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Three-colored Sancai glazed ceramics excavated from Bohai sites in Primorye (Russia)

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ABSTRACT

This paper presents the analytical results of polychrome and monochrome lead-glazed ceramic classified as Sancai that was excavated from the Bohai sites of Kraskino and Gorbatka walled towns, and the Chernyatino-2 settlement (Bohai layer) (Primorye, Russia). Thirty ceramic fragments were analyzed using non-destructive X-ray fluorescence analysis (pXRF), optical microscopy, and scanning electron microscopy (SEM) with energy-dispersive x-ray spectroscopy (EDS). This work presents new data on the elemental composition of lead glazes and discusses some aspects of their technology, including assumptions about the medieval potters' skill level and technological awareness. Data pertaining to the sample's elemental composition indicates their origin from various workshops practicing different approaches to pottery production. These ceramics have no slip layer with the glaze coating having been applied directly onto the surface of the ceramic vessels. The intensity of the lead component in the glaze composition varies significantly, in the range of concentration between 36 and 79 wt%. Surface features of filling and shine, as well as the nature of glaze defects demonstrates a low probability of the peak firing approach that was applied in the technological process. The results presented in this paper contribute to expanding our understanding of the Bohai (CE 698–926) and Tang (CE 618–907) periods for Sancai ceramics.

1. Introduction

At the peak of it's growth, the Bohai State (CE 698–926) spread over a substantial territory that currently borders Russia, China, and North Korea (Fig. 1). The prominent populations that participated in the formation of the polyethnic Bohai State were contributed by the Sumo Mohe tribes, and the Koguryo people, around whom a number of other related tribes were united. The territorial-administrative structure in Bohai was formed mainly in the second half of the eighth century under the influence of the Chinese Tang dynasty (CE 618–907). However, the Bohai leaders pursued an independent policy by forming separate alliances with other states, and the maintaince of close contacts through the exchange of diplomatic embassies in support of ~~a~~ particular forms of trade. The Bohai administration transported goods from the most remote regions of Northeast Asia, including China, the Japanese islands, the Korean Peninsula, Mongolia, and Central Asia. (Guochen and Guozhen, 1984; Shavkunov, 1994; Yufu, 1982). In conjunction with the transport of goods came new ideas and technologies, including mastering the technique of lead-glazed ceramics, similar to the Chinese tricolor glazed Sancai (Gelman, 1999a).

Sancai is a type of ceramics that is coated with both a polychrome and monochrome lead glaze (Cui et al., 2010a; Cui et al., 2010b; Feng et al., 2005; Lei et al., 2007; Li et al., 2006; Ma et al., 2014; Shen et al., 2018; Yong et al., 2005). Chinese Sancai pottery was fired in Gongyi/Huangue (Henan province), Neiqiu (Hebei province), and Huangbao (Shaanxi province) kilns and were made of kaolin clay and resulted in white vessel walls. Kilns in Neiqiu produced the famous Xing porcelain variety of ware. The Huangbao kilns are also known for the production of the famous Yaozhou celadon ware variety during the Tang (CE 618–907), Song (CE 960–1127) and Jin dynasties (CE 1115–1233). These products were exported to Japan and along the Silk Road to the Middle East (Iraq, Samarra – the residence of the Abbasids) and North Africa (Egypt, Fustat). It is already well known that the yellowish and reddish Sancai pottery originated from the Liquanfang (Shaanxi

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province) kilns, which was discovered by Chinese archaeologists in 1999 (Cui et al., 2010a). Chinese Sancai vessels were covered with a slip and fired in two stages: first at 1000–1100 °C, then the glaze was applied and fired at lower temperatures (Cui et al., 2010b; LEI et al., 2007). The prominent distinctive feature of Tang Sancai is the high concentration (over 50%) of lead oxide (PbO) in the glaze (Cui et al., 2010b).

Systematic long-term archaeological research conducted in the Russian Primorye territory permitted the assembly of more than 100 fragments of Sancai type ceramic fragments. There is evidence of this type of pottery in seven historic settlements of various administrative levels and solitary temples. The vast majority of these finds came from the Kraskino walled town, which has been under excavation since the 1980s.

The Kraskino walled town is located on the shores of Expedition Bay, near an estuary of the Tsukanovka (Yanchihe) River (Fig. 1). The center of the Yanzhou district (Salt District) was a part of the metropolitan area governed by the Eastern capital of Longyuanfu (the Baliancheng site near Hunchun, China), located about 50 km from Kraskino. This medieval city, covers an area of more than 13 ha and is encompassed by an encircling fortress walls extending 1380 m. This was an influential administrative center and functioned as an important commercial and craft center and, as well as a seaport, around which the land and sea roads led. Diplomatic and trade relations with Japan, China, and the United Silla Kingdom of Korea were maintained through this sea port, and its name is preserved in Chinese chronicles (Shavkunov, 1994). Lead-glazed pottery is often found in this ancient site in layers II–V, however, it is not nearly as numerous as ordinary earthenware.

One of the studied glazed ceramic samples comes from the Gorbatka walled town (area 10 ha, with a 1250 m perimeter of city walls), located in the Ilistaya River Valley, which flows into Lake Khanka. (Gelman et al., 2001; Gelman and Kojima, 2013). A fragment of the neck of a vase was found in a dwelling from the lowest layer in Gorbatka. Five periods of the functioning of this Bohai fortress have been established through archaeological excavations, which presumably was also the center of the district, judging by its size (Gelman et al., 2001). Another artifact was found in the Chernyatino-2 site, located in the Suyfun (Razdolnaya) River Basin (Nikitin et al., 2002).

The first assumption that Bohai people produced Sancai ceramics was put forward by the Russian researcher and leader of Manchurian archaeology in 1920–1950s, V.V. Ponosov, whose article was included in a report by Japanese archaeologists (Harada, 1939). The first analytical studies of a small number of samples (three Bohai samples with lead glaze) from the Superior Capital (Longquanfu) of the Bohai State were carried out by Yamazaki (Yamazaki, n.d.), who noticed the difference in the chemical composition of Bohai and Chinese Sancai vessels.

After many years of archaeological research in Bohai sites located in the Russian Primorye region, it became possible to conduct detailed visual, petrographic, and chemical studies, including attempts to clarify raw material distribution channels and identify glazed ceramics produced in the Bohai sites (Gelman, 1999b, 1999a). Suggestions have been made that the raw materials for lead-glazed goods could have come from a variety of sources, including northern and southern China, as well as the territory of Japan (Junko et al., 2015). However, a collaborative study with Japanese colleagues confirmed that lead-glazed pottery derived from Bohai sites differs from the Tang Sancai.

Nevertheless, lead-glazed pottery from Bohai sites, unlike Tang Sancai, has been insufficiently studied and there have been only a limited number of reports written. Since these reports include a number of inaccuracies, it is now of particular interest to investigate the technical and technological features of the Sancai vessels fabrication. To date, the assumption that the development of Sancai production in Bohai sites was based on the use of local resources, which is reflected in the appearance of Bohai glazed pottery, is still relevant (Gelman, 1999a). However, there is still no unequivocal conclusive answer regarding the origin of the Sancai in the Bohai sites. Sancai pottery kilns

