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METALLURGICAL CRUCIBLES OF THE GOLDEN HORDE (BASED ON MATERIALS FROM EXCAVATIONS OF A JEWELRY WORKSHOP AT THE TSAREVSKOYE SETTLEMENT)

Summary: The article is devoted to the study of metallurgical crucibles from the jewelry workshops of one of the capitals of the Golden Horde - Sarai al-Jedid - that had been producing gold jewelry in the 1340s-1370s. The chemical composition of the clay fabrics of crucibles and to a greater extent the composition of crucible slags formed in the contact zone between the vessel walls and their filling during melting was determined by scanning electron microscopy (SEM). The analyses let us reveal the composition of the crucible molding fabrics, which is almost identical to the composition of tableware from a nearby pottery workshop. The article also provides data on assay analysis of the workshop's products. The fine of the gold evidences that jewelers' skill and the quality of technical ceramics let them achieve great results.

Keywords: Golden Horde, 14th century, jewelry workshops, technical ceramics, crucibles

Introduction

Sarai al-Jedid – the Tsarevskoe settlement and the second capital of the Golden Horde in the Lower Volga Region (Figure 1) – is a unique monument in many respects. First of all, the huge city was obvious in the relief of the surface even before excavations and preserved evidence of topography and planning structure. According to written sources and numismatic data, Sarai al-Jedid is known as a rapidly emerging and flourishing city that existed for only a few decades in the 14th century – from the second half of the 1330s, the time of the reign of the Uzbek Khan, to the ruin of Timur in 1395.

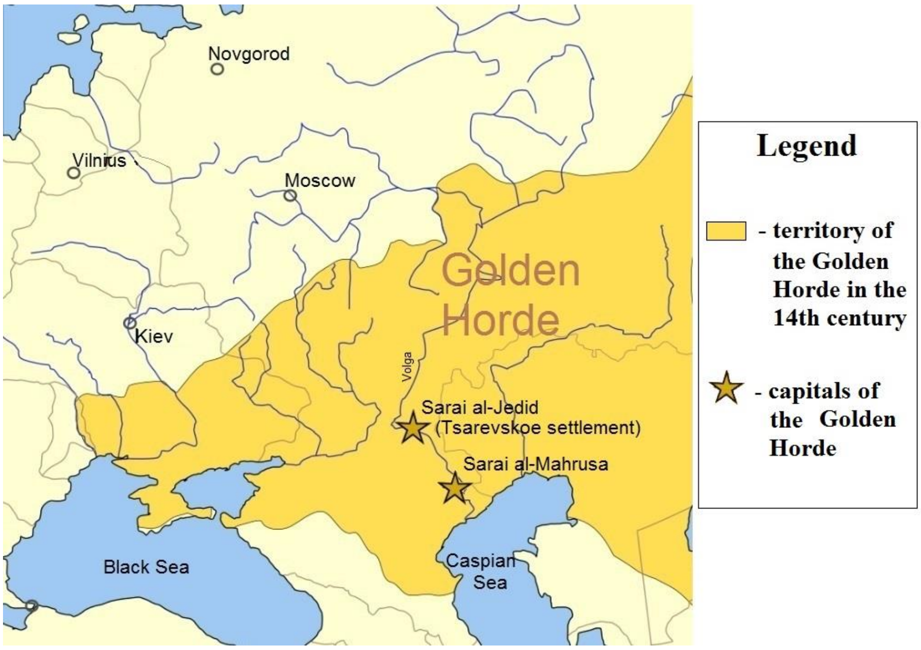


Figure 1: Map of the location of the Golden Horde capitals in the Lower Volga Region.

These factors were determinant when choosing the monument as the object of the first researches of the Golden Horde cities in the Volga region by the Moscow University archaeological expedition under the direction of G.A. Fyodorov-Davydov. In 1959, regular digging was started in the Tsarevskoye settlement, and from 1961 to 1968 a group from the Kazan University (supervised by I.S. Vainer) took part in the excavations (Figure 2). During these years the layout of the city, the type of constructing, fortification and water supply system were determined. Craft workshops – a large tile workshop in the potters' quarter in the central part of the city and three rich estates with workshops in the South-Eastern suburbs – were explored. Several types of production were organized in the estates: pottery (glazed dishes) production (Valiulina and Nuretdinova 2021), bone-carving and jewelry making (Valiulina 2020). Two successive gold-making workshops (Homestead II and Homestead III), according to numismatic material, functioned from the 1340s to the 1370s (Fyodorov-Davydov et al. 1974: 113). The neglected Homestead III survived until 1395. According to G.A. Fyodorov-Davydov, life in the suburbs after the raid of Timur's troops did not stop completely and the remaining residents of the quarter cleaned the territory of the homesteads. However, the former intensity of life was not observed, the quarter emptied and fell into decline.

At the initial stage of jewelry production in Homestead II, a workshop (380x170 cm) was located next to a residential dugout and at the distance from the rich house of the owner of the homestead; the jeweler probably lived in the dugout and was a dependent person. At the next stage in the 1360s-1370s, Homestead III appeared: a wooden house and a workshop next to (640x700 cm) were built there and that was the workshop of a free master.

