchers distinguish several types of medieval glass, depending on the main glass-forming substances (see Table 1).

Table 1. The chemical composition of the Byzantine, West-European, and ancient Russian bracelets found on the territory of the Vladimir-Suzdal principality. The table is based on A.V. Liadova’s research data

№	Origin	Type of glass composition	Na_2O, %	CaO, %	K_2O, %	PbO, %
1	Byzantine	Na-Ca-Si	14–20, 4	10–20, 5	2–3, 7	0–0.9
2	West-European	K-Ca-Si	0–2	19–32	7–9, 4	0–0.17
3	Ancient Russian	K-Pb-Si	0–0.4	0–3	4–20	10–44
4	Ancient Russian	Pb-Si	0–0.1	0.1–3.3	0–1.5	36–60

Table 2. The chemical composition of the pre-Mongol bracelets from Dubna

Sample, №	Type of glass composition	R_2O	RO	R_2O/RO	K_2O/Na_2O	CaO/Na_2O	(Na_2O+CaO)/K_2O	Na_2O	MgO	SiO_2	K_2O	TiO_2	MnO	FeO	CaO	Sum of oxides	PbO_{theor}
		mg/kg	mg/kg					%	%	%	%	%	%	%	%	%	%
1	3	410100	20800	20	401	19.4	0.05	0.10	0.10	34	41	0.09	0.006	0.2	2.0	78	22
2	3	532900	14600	37	157	3.9	0.03	0.34	0.15	33	53	0.14	0.335	0.7	1.3	89	11
3	4	26900	1820	15	12	0.5	0.13	0.21	0.07	19	2	0.06	0.005	0.2	0.1	22	78
4	3	510500	7190	71	187	2.4	0.02	0.27	0.06	30	51	0.11	0.022	3.5	0.7	86	14
5	3	465500	19800	24	447	18.2	0.04	0.10	0.09	36	46	0.08	0.005	0.2	1.9	85	15
6	4	15400	2110	7	8	0.7	0.22	0.17	0.08	20	1	0.05	0.003	1.3	0.1	23	77
7	3	361900	12800	28	425	14.1	0.04	0.09	0.08	31	36	0.08	0.004	0.3	1.2	69	31
8	4	15000	1850	8	9	0.7	0.20	0.15	0.07	22	1	0.05	0.004	1.6	0.1	25	75
9	4	13000	1270	10	3	0.3	0.42	0.32	0.03	16	1	0.06	0.001	0.1	0.1	18	82
10	4	17000	1770	10	8	0.5	0.19	0.19	0.07	17	2	0.05	0.003	0.2	0.1	19	81

Sample, №	Type of glass composition	Continuation															
		Mass fraction, mg/kg															
		Na	Na_2O	Mg	MgO	Si	SiO_2	K	K_2O	Ti	TiO_2	Mn	MnO	Fe	FeO	Ca	CaO
1	3	378	1020	585	968	161000	343300	170000	409100	560	930	47	61	1690	2170	14200	19800
2	3	1250	3370	900	1489	155000	330500	220000	529500	810	1350	2600	3350	5200	6680	9350	13100
3	4	773	2080	450	744	88400	188500	10300	24800	340	570	40	51	1340	1720	775	1080
4	3	1010	2720	360	596	142000	302800	211000	507800	660	1100	170	220	26900	34560	4720	6590
5	3	386	1040	525	869	170000	362500	193000	464500	470	780	36	47	1410	1810	13500	18900
6	4	633	1710	500	827	93400	199200	5710	13700	320	530	25	32	10400	13360	920	1280
7	3	314	850	460	761	144000	307100	150000	361000	490	820	28	37	1970	2530	8600	12000
8	4	564	1520	440	728	101000	215400	5620	13500	280	470	34	44	12300	15800	800	1120
9	4	1170	3150	160	265	77100	164400	4080	9820	360	600	11	14	650	840	720	1010
10	4	705	1900	445	736	79200	168900	6260	15100	300	500	25	32	1430	1840	740	1030

A large difference in the values of Na_2O and CaO is caused by the fact that the first type of glass may be either with Na_2O or CaO predominance or with approximately equal percentage values for both oxides.

A comparison with the Byzantine (Na-Ca-Si) type and two ancient Russian types (K-Pb-Si and Pb-Si) was actual for this study. Presence or absence of lead in a glass is important in determining the type of glass. Lead (Pb) is not determined using NAA. However, since PbO is one of the major oxides of the continental crust [6], we can find the value of possible content PbO_{theor} in percentages by summing the values of percentages of the remaining major detected oxides: Na_2O, MgO, SiO_2, K_2O, TiO_2, MnO, FeO, CaO and subtracting the received amount from 100%.

The calculation results are shown in Table 2.