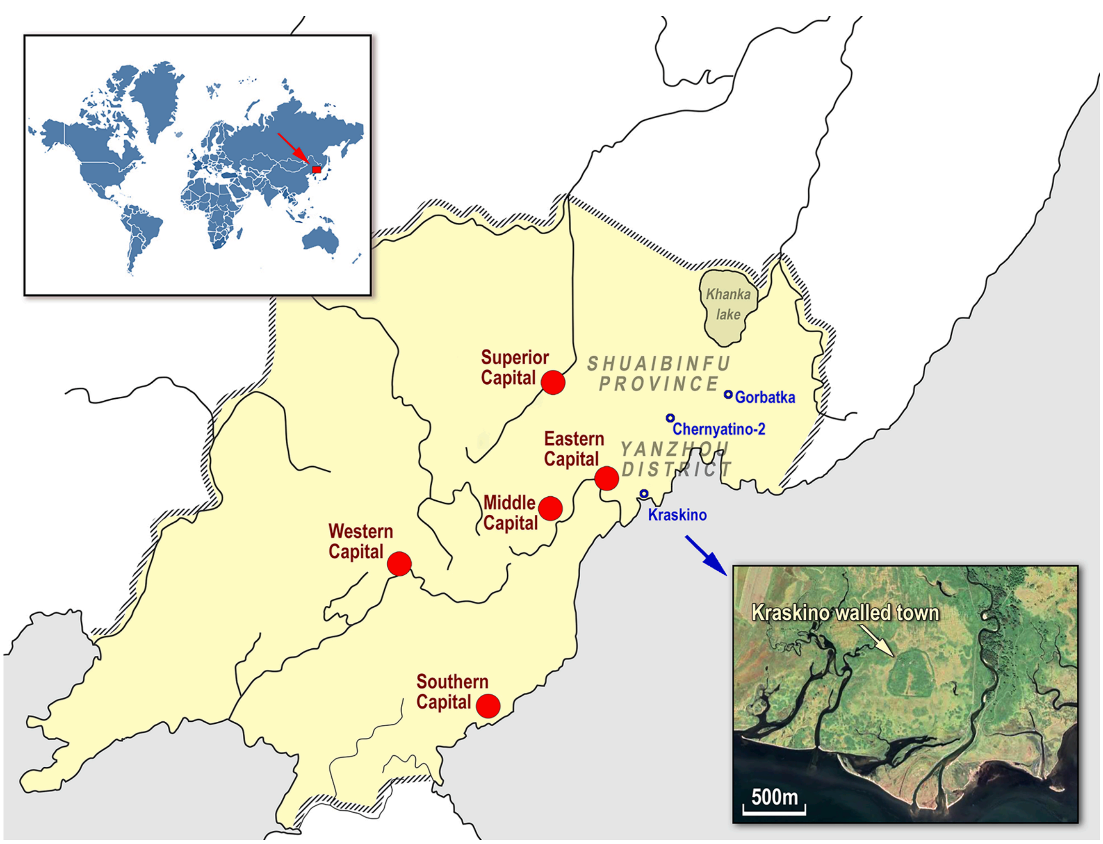

Fig. 1. Map of the Bohai State's territory (CE 698–926) with the insert of a satellite photo of the Kraskino walled town.

have not yet been found within the borders of the Bohai State. However, judging by the scale of the use of glazed tiles and architectural details of the palaces in the capital cities and the quantity of the final products produced, it is likely that the production sites were located close to the destination for consumption.

This research project examined 30 fragments of Sancai pottery collected during excavations of Bohai sites in Russian Primorye. The chemical composition of the ceramic materials and their glaze coating was determined.

2. Experimental

The 30 fragments of Sancai pottery collected during the excavations of three Bohai sites were initially macroscopically examined and described with the naked eyed and photographed (Fig. 2).

Separate areas of each ceramic fragment were examined for elemental composition using a handheld portable X-ray fluorescence (pXRF) analyzer Olympus Delta Professional DP 4000 (Japan). Measurements were taken through a PRO 6 Prolen U8990460 (6 µm) window, in dual beam mode for 40 s (10 and 30 s). When performing measurements, preference was given to flat and smooth areas with a study surface larger or comparable to the area of the pXRF analyzer window. The analytical mode of the pXRF instrument selected for the analysis is Two Beam Mining. The spectrometer calibration algorithm is based on the principle of Fundamental Parameter Calibration. To produce elemental concentrations the pXRF analyzer uses the measured intensity of each element's fluorescence from the sample, and the calibration data, coming from the analyses of standard reference materials.

The ceramic shards, glaze coating, and mixed (shards/glaze) surfaces were analyzed. It is well known that for museum collections and archaeological objects the use of destructive methods of analysis is very limited. Non-destructive pXRF analysis has become widespread and popular in the field of historical, cultural, and art research, providing accurate results despite its usability (Forster et al., 2011; Goren et al., 2011; Ioannides et al., 2016; Marghussian et al., 2017; Tykot, 2016; Wilke et al., 2016). In this study, pXRF was applied to quickly and affordably determine the elemental composition of the material and to form further questions and targets for microanalysis, which will be performed in the following studies using geochemical trace element identification methods. The use of the pXRF allows us to distinguish composite groups of elements with high sensitivity. In particular, the most accurate measurement is provided for elements with an atomic number over 26.

Determination of the main components of the system and the impurity components, as well as comparison of their concentration ratios, was performed using visualization of data from a portable handheld pXRF analyzer by descriptive statistics plotting box-and-whiskers diagrams, showing: *(1)* center statistics (median and mean); *(2)* range statistics (lower and upper quartiles); *(3)* minimum and maximum sample values; *(4)* lower (25%) and upper quartile (75%) points, which contain, respectively, 50% (interquartile range) of sample concentration values for each chemical element; and *(5)* outlier points, the strong outlier value of the observed value that stands out from the total sample. This type of diagram is well-proven for analyzing large data sets, as it is one of the easiest and most accessible ways to identify the asymmetry of values in a statistical sample (Henderson, 2006). Among other

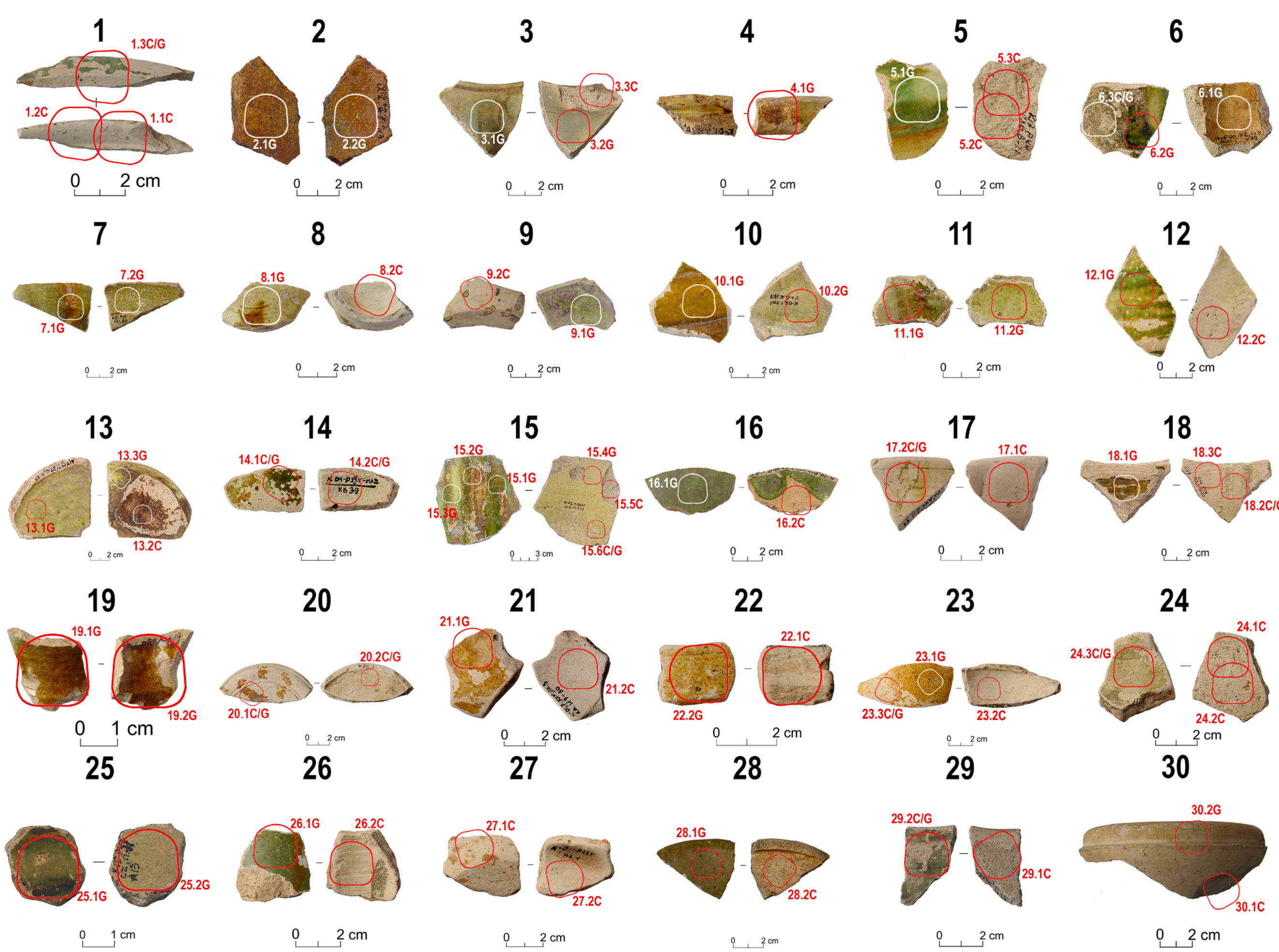

Fig. 2. Three-colored glazed ceramic shards of the Sancai type from the Bohai archaeological sites with pXRF analyzer measurement areas identified.