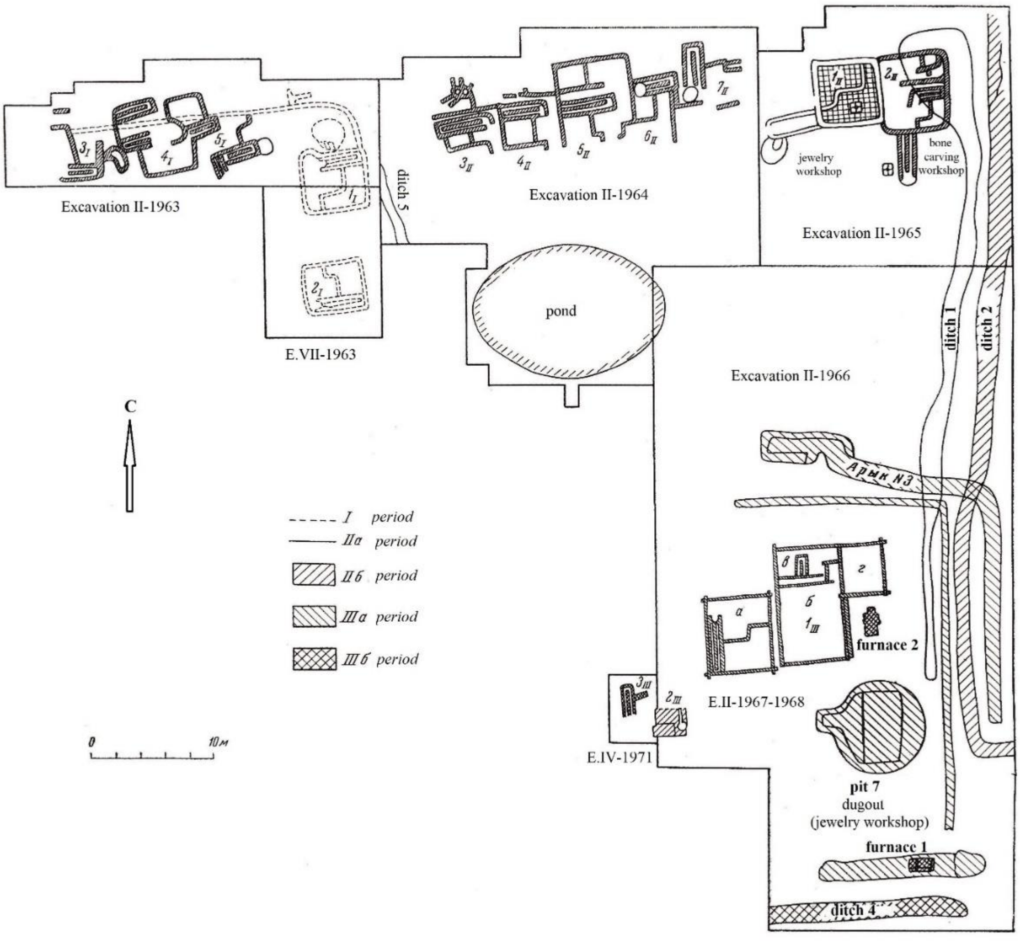


Figure 2: Layout of the excavations of the Tsarevskoye settlement.

The excavations presented the remains of thermal-and-technical constructions – furnaces, jewelry tools, numerous production wastes – golden plates' cuttings, wire, and finished products made of gold (overlay, turquoise set in gold, six-petal rosette, ring, miniature carnations) (Figure 3). The goldsmith's workplace is marked by drops of gold on pieces of stove plate and clay coating in kilns, on the fragments of household utensils and inside melting vessels – crucibles (Figure 3). In total, 137 crucibles of various degrees of preservation were found in workshops; the whole collection is stored in the Archaeological Museum of Kazan University (Inventory number AKYKP 358) (Valiulina and Nuretdinova 2022).

The results of X-ray analysis of 17 gold samples from the workshops, including 5 gold drops from crucibles, were given in the preliminary publication on the results of the unearthing. In all samples, the content of gold is 90-99%, silver is presented as natural impurity to the gold, and impurity of copper, which, according to the authors of the study, was added during the melting process in the crucibles, were found. The limited capabilities of X-ray diffraction analysis did not allow us to give full characteristic of the alloys, and the analysis of technical ceramics was not performed (Vainer and Krinari 1974: 126–129). The assay analysis carried out in the framework of our study supplemented and clarified the previously obtained data (Table 1).