Finally, we can summarize the following results:

1. The K_2O:Na_2O ratio is always greater than three in all the bracelets; the K_2O:CaO ratio is always greater than nine; even the K_2O/(Na_2O + CaO) ratio is greater than two in all cases. In addition, the PbO_{theor} value is very large (11–82%) too. It may safely be said that the analyzed fragments of bracelets do not belong to the Byzantine glass type (Na-Ca-Si).

2. The R_2O:RO ratio of the prescribed norms of the main alkaline and alkaline-earth oxides ((Na_2O + K_2O)/(MgO + CaO)) is more than seven in all cases. This clearly indicates that no Byzantine prescribed norms were used.

3. Recalculation of oxide mass fraction values in percentages allows one to distribute the analyzed bracelets by types:

• Bracelets №1, №2, №4, №5, №7 belong to the ancient Russian potassium-lead-siliceous (K-Pb-Si) type, because the K_2O percentage in these bracelets is more than 36% in all cases. Researchers consider that such glass composition was used in the metropolitan workshops of ancient Rus' in Kiev, as well as in Novgorod [4]. It is also interesting that the K_2O percentage in Dubna bracelets is much higher than the values that are common to similar bracelets in other cities of Vladimir-Suzdal Rus' (see Table 1).

• Bracelets №3, №6, №8, №9, №10 belong to the ancient Russian lead-siliceous type (Pb-Si) of glass. The K_2O content in these bracelets does not exceed 2.5%. But the value of Na_2O and CaO is also very small (the Na_2O value is less than 0.35%, CaO is less than 2%). And as the theoretical percentage of lead oxide is very high — PbO_{theor} (75–82%), it allows one to affirm that these bracelets belong to Pb-Si type. According to Liadova [4], lead-siliceous glass was produced only in the provincial workshops in Novgorod, Smolensk, and Polotsk.

During the research the main elements responsible for the colors of the pieces of bracelets also were identified — iron oxide II (the fragments of green bracelets) and iron oxide III (dark brown and black ones), see Fig. 3. The complete absence of such popular element for glass coloring in Byzantium as copper among the

Fig. 3. Bracelets №2, №4, №9 from Dubna

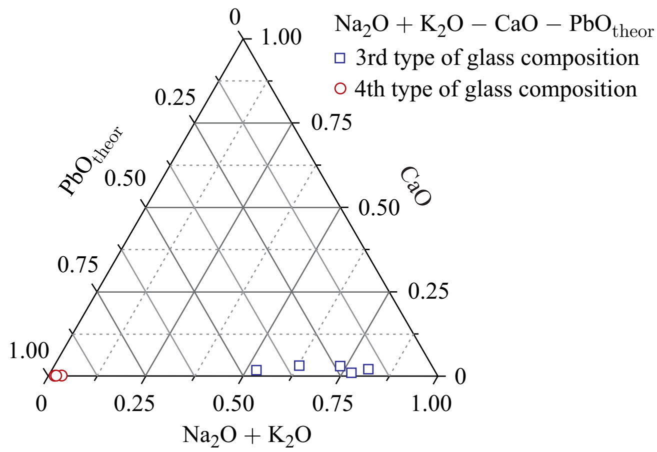

Fig. 4. Ternary diagram $Na_2O + K_2O - CaO - PbO_{theor}$

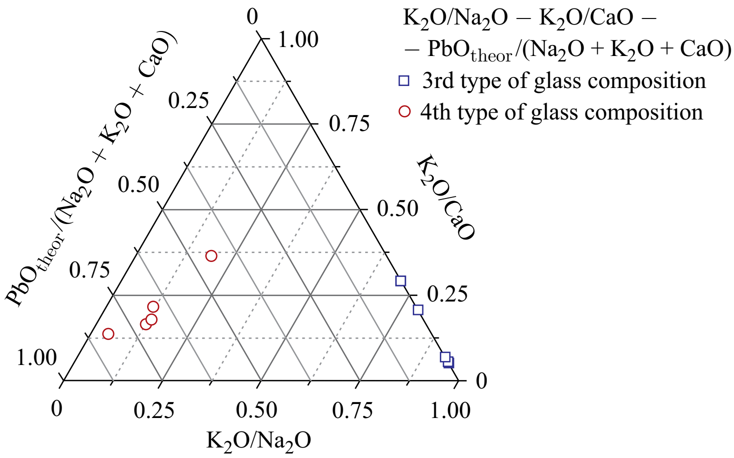

Fig. 5. Ternary diagram $K_2O/Na_2O - K_2O/CaO - PbO_{theor}/(K_2O + Na_2O + CaO)$

results of NAA (although the NAA can determine its presence), confirms the ancient Russian origin of the studied samples once again.

Thus, it can be concluded that the selected group of bracelets was created in the ancient Russian workshops. Half of the bracelets belongs to the potassium-lead-siliceous type and was created in the workshops of Kiev or Novgorod. Another part of the bracelets belongs to the type of lead-siliceous glass and was created in the provincial ancient Russian workshops, see Figs. 4 and 5.

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