applications, scatter diagrams effectively describe ceramic materials of both archaeological origins (de Dios et al., 2018; Zhushchikhovskaya and Buravlev, 2021) and advanced technical applications (Papynov et al., 2020; Shapkin et al., 2021).

The microstructure was studied using a Carl Zeiss Axiovert 40 MAT microscope equipped with an AxioCam ERc 5 s digital camera (by Carl Zeiss MicroImaging GmbH, Germany) and AxioVision 40 software version 4.8.2.0. Scanning electron microscopy (SEM) was performed on a Carl Zeiss Ultra 55 scanning electron microscope (SEM, Germany), with the prefix for energy-dispersive X-ray microanalysis (EDS) Bruker (Germany).

The percentage of open pores (water absorption) of samples was determined for the most representative samples, visually and qualitatively different in the characteristics (color, surface roughness, visually distinguishable grain size, etc.). The method of determining the percentage of open pores is as follows: the sample was placed in a container and poured into the water at 25 °C, in this state, the sample was kept 10 min, then the water was heated to boiling temperature and the system was kept in this state for 120 min. The sample cooled to room temperature and was dried with a dry cloth and weighed to the accuracy of 0.01 g. The difference in weight before and after boiling, shown in percentage (%), characterizes the degree of open porosity of the shard.

3. Results

The Kraskino ancient site is located on Expedition Bay of Posiet Bay (west coast of the Sea of Japan). Many years of excavation experience conducted in this site testifies to the destructive effects of the acidic soils of this coastal area on the materials composition of the ancient remains. Contrary to long-term observations, the samples of glazed Sancai ceramics recovered from the territory of the Kraskino ancient site, where a high level of groundwater is often preserved, exhibit relatively good preservation, as a result of relatively high firing temperatures (850–1000 °C). This agrees with the data in earlier research (Junko et al., 2015) and was confirmed by the results of measuring the mass of several samples during the evaluation of the water absorption factor (Table 1).

The artifacts exhibited no rehydration or surface softening, which is expected for insufficiently fired ceramics that have undergone prolonged exposure to moist and salt-ladened soils. Bohai products that contain lead glazes are soft and visually look either beige or grayish/grayish-white. Based on the results presented in Table 1, the two types of ceramic shards in the example of objects No. 2 and 20 fall within the range of optimal porosity (8–12%). The rest of the items (No. 6, 8, 22) are close to the optimal value with a deviation up to 3% of the upper limit. This indicates close to optimal requirements for bisque firing, which provides indirect evidence of a sufficient level of technology prowess.

The results of the pXRF data for the ceramic shards are presented in Table 2 and graphically visualized in Fig. 3. Despite the reasonably high concentration of iron in the ceramic shards, the samples visually do not reveal different red-burning clay, which may result from a specialized approach to the selection of raw materials and a relatively low firing temperature (<900 °C). However, master craftsmen worked alternately with red and white clay. In particular, this is evidenced by

Table 1
The results of measuring the weight of Sancai ceramics in the process of evaluating the water absorption coefficient.

Fragment of Sancai ceramic item, No.	Δm, %
2	10.27
6	13.85
8	15.03
20	12.00
22	13.19

Table 2
The chemical composition of ceramic shards obtained via non-destructive pXRF-analysis of three-colored glazed ceramics of the Sancai type from the Bohai Kraskino archaeological site.

Area, #	Chemical Elements, wt%																				
	Si	Al	Fe	Ti	Pb	Cu	Mn	Zn	Mg	Sb	Sn	P	S	Zr	Nb	Hf	Bi	Cd	V	Cr	Ni
13.2–C	37,61	15,62	11,25	2,24	0,19	–	0,23	0,11	–	–	–	32,44	–	0,31	–	–	–	–	–	–	–
1.1C	58,06	29,01	8,51	2,07	1,31	–	0,26	–	–	–	–	0,56	–	0,20	0,02	–	–	–	–	–	–
1.2C	58,99	29,23	7,97	2,02	0,92	–	0,14	0,07	–	–	–	0,51	–	0,13	0,02	–	–	–	–	–	–
3.3C	57,12	25,23	12,08	1,99	0,94	–	0,30	0,05	–	–	–	2,13	–	0,15	0,01	–	–	–	–	–	–
5.2–C	51,14	33,71	10,12	2,35	0,17	–	0,15	0,04	–	–	–	1,82	0,23	0,22	0,01	–	0,04	–	–	–	–
5.3–C	50,39	33,79	10,70	2,57	0,14	–	0,15	0,05	–	–	–	1,75	0,17	0,26	–	–	0,03	–	–	–	–
8.2–C	48,43	22,56	15,46	5,95	0,83	–	0,39	0,13	–	–	–	2,97	2,61	0,67	–	–	–	–	–	–	–
9.2–C	61,49	22,83	10,44	1,84	1,94	–	0,18	0,12	–	–	–	1,00	–	0,16	–	–	–	–	–	–	–
12.2–C	48,85	30,43	9,00	3,57	0,41	–	0,10	–	–	–	–	6,58	0,79	0,21	0,02	–	0,04	–	–	–	–
15.5–C	50,37	30,04	13,33	2,30	0,51	–	0,09	0,05	–	–	–	2,15	0,99	0,17	–	–	–	–	–	–	–
16.2–C	50,73	26,73	16,54	2,07	2,26	0,04	0,10	0,06	–	–	–	1,29	–	0,18	–	–	–	–	–	–	–
17.1–C	59,60	23,54	9,43	2,82	0,75	–	0,08	0,03	–	–	–	3,12	0,45	0,16	0,02	–	–	–	–	–	–
18.3–C	48,97	35,44	10,05	2,52	1,50	–	0,07	0,05	–	–	–	1,11	–	0,17	–	–	–	–	–	0,07	0,05
21.1–C	56,73	26,37	12,90	2,48	0,10	–	0,13	0,06	–	–	–	0,61	0,45	0,17	–	–	–	–	–	–	–
22.1–C	58,19	27,61	8,92	1,90	0,06	–	0,15	0,04	1,91	–	–	0,69	0,32	0,12	0,01	–	–	–	0,08	–	–
23.2–C	56,77	23,9	14,08	2,55	0,16	–	0,27	–	–	–	–	0,32	1,72	0,21	0,02	–	–	–	–	–	–
24.1–C	59,63	29,61	6,63	2,80	–	–	0,12	–	1,49	–	–	0,64	0,21	0,36	–	–	–	–	–	–	–
24.2–C	58,37	29,76	6,38	2,75	0,03	–	0,12	0,04	–	–	–	0,62	0,20	0,24	–	–	–	–	–	–	–
26.2–C	59,93	23,07	11,99	2,33	1,64	–	0,09	0,05	–	–	–	0,68	–	0,20	0,02	–	–	–	–	–	–
27.1–C	59,02	26,72	10,4	2,13	0,31	–	0,12	0,04	–	–	–	0,41	0,72	0,12	0,01	–	–	–	–	–	–
27.2–C	54,77	25,65	14,42	2,66	0,22	–	0,21	0,05	–	–	–	0,56	1,26	0,20	–	–	–	–	–	–	–
28.2–C	59,70	26,41	9,41	1,92	1,38	–	0,12	0,07	–	–	–	0,79	–	0,16	0,02	–	–	–	–	–	0,02
29.1–C	57,58	29,09	8,36	2,75	0,14	–	0,12	0,05	–	–	–	0,57	1,00	0,31	0,01	–	–	–	–	–	0,02
30.1–C	60,38	26,23	9,33	2,00	0,68	–	–	0,03	–	–	–	1,20	–	0,14	0,01	–	–	–	–	–	–