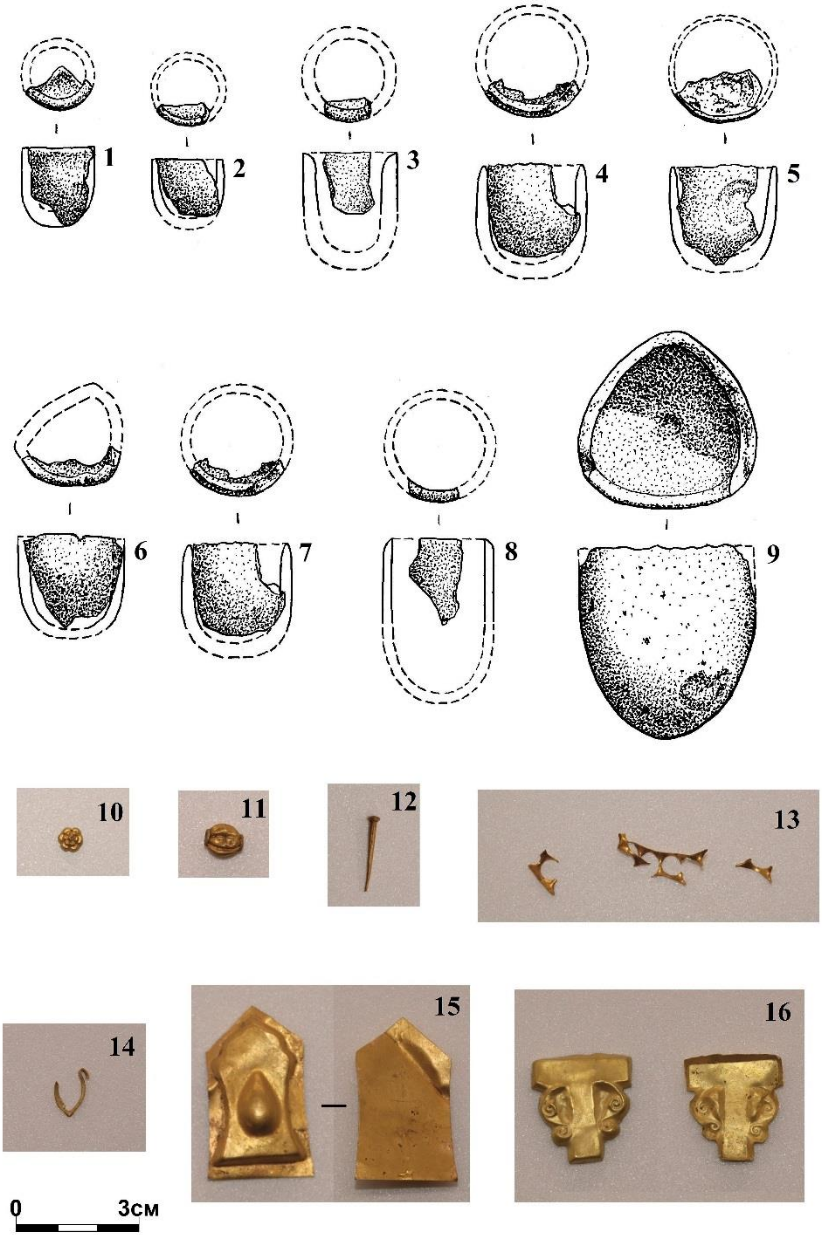


Figure 3: Crucibles (1-9) and golden products (10-16) from Tsarevskoye settlement workshops. Drawing by A.R. Khisamova, photo A.R. Nuretdinova.

Crucibles as vessels for melting metal are characterized by special qualities. They must have had special physical and chemical properties: they were to be resistant to high temperatures, provide the melting speed, and be able to control the melting process. In many ways, the properties of crucibles depend on the composition of the clay, the shape and method of temperature effect (Yeniosova and Rehren 2011: 244).

The article aims to determine the chemical composition of the clay fabrics of the crucibles, and to a greater extent, the composition of crucible slags formed in the contact zone between the walls of vessels and their filling during melting.

Table 1

Results of assay analysis of workshops' production from Tsarevskoye settlement.

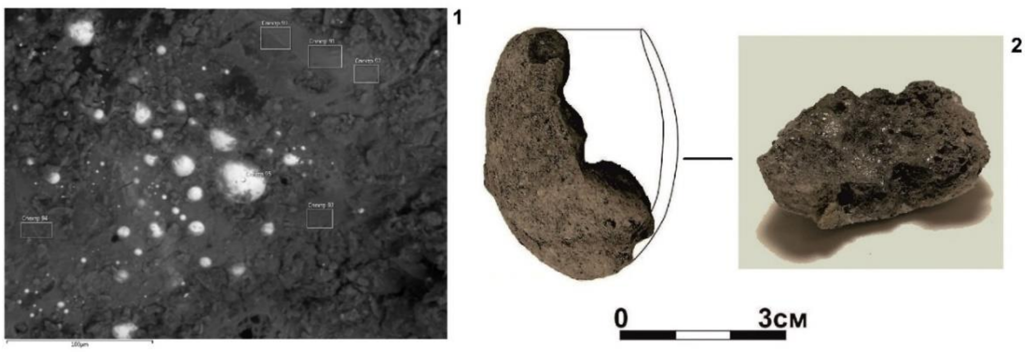
name	picture	composition		
		Au	Ag	Cu
onlay	Figure 3, 10	96 %	-	4 %
bead	Figure 3, 11	95 %	3 %	2 %
eardrop	Figure 3, 12	90 %	7 %	3 %
offcut	Figure 3, 13	96 %	3 %	1 %
offcut	Figure 3, 14	80 %	17 %	3 %
onlay	Figure 3, 15	93 %	4 %	3 %
onlay	Figure 3, 16	80 %	18 %	2 %

Methods

Crucible material was examined by scanning electron microscopy (SEM) using a Carl Zeiss EVO 50 with an X-ray microanalyzer (Bruker EDS). The studies were carried out at accelerating voltages of 20 kV in order to increase the sensitivity of such elements as Pb, Sn, Sb, As, Ba. The current mode ranged from 5 to 12 nA for a better terrain / analysis ratio. The microscope imaging mode involves electron backscattering (BSE). This mode allows you to most accurately distinguish the phase composition in the samples (layers, inclusions). Data on quantitative and qualitative analysis are presented in the form of oxides (Table 2). To process the experimental data and determine the composition directly during the measurements, we used a calculation algorithm based on the ZAF model diagram, which takes into account corrections for the arising effects of generation and absorption of characteristic x-ray radiation, as well as for fluorescence from characteristic x-ray radiation or bremsstrahlung. To obtain reliable results, each sample was studied by 5 spectra (Figure 4), followed by the calculation of average values, the results are presented in Table 2.