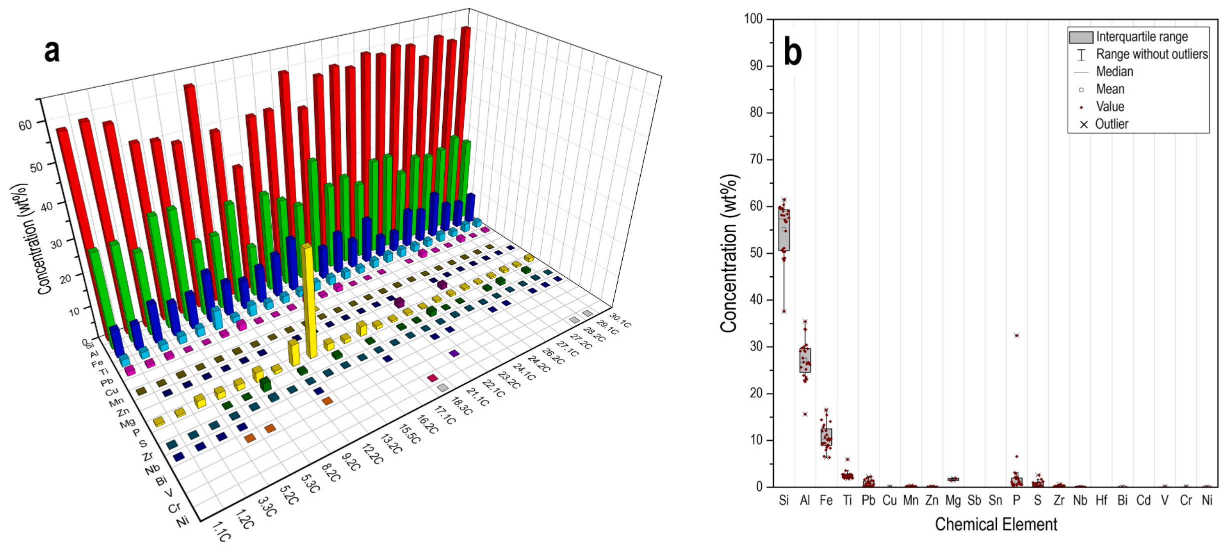

Fig. 3. Chemical composition of ceramic shards *(a)* and box-and-whisker plots *(b)* for the data obtained via non-destructive pXRF-analysis of three-colored glazed ceramics of the Sancai type from the Bohai Kraskino archaeological site.

the trace of red-burning clay in a fracture of piece No. 30 (Fig. 4), formed as a result of accidental mixing in the process of kneading the clay mass. The ceramic mass lacks copper-based compounds in its composition (an exception is the fragment of item No. 16) and, according to the pXRF data, has stable impurities of manganese (Mn), zinc (Zn), zirconium (Zr), and less stable impurities of magnesium (Mg), neodymium (Nd), bismuth (Bi), vanadium (V), chromium (Cr) and nickel (Ni). The surface is also contaminated with impurities of phosphorus (P) and sulfur (S). The ceramic surface of object No. 13 (area 13.2C) is a continuum of loose iron and phosphorus compounds, which were formed when the material came into contact with the soil after the loss of its glaze coating. The loss of glaze coating is only represented in fragment No. 13, due to the specific conditions caused by an extended period in the ground for this particular item.

Over the past 40 years of research conducted in the Bohai sites, petrographic studies of ceramics that have been carried out occasionally have shown that the ceramic shards of Sancai from Bohai sites of Primorye are hydrosludite. The shards themselves were fired in the temperature range of 850–900 °C. Thus, the firing temperature of ceramics corresponds to the melting temperature of the glaze. Sand is present in the shards in small amounts, and their composition can be either as quartz-feldspar or quartz. The quartz sand occasionally contains plagioclase, as well as an admixture of muscovite and zircon. One of the shards contains mullite. The sand granular size is predominantly 0.3–0.5 mm.

For all artifacts, a layer of polychrome glaze was applied only to the outer surface. Brown, yellow, and green glazes are darker and duller than the Chinese Sancai. The difference in thickness of the glaze layer on the inner and outer surface indicates a multi-layer coating of the outer side, applied by either immersion or brush. The vessels were covered on the inside with a thin layer of light green or light yellow glaze. The bonding of ceramic and glaze under conditions of thermal influence at the firing stage obtained a high residual thermal stress at the interface of their contact surface. The potter's selective approach to the choice of raw materials and use of the method of glaze application to the fired vessels allowed a reduction of the influence of destructive effects from the coefficient of thermal expansion (CTE). However, even for prestige products like Sancai ceramic vessels, it is inevitable that failures will occur as a result of uncompensated mechanical stresses, both in the joints themselves and in the glaze layer throughout their entire application. It was reasonable to compensate for inconsistencies between the CTE of the ceramic and the glaze with an intermediate damping layer, which can be used to compensate for the described load. None of the 30 fragments analyzed identified the presence of a slip. This fact is one of the primary pieces of evidence distinguishing the samples from the Chinese ones. Some of the glazes have an iridescent effect. There is a predominant use of non-transparent green glaze of different shades in most cases, without a gloss. Even the brightest glaze surfaces of the selected samples look darker compared to the Sancai from the Tang, Japanese, or Lao kilns.

Fig. 4. Traces of red-burning clay in a fracture of the ceramic shard of object No. 30.

All sample items have a crazing of the glaze (Fig. 5*a*). The surface of the glaze layer is characterized by a variety of defects in the form of a developed network of cracks formed due to the accumulation of stresses. The bond between the glaze and the pottery varies: there is an easy to separate glaze as well as a difficult to separate one without causing obvious damage to the visual aspect of the item. There are fragmentary absences of the glaze layer, separated from the ceramic surfaces by small fragments along the edges of the cracks (Fig. 5*b*), including traces of mechanical friction (Fig. 5*c*). These characteristic are present on a number of examined shards. Mechanical decay of the glaze coating occurs more easily in areas with the roughest surface of the ceramic shards exist as a result of the crystallization of salts inside their porous structure (Cronyn, 1990). Individual fragments of the items may have cracks in the lead glaze layer of about 3 μm. The width of the cracks affects the ability of moisture, with various compounds, dissolve and penetrate into the soil solution to the glaze/ceramic interfaces. This decay proceeds with the greatest intensity under rapid changes in moisture, for example, in well-ventilated soils. After the cleaning processing, which involves