Morphology

All crucibles from jewelry workshops have been remained as fragments (Figure 3) of varying degrees of preservation; whole forms are represented by drawings in the General Table of Finds in an early publication (Fyodorov-Davydov et al. 1974: tab. V: 28, 29); these are triangular and cylindrical crucibles. Unfortunately, the triangular crucible was not available for our study. Several fragments preserved a complete profile of vessels, i.e. being "archaeologically full" they provide information about the height and diameter for rather reliable graphical reconstruction (Figure 4: 2). Thus, the safety of the material does not let us either perform a strict systematization of products or create a typology and establish quantitative ratios of different types. Based on the available data, at least three types of crucibles can be distinguished: 1 – cylindrical (2 subtypes) with a rounded bottom and a conical bottom, 2 – egg-shaped – with a rounded bottom, slightly rounded walls and a narrowed opening (Figure 3-8) and 3 – triangular with a rounded bottom. All crucibles were small in size, if the height is difficult to judge, whole samples show 5-6.5 cm, the information about the edge diameter is more reliable: the diameter of the crucibles varied from 3 to 5 cm. Crucibles are thin-walled, the wall thickness was 3-5 mm, increasing in the bottom part. Miniature crucibles correspond to small volumes (portions) of the noble metal used by the jeweler, and thin walls facilitate heat exchange and increase fire resistance (Bayley and Rehren 2007: 47).



3

АКУКП-358/1	Na	Mg	Al	Si	P	S	K	Ca	Ti	Mn	Fe	Co	Cu	Zn	Sn	Sb	Ba	Pb	Ag	Au
Spectrum 90	3,26	1,79	8,29	53,56	5,34	0,46	3,26	12,06	0,36	0,30	8,77	0,12	0,27	0,12	0	0,43	0,24	0,60		
Spectrum 91	4,97	2	7,58	54,2	3,05	0,37	4,18	11,16	0,4	0,24	9,21	0,15	0,27	0,18	0	0,51	0,16	0,37		
Spectrum 92	2,63	2,19	8,61	51,45	3,14	0,53	4,86	13,21	0,43	0,32	10,11	0,08	0,6	0,00	0,21	0,52	0,08	0,22		
Spectrum 93	2,98	2,38	10,37	54,13	4,06	0,81	3,37	12,83	0,43	0,23	6,28	0,02	0,45	0,00	0,17	0,51	0,31	0,15		
Spectrum 94	1,68	1,67	9,73	57,06	5,68	1,17	2,23	12,59	0,28	0,12	5,81	0,00	0,37	0,00	0	0,42	0,27	0,47		
Average	3,10	2,01	8,91	54,08	4,25	0,67	3,58	12,37	0,38	0,24	8,04	0,07	0,39	0,06	0,08	0,48	0,21	0,36		
Standard deviation	1,20	0,29	1,12	2	1,22	0,33	0,99	0,80	0,06	0,08	1,89	0,06	0,14	0,09	0,11	0,05	0,09	0,18		
Spectrum 95	0,76	0,9	3,80	14,88	1,92	1,81	1,41	7,11			2,68		0,66						2,42	61,42

Figure 4: Scanning electron microscopy and photo of crucible no. 1 (AKYKP-358/1).

The surface of the crucibles is even, rather smooth, brown or brown-gray outside and dark gray inside. All samples of the collection from Tsarevskoye do not have vitrification (glazing) either of the external or internal surface. When zooming in on the inner surface of the crucible wall, one can clearly see quartz grains, dark coal (?) clusters, angular shiny scales of muscovite mica and droplets-balls of gold of different size in the composition of ceramic slag in most crucibles (Figure 4: 2).

Results and discussion

The chemical composition of the crucibles' material (Table 2) shows that they are of common raw material with earthenware and other products from the pottery workshop in Homestead II: nozzles, three-horned stands for firing glazed dishes, matrix forms for making relief stamped ornaments (Valiulina and Bocharov, 2020). The fabrics of both crucibles and earthenware is characterized by a high concentration of alumina, calcium, and iron with an average content of alkalis of 6 % (Table 2). Only a large amount of aluminum oxide is useful from this list for producing refractory vessels. Therefore, the master should have introduced necessary technological additives into the fabrics to increase the refractoriness of vessels in accordance with the crucibles' targeting. It is important that 5 crucibles taken for analysis demonstrate a lack of standardization in this process – technological additives are individual in almost every sample. Perhaps the master was searching for the optimal composition, which obviously characterized the craft tradition that had not yet developed. However, this diversity may reflect the slag inclusions obtained while using the crucibles.

Table 2

The chemical composition of the material of crucibles and gold inclusions according to the results of SEM.

		Na	Mg	Al	Si	P	S	K	Ca	Ti	Fe	Cu	Zn	Sn	Sb	Pb	Ag	Au
1	**AKY KP-358/1**	3,10	2,01	8,91	54,08	4,25	0,67	3,58	12,37	0,38	8,04	0,39	0,06	0,08	0,48	0,36		
2	Standard deviation	1,20	0,29	1,12	2	1,22	0,33	0,99	0,80	0,06	1,89	0,14	0,09	0,11	0,05	0,18		
3	Spectrum (Au)	0,76	0,9	3,80	14,88	1,92	1,81	1,41	7,11		2,68	0,66					2,42	61,42
4	**AKY KP-358/19**	4,36	2,93	11,54	34,68	0,94	0,53	1,06	20,62	0,27	5,77	9,14	0,01	0,18	0,74	6,35		
5	Standard deviation	0,26	0,27	0,97	0,94	0,33	0,29	0,1	0,77	0,04	0,4	0,56	0,02	0,08	0,15	0,95		
6	Spectrum (Au)	2,02	0,83	3,21	8,74	0,18	1,75	0,34	4,43		1,53	6,06					8,89	58,72
7	**AKY KP-358/25**	4,59	2,9	14,22	45,54	1,11	1,09	3,1	17,93	0,40	5,61	0,89	0,04	0,45	0,47	0,59		
8	Standard deviation	0,72	0,24	0,84	2,82	1,02	0,42	0,29	3,39	0,08	0,45	0,03	0,03	0,16	0,09	0,07		
9	Spectrum (Au)	2,68	1,62	8,55	21,17	0,57	1,98	1,69	8,65		3,16							49,41
10	**AKY KP-358/31**	3,27	5,25	13,46	50,62	0,21	0,44	1,53	14,11	0,55	7,53	1,16	0,02	0,23	0,51	0,37		
11	Standard deviation	0,23	0,47	0,71	2,04	0,33	0,04	0,35	0,2	0,17	2,67	0,18	0,03	0,05	0,07	0,08		