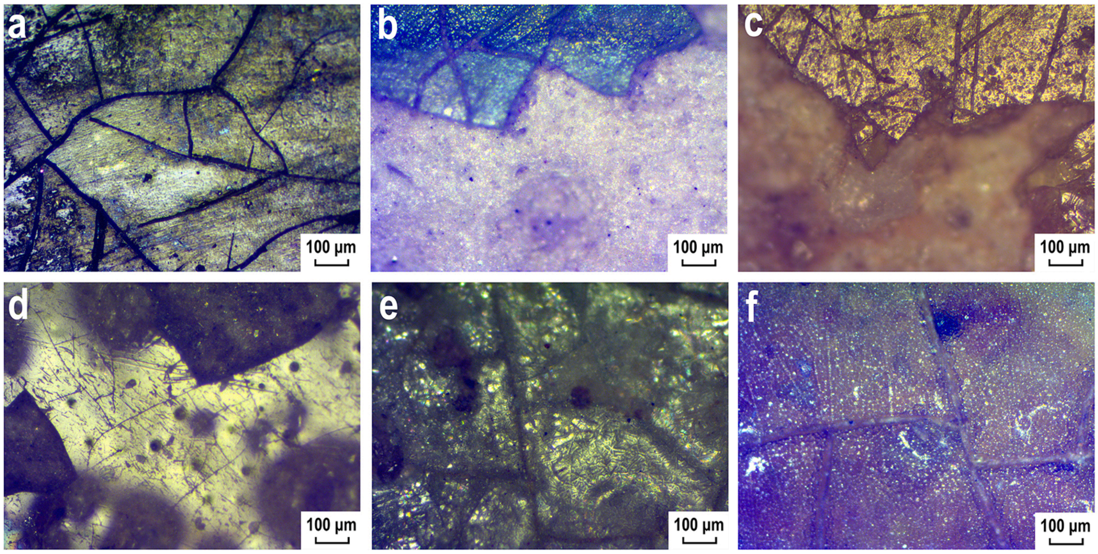

Fig. 5. The fracture and surface defects of the glaze layer of tricolor ceramics of the Sancai type from the Bohai site in Kraskino: a – the network of cracks on the surface of the glaze coating of object No. 10; b – fragmentary delamination of the glaze from the ceramic shards on the borders of defects (object No. 1); c – loss of part of the glaze coating on the borders of the cracks (object No. 14); d – air bubbles in the glaze layer on the object No. 23; e – defects of the rising surface of the glaze layer of object No. 24; f – traces of surface erosion, resulting in an irregular color coating with the effect of silvering (fish scales) of object No. 21.

thoroughly rinsing the objects, the effect of this decay factor is reduced.

In some cases, the thickness of cracks in the glaze layer can reach 55 μm, indicating the poor barrier-coating ability of the glaze films that once sealed the surface of the ceramics while they were in the ground. Another defect in the glaze is spherical bubbles of varying sizes. Gas bubbles affect the way light spreads in the glaze. In the studied objects, bubbles are formed through boiling the glaze and as a consequence of the release of gases from the shards (mainly carbonates) released during the process of dissociation of raw materials (Fig. 5*d-e*). A glaze layer containing many tiny bubbles looks shiny because the smooth interfaces between air and glass serve as reflective surfaces. In modern ceramic manufacturing, the peak firing approach and under-firing of carbonate-saturated shards is a way of matting glazes to avoid opacifiers. Possibly, this technique may have been used deliberately in some cases. Hypothetically, this solution could have been arrived at by experimental analysis. In addition, it should be noted the surface erosion, resulting in an irregular color coating resulted in a silvering effect («fish scales») (Fig. 5*f*). Particularly noteworthy is the absence of signs of long-term contact with seawater since the surface of the glaze layer has no black sulfide spots, which are typical for lead products found in seawater. This is appropriate since the ground layer at the Kraskino walled town is filled with fresh water. However, the groundwater stands high, and the change in winter and summer temperatures is harmful to the lead glaze. When evaluating the impact of unfavorable conditions in the ground layer, the material is sufficiently resistant to the effects of aggressive environmental conditions.

Glazes differ in thickness, density, color saturation, and composition. The results of the elemental composition of the glazed surface of the objects are presented in Table 3 and visualized in Fig. 6.

First of all, the high concentration of Pb in the composition of the glaze layer should be noted (Fig. 6*a*). The box-and-whiskers diagram plots the results of the analysis of elemental composition that shows a high degree of dispersion of the values of Pb in the glaze layer in the range of values from 36 up to 79 wt%. Also, the asymmetry of the distribution of values relative to the median (Fig. 6*b*) indicates the difference in technological approaches to the quantitative level of the main component for the production of frit.

Since the Pb concentration influences the melting temperature of the glazes, such significant differences indicate various optimal temperature ranges for softening, melting, and flowing under thermal influences. At a specific firing temperature, the glaze materials containing different concentrations of Pb will exhibit different behaviors as it gradually flows from the solid to the plastic state and then to the liquid (syrup-like) state. Thus, for example, several objects have a smooth coating in the state of the tension phase of the glaze mirror with good filling and surface gloss. This surface quality is obtained by controlled exposure of the glazes in a molten state with uniform heating of the entire mass of the product. The well-preserved coating, absence of pores filled, in particular, with residues of interacting agents with the substance of the soil solution, indicates that it is impossible to obtain a comparable coating under peak firing approaches. However, the repeated firing of one of the micro samples showed that the glaze layer at 800 °C changed the topography of its surface (became smooth), while in connection with access to air, the shards changed their color to a reddish pink. This may be the result of increased acidity, due to increased silica content while maintaining a constant composition of the bases, which corresponds to an increase in refractoriness and the viscosity of the glaze. In this case, the possibility of vitrification of glazes increases, which outwardly may be reflected in their opacity and loss of gloss.

Since the presence of Cr in the composition of the glazes has not been determined, it is likely that the green color is due to compounds of iron and copper. Iron oxides are present in all samples. Copper oxides are predominantly present in green and green–brown samples and are also identified in distinctly brown glazes. The concentration of Cu in areas with deep non-transparent green glaze stains is over 2.5%. The color variations in the glaze do not present the blood-red hues characteristic of the presence of Cu_2O copper oxide because Cu_2O quickly oxidizes into CuO oxide, which imparts a blue or green color. Preventing the oxidation of Cu_2O to CuO is possible by heating in a reducing environment (by adding tin oxide, coal, etc.) to 400–500 °C. Brown and mixed glazes are characterized by the presence of P, which is found in poorly soluble compounds with iron $FePO_4$ formed in the soil (Junko et al., 2015). Iron phosphate makes yellow and brown glazes darker and gives the surface a brittle texture. For green glazes, the presence of phosphorus is not common. Green glazes are poorer in the composition of impurities than brown glazes. This is associated with the higher chemical activity of iron.

Also, among the areas examined, the present study highlights the analysis of surfaces that do not allow the unique assignment of results with their categorical affiliation to only the ceramic or only the glaze

Table 3
Chemical composition of glaze obtained via non-destructive pXRF-analysis of three-colored glazed ceramics of the Sancai type from the Bohai Kraskino walled town.