12	Spectrum (Au)	1,88	1,35	3,65	12,51	0,00	1,51	0,79	3,99		3,42	2,67					3,77	64,21
13	**AKY KP-358/107**	3,68	2,88	28,05	49,13	0,17	0,77	1,76	8,25	1,17	1,97	0,48	0,02	0,13	0,27	0,14		
14	Standard deviation	0,20	0,35	2,07	3,07	0,04	0,14	0,27	1,43	0,64	0,31	0,09	0,02	0,08	0,07	0,03		

Of all the samples, crucible no. 107 is the most consistent in composition with the technological standards of refractories. The crucible material is rich in alumina –28.05 %; this is a high concentration level for unused vessels (Martinon-Torres and Rehren, 2009) and the lowest level of iron oxide in the sample – 1.97 % (Table 2: 13). The crucible has an equally smooth surface inside and outside, without bubbles, cavities and traces of metal – gold droplets. All these features and the chemical composition of the crucible material allow us to conclude that the crucible was not used.

Sample no.1 is characterized by a significant amount of phosphorus –1.33 %, that is, more than 3 times higher the average value and an increased content of potassium (Table 2: 1). These data indicate the addition of vegetable ash to the clay; the additive is known to have been used by artisans (Martinon-Torres et al. 2008) for creating of recovery conditions in the crucible (Bayley and Rehren 2007: 47).

Crucible no. 31 is characterized by an increased level of magnesium oxide of 5,25 % (twice higher than the average percentage), possibly due to the introduction of a mineral additive of magnesia-ferruginous silicate (olivine, chrysolite), aimed at increasing heat resistance (Table 2: 5).

Two crucibles no. 19 and 25 are both characterized by a high percentage of calcium oxide 20.62 % and 17,93 %, respectively; in both cases we can assume the presence of bone ash, another typical additive for making refractories, especially specialized in cupellation. Bone ash and wood ash were used to make crucibles in the alchemy laboratory in Oberstockstall (Osten 1998). Probably this multi-step procedure was not completed in crucible no. 19, unlike crucible no. 25 (Table 2: 7,8; 3,4). The large amount of calcite or lime could be a component of slag (Martinon-Torres and Rehren 2007: 86).

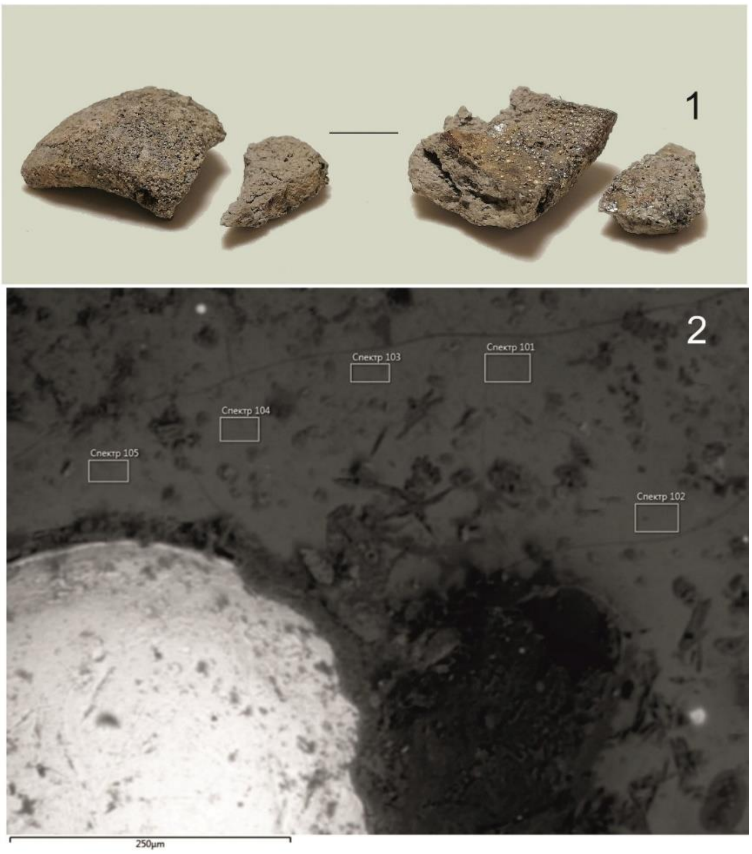


Figure 5: Scanning electron microscopy and photo of crucible no. 19 (AKYKP -358/19).

The absence of vitrified slag on the surface of the crucibles (Figure 3) is determined by a set of technological conditions, including, probably, the metal for which they served. The same feature is noted in the workshop of the Bilyar alchemist, where of 8 crucibles only 2 fragments belonging to one vessel contained vitreous slag. The fact that the Bilyar alchemist worked with gold is evidenced, in particular, by the assay stones found in the workshop. Some of them retained distinct strokes of gold, which let us determine high concentration of gold - 850 and 950 fines (Valiulina 2005: 156-157, fig. 44; Valiulina 2016: 265-266, fig. 19a, 19b: 8-14). But the three Bilyar crucibles retained traces of brass and also did not have vitreous slag.

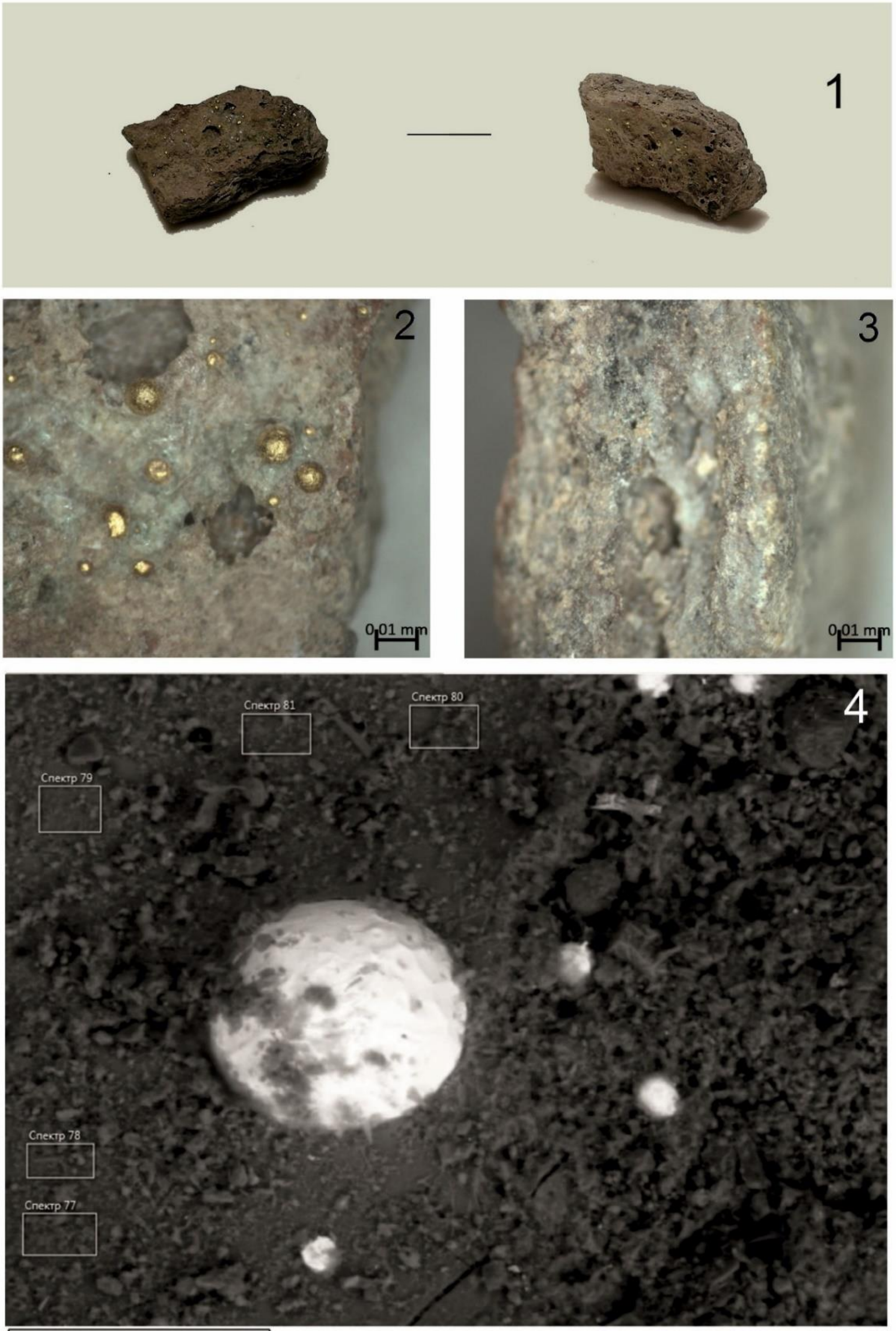


Figure 6: Scanning electron microscopy and photo of crucible no. 25 (AKYKP -358/25).