Area, #	Color	Chemical Elements, wt%																				
		Si	Al	Fe	Ti	Pb	Cu	Mn	Zn	Mg	Sb	Sn	P	S	Zr	Nb	Hf	Bi	Cd	V	Cr	Ni
2.1G	Brown	17,98	3,50	2,34	0,53	72,54	–	–	0,43	–	1,31	1,02	0,34	–	0,02	–	–	–	–	–	–	–
2.2G	Brown	21,63	4,00	3,35	0,95	66,85	–	–	0,41	–	1,31	0,94	0,47	–	0,09	–	–	–	–	–	–	–
4.1–G	Brown	22,10	16,62	12,68	2,26	37,71	–	0,21	–	–	–	–	6,81	–	0,75	–	0,86	–	–	–	–	–
6.1–G	Brown	17,99	3,40	2,85	0,37	68,97	0,94	0,04	0,11	–	–	–	5,31	–	0,02	–	–	–	–	–	–	–
19.1–G	Brown	26,76	4,09	1,93	0,67	63,36	1,75	–	–	–	0,69	0,45	0,20	–	0,10	–	–	–	–	–	–	–
19.2–G	Brown	20,67	11,67	5,13	2,04	57,08	2,61	–	–	–	–	–	0,30	–	0,47	–	–	–	–	–	–	0,03
7.1–G	Brown/green	17,35	4,59	2,05	0,59	73,03	0,72	–	–	–	0,22	–	1,42	–	0,03	–	–	–	–	–	–	–
11.1–G	Brown/green	27,19	6,12	3,02	0,57	61,42	0,55	–	0,05	–	0,18	–	0,61	–	0,04	–	–	0,25	–	–	–	–
8.1–G	Brown/green	40,14	3,22	1,05	0,22	54,56		–	–	–	0,24	–	0,53	–	0,04	–	–	–	–	–	–	–
3.1G	Green	49,96	3,62	2,68	0,28	41,47	0,80	–	0,04	–	0,22	–	0,91	–	0,02	–	–	–	–	–	–	–
3.2G	Green	49,25	1,35	0,78	–	47,95	0,20	–	–	–	0,18	–	0,27	–	0,02	–	–	–	–	–	–	–
5.1–G	Green	35,30	3,21	0,90	–	58,53	1,57	–	0,30	–	0,19	–		–	–	–	–	–	–	–	–	–
6.2–G	Green	27,21	2,68	2,08	–	63,92	1,94	–	0,12	–	0,17	–	1,88	–	–	–	–	–	–	–	–	–
7.2–G	Green	16,96	4,29	1,16	0,40	75,53		–	–	–	0,45	–	0,68	–	0,11	–	0,42	–	–	–	–	–
9.1–G	Green	28,64	3,46	1,75	0,42	62,41	0,99	–	–	–	0,48	0,19	1,57	–	0,09	–	–	–	–	–	–	–
10.2–G	Green	39,17	3,36	1,24	0,38	55,03	0,23	–	–	–	–	–	0,60	–	–	–	–	–	–	–	–	–
11.2–G	Green	23,42	3,75	0,56	0,26	71,14	0,20	–	–	–	0,34	–	0,26	–	0,08	–	–	–	–	–	–	–
12.1–G	Green	18,43	4,15	1,04	0,25	74,75	0,85	–	–	–	0,22	–	0,31	–	–	–	–	–	–	–	–	–
13.1–G	Green	11,88	1,67	0,49	–	78,73	0,16	–	–	–	0,14	–	6,93	–	–	–	–	–	–	–	–	–
15.3–G	Green	20,47	4,58	1,05	0,29	72,40	0,24	–	–	–	0,17	–	0,80	–	–	–	–	–	–	–	–	–
16.1–G	Green	36,50	5,99	1,69	0,33	54,07	1,09	–	–	–	–	–	0,33	–	–	–	–	–	–	–	–	–
25.1–G	Green	38,34	6,77	2,03	0,43	50,42	0,41	–	–	–	0,13	–	1,23	–	0,02	–	–	0,22	–	–	–	–
26.1–G	Green	38,87	6,35	1,94	0,32	51,55	0,56	–	–	–	0,12	–	0,26	–	0,04	–	–	–	–	–	–	–
28.1–G	Green	44,22	4,19	1,84	0,18	48,89	0,13	–	–	–	–	–	0,55	–	–	–	–	–	–	–	–	–
13.3–G	Brown/green	24,91	4,71	2,17	0,30	59,92	0,14	–	–	–	0,14	–	7,69	–	0,02	–	–	–	–	–	–	–
15.1–G	Brown/green	18,59	6,11	2,70	0,57	68,96	0,68	–	0,06	–	0,26	–	2,03	–	0,04	–	–	–	–	–	–	–
15.2–G	Brown/green	16,37	10,01	6,27	1,33	55,96	0,46	–	0,05	–	0,33	–	8,74	–	0,13	–		0,35	–	–	–	–
18.1–G	Brown/green	21,75	7,16	3,37	0,72	63,78	0,71	–	0,06	–	0,22	–	2,18	–	0,05	–	–	–	–	–	–	–
21.1–G	Brown	42,21	3,33	3,49		49,91	–	–	–	–	0,31	–	0,72	–	0,03	–	–	–	–	–	–	–
15.4–G	Green	22,53	3,65	0,96	0,38	70,45	–	–	–	–	0,55	0,24	0,39	–	0,07	–	0,62	–	0,16	–	–	–
25.2–G	Transparent	20,83	4,72	1,31	0,35	71,40	–	–	–	–	0,36	–	0,65	–	0,05	–	0,33	–	–	–	–	–
22.2–G	Brown	47,84	5,90	3,00	0,59	41,66	–	–	–	–	0,23	–	0,38	–	0,08	–	0,32	–	–	–	–	–
23.1–G	Brown	36,67	4,40	3,12	0,39	53,77	–	–	–	–	0,42	0,16	0,41	–	0,11	–	0,55	–	–	–	–	–
10.1–G	Brown	16,85	3,66	1,55	0,31	76,60	0,44	–	–	–	–	–	0,59	–		–	–	–	–	–	–	–
30.2–G	Brown	28,97	10,39	3,90	0,94	53,88	0,08	–	–	–	0,49	–	1,22	–	0,13	–	–	–	–	–	–	–

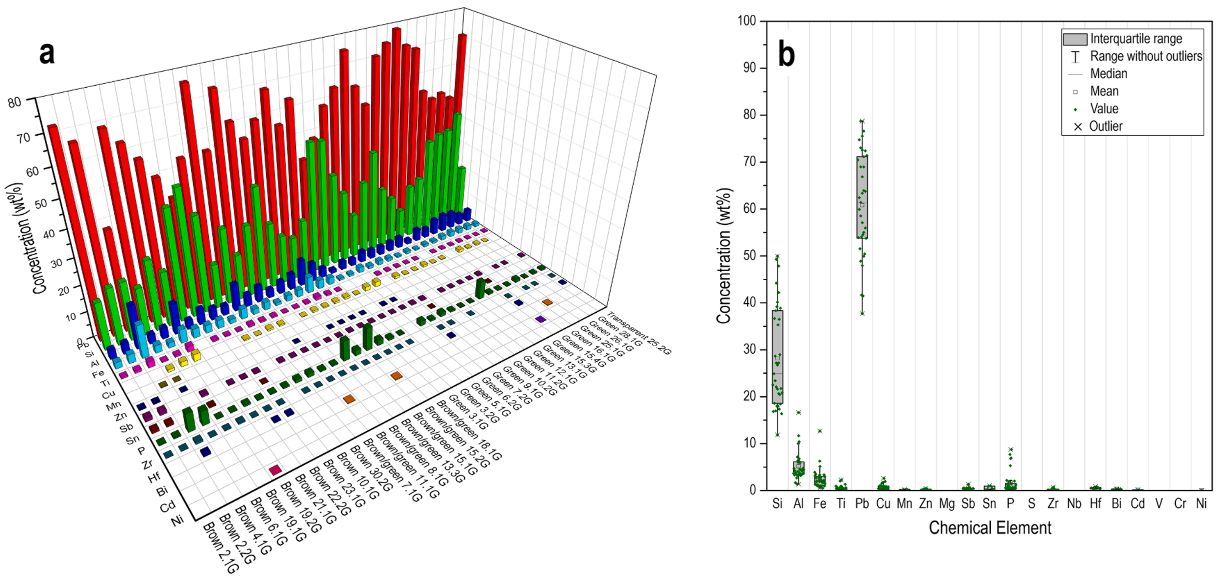

Fig. 6. Chemical composition of glaze *(a)* and box-and-whisker plots *(b)* for the data obtained via non-destructive pXRF-analysis of three-colored glazed ceramics of the Sancai type from the Bohai Kraskino walled town.

type (Table 4). These data are presented for qualitative interpretation of the glazed surfaces for the likely color-forming elements.

The present study attempts to analyze the chemical composition of glaze coatings by non-destructive analysis of the surface without prior preparation of a particular sample with a clearing procedure that would result in a slightly polished finish. Thus, the SEM-EDS results of the partially fractured glaze coating analysis on the example of fragment No. 10 (Fig. 7) shows the differences in the chemical composition in the morphologically different areas. Such a structural and chemical heterogeneity of the glaze coating increases the difficulty of comparing Sancai glazes using the in-situ approach to analyze local surface areas without prior preparation. A difficulty in the comparison also causes the need to consider the composition of the glaze regarding the dyeing effect of metals with variable valence. Shifting equilibrium $2Fe_2O_3 \rightleftarrows 4FeO + O_2$ leads to varying colors of the glaze melt depending on the gas atmosphere of the furnace due to the predominance of FeO or Fe_2O_3. Iron oxide gives a minimum absorption in the yellow part of the spectrum, while oxides give a minimum absorption in the blue-green part of the spectrum. The phenomena of light absorption caused by the combined action of staining oxides are due to the formation of spinel-type compounds that provide a stable, consistent brown glaze color.

In order to validate the pXRF results, several tiny glaze samples were taken in areas where it was possible to separate the glaze easily from the surface of the ceramic shard without damaging the object and leaving spots of destructive intervention. This approach could not be applied to the entire collection because of the requirements dictated by the policy of handling valuable rare artifacts under study. The samples taken were analyzed after prior polishing of the surface to remove the outer layer, which could contain traces of corrosion, the formation of which is inevitable in conditions of prolonged exposure to soils and constant contact with aggressive agents in the soil solution. The results of this comparison are presented in Table 5.

As shown in the comparison of results presented in Table 5, the presence of such chemical elements in the composition of the glaze as Mn, Nb, Cd, Cr, Ni, and S is not detectable in the local analysis of the chemical composition of the glaze in the case of preliminary removal of the outer layer by polishing. The presence of the elements in the pXRF spectrum can be neglected because they are the consequence of contamination of the surface by soil residues penetration the near-surface layer, as a result of a long slow destructive process. The results of this analysis indicates a pronounced correlation in the different concentrations of Fe and Cu in the microsamples of glaze color characterized as brown or green, respectively. The concentration of Fe in the composition of the glaze exceeds the concentration of Cu, and for samples of green color to the contrary. For the brown glaze sample taken from the 20.1-C/G area, a relatively high phosphorus concentration in the microsample correlates with a high concentration of the presence of the Fe component, which in the local analyzed areas slightly exceeds the value of the intensity of the presence of iron established by pXRF. In general, comparing the results obtained by the two methods, it is fair to state that the values obtained are correlatable and do not contradict each other.

4. Discussion

The quality of ceramics depends on the effect of the quality of its technological operations during fabrication. Ancient potters had to contend with a lack of repeatability of results. This likely depended on how stable the chemical compositions of the initial components of the glazes were. Also, to a much greater extent, on how well they understood the technological principles of the firing processes associated with the intentional formation of certain reducing, oxidizing, or neutral atmosphere conditions inside the furnace chamber. In the contemporary context, the quality and repeatability of the result are achieved by the precise control of firing parameters, which were not available to potters in ancient times due to their limited understanding of the physical and chemical foundations of the technological technical processes of ceramic fabrication. The same starting material can yield several different final products with the application of different technologies (Colomban et al., 2003). Varying the temperature of the operating parameter in the range from 10 to 15 °C in the firing process can lead to a significant change in color characteristics in the same composition of the glaze. The environment will have an even more significant influence on the process of firing.

It should be noted that accurate temperature and oxygen concentrations and their maintenance in the furnace, even during contemporary applications, are challenging. We tend to believe that each master (artistan) consistently maintains an individual specificity of his work. The craftsman is not expected to make mistakes that affect the quality and visual aspect of the goods he makes. In this regard, objects of arts and crafts could be "lucky" or "unlucky" dependent on their level of skill and working attitude, technological approach, quality of raw materials,

Table 4
Chemical composition of simultaneous exposure to both the glaze and the surface of the ceramic shard in the measurement of area obtained via non-destructive pXRF-analysis of three-colored glazed ceramics of Sancai from the Bohai Kraskino walled town.

Area, #	Color	Chemical Elements, wt%																				
		Si	Al	Fe	Ti	Pb	Cu	Mn	Zn	Mg	Sb	Sn	P	S	Zr	Nb	Hf	Bi	Cd	V	Cr	Ni
20.1–C/G	Brown	42,59	26,07	6,25	3,25	11,33	–	–	–	–	–	–	10,01	–	0,36	–	–	–	–	0,14	–	–
14.1–C/G	Dark green	30,88	21,44	4,00	1,34	39,82	1,09	0,06	0,10	–	0,28	–	0,39	–	0,40	–	–	0,20	–	–	–	–
1.3C/G	Green	38,02	20,46	5,05	1,38	33,34	0,61	–	0,06	–	–	–	0,88	–	0,20	–	–	–	–	–	–	–
6.3–G	Green	8,89	1,15	1,70	0,20	83,20	0,07	–	0,05	–	–	–	4,74	–	–	–	–	–	–	–	–	–
17.2–C/G	Green	38,10	15,28	6,80	1,33	35,27	0,48	–	–	–	0,37	–	1,64	–	0,26	–	–	0,34	–	0,13	–	–
24.3–C/G	Green	37,46	12,09	3,34	1,44	44,22	0,22	–	–	–	0,30	–	0,30	–	0,36	–	–	0,27	–	–	–	–
29.2–C/G	Green	56,07	29,43	7,95	2,81	2,29	0,06	0,07	0,06	–	–	–	0,88	–	0,37	0,02	–	–	–	–	–	–
15.6–C/G	Ligth green	23,78	17,60	6,79	1,29	47,40	–	–	–	–	0,52	–	1,21	–	0,29	–	0,98	–	–	0,14	–	–
20.2–C/G	Transparent	45,87	22,05	6,88	3,49	14,94	–	–	–	–	–	–	6,35	–	0,42	–	–	–	–	–	–	–
18.2–C/G	Transparent light green	46,54	29,98	9,00	2,23	10,72	–	–	–	–	–	–	1,01	–	0,25	–	0,27	–	–	–	–	–
14.2–C/G	Transparent very light green	57,95	28,02	8,18	3,30	1,20	–	0,10	0,05	–	–	–	0,78	–	0,40	0,02	–	–	–	–	–	–
23.3–C/G	Yellow	51,43	23,30	8,42	1,42	14,17	–	0,10	–	–	–	–	0,59	–	0,20		0,26	–	–	0,11	–	–

cleanliness of the workplace, etc. There are too many unintentional and random actions in craft fabrication that can lead to unsystematic errors. For this reason, one should always be particularly critical of definite conclusions about the technology of the archaeological pottery-making process.

The pottery fabrication method involves a lot of handwork. Most of the studied vessels of the Sancai fragments were made on a potter's wheel. Efforts to estimate the probable height of these vessels is impossible. Among the ceramic fragments under consideration, there are specimens with fairly thick walls. For example, the wall thickness of fragment No. 11 suggests that it may be of a larger product. The thin wall of a fragment implies a high degree of probability that the vessel was small in size. There is a significant variation in wall thickness values for many items, which indicates unambiguously that the products belong to different production batches.

It should be noted that the thinner the wall of the ceramic vessel, the lower its thermal inertia. Differences in the degree of heating can yield a difference in color on thick and thin walls. Regardless of the nature of the substance, the outer surface of the item cools faster than the inner. With its very low thermal conductivity, the glaze can undergo considerable stress when it cools rapidly. If the coefficient of thermal expansion of the ceramic is lower than the glaze, then the glaze is stretched when cooling and undergoes tensile stress. Since free displacement along with the surface contact is impossible, and the solidified glaze resists tearing is much weaker than compression, the inelastic glaze fractures when it reaches stresses that exceed allowable elasticity and strength limits.

The chemical composition of the analyzed samples of Sancai ceramics agrees with the majority of previously published scientific works and does not provide reasons to suggest new theories and hypotheses that would contradict the currently established view of this type of ceramic composition. However, some findings deserve a deeper examination and should be considered in subsequent studies as points of focus in the analyses of elemental compositions. It is noteworthy to observe that in most cases the glaze surface contains antimony (Sb) reaching concentrations up to 1.3 wt%. In earlier work on the composition of Sancai glazes from Bohai sites, the level of Sb was not determined (Junko et al., 2015). The same observation applies to a number of works conducted on the Tang Sancai (Ma et al., 2014; Yong et al., 2005). In discussing the presence of this element in the composition of the material under study, we can turn to modern ceramics to find a possible appropriate answer. In the practice of contemporary ceramic manufacturing Sb is used mainly in the form of Sb_2O_3 oxide (or $NaSbO_3$ sodium metamagnesic acid) and is added in an amount of approximately 7–9%, which significantly exceeds the concentrations determined in the samples studied. Antimony can play the role of a coloring element in the lead glaze due to the crystallization during the yellow phase $Pb_2Sb_2O_7$. A possible effect of this process is to give the glaze a light honey-type color. All Sb compounds are sensitive to a reducing atmosphere. The metallic Sb, which is reduced in the process, like lead, gives the glaze a dirty grayish color. The sulfurous Sb gives out S in the form of gas during the firing, which makes the glaze foamy. With a long firing the glaze sinks and becomes smooth. With rapid cooling, however, the foam may form on the surface of the glaze. Antimony oxides can greatly increase the refractoriness and viscosity of the glaze, making it difficult to work while in the molten state. However, Sb cannot be categorically disregarded because its toxic properties do not apply to household ware.