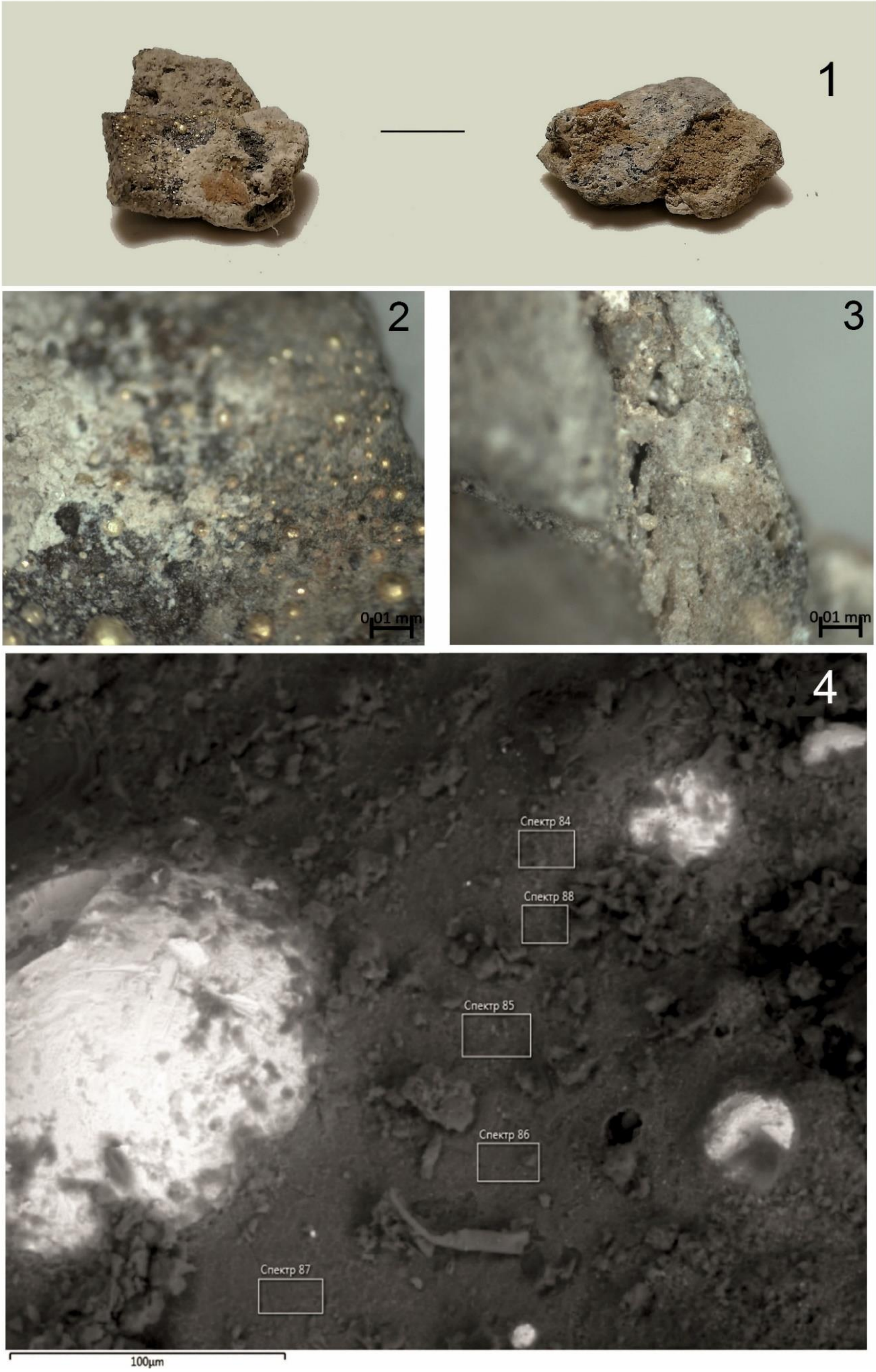


Figure 7: Scanning electron microscopy and photo of crucible no. 31 (AKYKP -358/31).

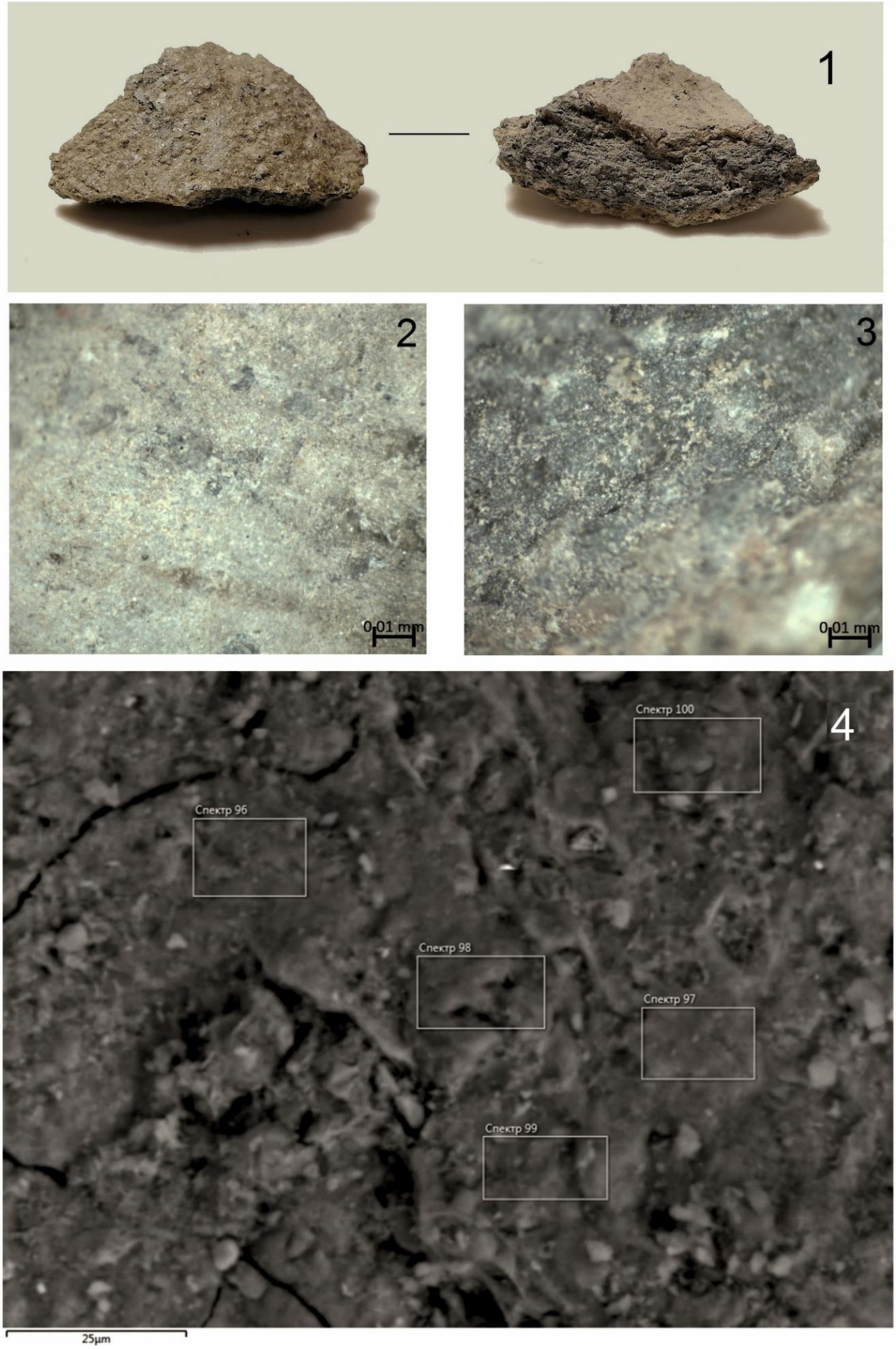


Figure 8: Scanning electron microscopy and photo of crucible no. 107 (AKYKP -358/107).

Analysis of the crucibles of the Tsarevskoye settlement workshop allowed us to obtain information about the slag on their inner surface. This slag usually carries the most metallurgical significant information (Martinez-Torres and Rehren 2007: 86).

The results of the analysis showed the presence of sulfur in all samples in the range of 0.44-1.09 %, while in all samples of gold balls on the inner surface of the crucibles (except for no. 107, where no gold was found), the concentration of sulfur is 2-3 times higher than that of the matrix. The fact of sulfur presence in clay itself is not surprising, it is found in sand, clay and, accordingly, in the products of the Golden Horde workshops – glazes, ceramics, glass – sulfur compounds are a regional geochemical feature of the raw material base of the Lower Volga region. But an increased amount of sulfur in the metal indicates its deliberate technological addition. Sulfur has been used to refine gold since ancient times. Theophilus mentions sulfur when working with gold at least in three chapters of his work "On Making a Golden Cup", where he recommends to use sulfur for improving the plasticity of the metal, namely in chapters LXVIII and LXIX – "How to Separate Gold from Copper" and "How to Separate Gold from Silver" (Theophilus 2008: 291, 320-321). It is important that pieces of sulfur were found at the sites of workshops from Tsarevskoye (II-1967/1968, 3/213), sulfur was also found in the materials of the alchemist's workshop in Bilyar (Valiulina 2005). T. Rehren cites the opinions of authoritative researchers in this regard and mentions the use of antimonite – antimony sulfide (antimony luster, or the mineral stibnite Sb2S3) as a separating agent of gold from silver (Rehren 1996: 138). The antimony as well as sulfur is found in the composition of the crucible fabrics, but it is not registered in golden balls (Table 1). The presence of copper in golden balls on the walls of the crucibles is also explained by a technological additive. Sulfur, copper, and a significant percentage of silver in gold show an incomplete cupellation process. And silver is present as silver sulfide in samples no. 1, 25, 31 (Table 2: 3,4; 7,8), or silver nitrate (Rehren 1996: 140), as in sample no. 19 (Table 2: 4), where in addition to a large amount of silver (8.89 %) a significant concentration of nitrogen (2.96 %) is found (Table 2: 4).

Conclusion

Crucibles from jewelry workshops of the Tsarevsky settlement are stratified and provided with a wide context: technological, numismatic, household; they are a part of a manufacturing complex in its development, implying the changing social conditions of handicraft organization. It is especially important that the craft complex, in addition to jewelry making, included pottery workshops for the production of glazed dishes, which provided a comparative material. All these circumstances open great prospects for further research of crucibles.

A comparative analysis of the composition of the crucible fabrics and the products of the pottery workshop made it possible to determine the local production of crucibles, although it is a well-known fact that these products necessary for metallurgical production could have been a subject of trade (Martinon-Torres and Rehren 2009).

The composition of the molding fabrics of crucibles, which is almost identical to the composition of tableware, does not allow us to consider them fully fireproof vessels; it is more correct to call them technical ceramics. Examples of such crucibles are known in scientific literature (Rehren 1996). However, the crucibles from Tsarevskoye settlement, being not quite refractory, performed their functions well.

The fact that the crucibles from Tsarevskoye workshops coped with the tasks of cupellation - cleaning gold from ore impurities, melting and casting - is evidenced by the high fine of jewelry, cuttings, wire, and drops of gold (Table 1). At the same time, attention is drawn to the obvious wastefulness of the master when working with noble metal, which is usually not a characteristic of goldsmiths.

Clay crucibles were obviously made by the goldsmiths themselves, because of their complete absence in the potteries located nearby.

In all aspects of studying the syncretic culture of the Golden Horde, the identification of origins of cultural traditions is of particular importance. Nowadays, the lack of analytical data on materials from Central Asia and Transcaucasia is a constraining factor for solving this problem in handicraft and, in particular, in search of technological traditions. In addition, expanding the complex of methods and analytical base on the crucibles from both the Tsarevskoye settlement and other cities – craft centers of the Golden Horde – is the top priority in this field.

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ФАКТОРЫ ПСИХОЛОГИЧЕСКОГО БЛАГОПОЛУЧИЯ У ПОДРОСТКОВ: ОЦЕНКА И ПРАКТИЧЕСКОЕ ЗНАЧЕНИЕ

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Аннотация. Статья посвящена анализу факторов, влияющих на психологическое благополучие подростков и разработке практических методов его поддержки. Рассмотрены основные аспекты, включая роль семьи, школьной среды, социальных связей и эмоциональной стабильности в формировании психического здоровья подростков.

Семейная поддержка играет значимую роль в эмоциональной стабильности подростков и формировании их уверенности. Школьная среда и роль педагогов также оказывают влияние на эмоциональное состояние и успешное адаптирование учащихся. Социальные связи и эмоциональная стабильность имеют ключевое значение для общего психологического благополучия подростков.

В заключении подчеркивается необходимость комплексного подхода к поддержке психологического здоровья подростков, включающего различные аспекты их жизни с целью обеспечения полноценного развития и укрепления эмоциональной стабильности.

Ключевые слова: школа, подростки, психология, благополучие, семья, поддержка.