Titanium oxide TiO_2 is very sensitive to changes in the gas atmosphere. In the presence of reducing agents TiO_2 is easily reduced to a blue color Ti_2O_3. The high refractive index of TiO_2 makes it a valuable component for matting glazes. The most undesirable titanium dioxide impurities for bright glazes are iron oxides, as they give the glazes a yellowish hue.

The Zn presence was previously identified in glazes of Tang Sancai samples, as well as in glazes from the Nara and Heiyang eras in Japan (Junko et al., 2015), which may be since zinc is part of both the

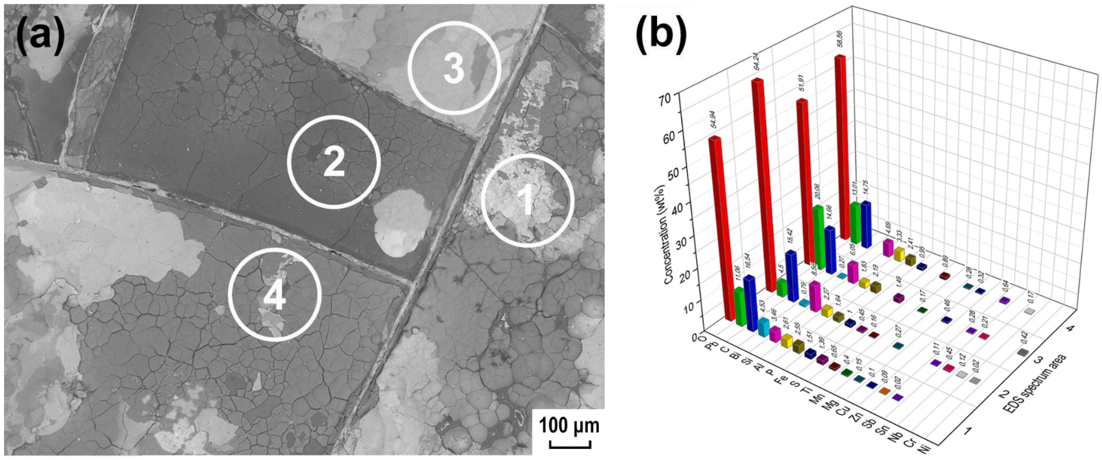

Fig. 7. SEM-EDS non-destructive analysis of the surface without prior preparation of a particular sample with a clearing procedure and a slightly polished finish: (*a*) morphology and (*b*) chemical composition of mixed type glaze of object No. 10.

transparent glaze base and the pigment component. In work conducted by Junko et al. (2015) 7 of 22 samples had zinc in the range of 0.08–0.19 wt%. Since ZnS sphalerite usually accompanies PbS, it is reasonable to assume that zinc is part of the transparent base. The addition of zinc oxide to green glazes contributes to the gloss and color saturation of this glaze. However, the deliberate use of zinc at the time of the Bohai State is doubtful. The initial raw material for the preparation of the base of lead glaze was most likely the most common hydrothermal sulfide – galena (lead sulfide (II) – PbS). This often occurs as dense grain masses of lead-gray color together with sphalerite (ZnS), pyrite (FeS_2), chalcopyrite ($CuFeS_2$), quartz (SiO_2), fluorite (CaF_2) and carbonates. Most likely Zn enters the glaze in the form of sphalerite together with galena.

The addition, Zr has a good effect on the consistency of the CTE of the glaze. Zr grains are contained in the and clay in concentrations of up to 3%, Zr do not affect the color. If the glaze is melted with water, after a month it will be impossible to stir because of the strong thickening process. Therefore, in contemporary ceramic manufacturing, a portion of the same clay (up to 5%) from which the vessel is made is added to the glaze solution, which allows the glaze to remain suspended while being easily stirred. Zirconium dioxide ZrO_2 is known as the rare mineral badelite ZrO_2, but is mainly used as the zircon mineral $ZrO_2{\cdot}SiO_2$. ZrO_2. Low coefficient of thermal expansion is responsible for the high thermal resistance it imparts to the glaze. The melting point of pure ZrO_2 is about 2900 °C, in the presence of impurities – from 2700 to 2900 °C (80–98% ZrO_2). Therefore, it makes the glaze more refractory. Like other oxides of the fourth group of the periodic system of elements, ZrO_2 increases the viscosity of the glaze and increases the temperature range of viscosity change.

Cadmium (Cd) sets the red color of the glazes, but at the concentrations determined in this study, it has no significant effect on the color. Vanadium (V) contributes to the yellow color of the glazes and in the samples studied its presence is characteristic for glazes with a light brown hue. Nickel oxides can be present mainly as Ni_2O_3 (dark gray to black) and NiO (green) in the glazes, with nickel oxide as the coloring agent, which gives the glaze different colors from violet to red-brown.

Mg is observed in two samples and the identified concentrations does not affect the quality of glazes. Special attention should be paid to the presence of Bi in the glaze, which was identified on items No. 11, 15 and 25 (Fig. 6), and also confirmed by EDS in object No. 13 (Fig. 8).

Ceramicists in medieval China, as is widely known, had an abundance of excellent refractory clay and materials that allowed them to turn their work into art (Vandiver, 1990). This process included the use of new materials and the invention or refinement of means to achieve new visual effects. Also, it is necessary to emphasize that comprehensive studies of ceramics include, among other things, the determination of the composition of ceramic masses belonging to certain geological provinces. In general, the raw materials for ancient Chinese fired pottery can be broadly divided into two categories: weathered acidic igneous rocks used in southern China, and sedimentary coal clay used in northern China (YANYI, 1987). The differences in the raw materials used in southern and northern China are due to differences in the geological structure of the two areas. This led to the emergence of different ceramic technologies in the North and the South. Studies to determine if the raw materials belong to a particular source are extremely complex, do not always allow unambiguous interpretation, and require the use of a set of analytical methods, including such as neutron activation analysis and/or inductively coupled plasma mass spectrometry (Cochrane and Neff, 2006; Hamdan et al., 2014; Kulkova et al., 2018; Spataro et al., 2015). Currently, Sr and Pb isotopic analysis that rely on the presence of sufficient contrast in the age of the geological formation is the most effective method for studying the origin of archaeological materials on a lead basis. This is used as a marker to indirectly estimate the source of silica in the glazes and compare fluxes (Freestone et al., 2003; Ganio et al., 2013; Henderson et al., 2005; Henderson et al., 2020b; Henderson et al., 2020a; Wedepohl and Baumann, 2000). Earlier, we conducted a study of the lead isotope in the composition of glazes of Sancai ceramic products from the Bohai sites of Primorye (Junko et al., 2015). The lead isotope ratios in the glaze material indicated several ore sources in northern and southern China. The possibility of a wider area is also indicated, including a suggestion of the probability of lead ores from Japanese sources. Lead glaze production in northern China may have developed since the Warring States (BC 475–221) period. The products of the Tang Sancai mark the culmination of this production and had a profound impact on time and space calculations (Tang, 2012). According to data presented in several studies conducted in China, lead-glazed materials from Bohai State Capitals could be made out of local iron-rich "red clay." In contrast, there is a high probability that the lead for these products may have been imported from Tang China and less likely from Japan, as assumed by Junko et al. (2015). However, the question of whether the glazed Bohai ceramics are either local or imported, as well as the possible transport routes by which the ceramics could get to the territory of modern Russian Primorye is still open to examination. It is very challenging to give an unambiguous answer to these issue, as the technological portraits of the studied Sancai products from the Bohai sites of Primorye are very diverse and leave considerable room for interpretation. A potential option for expanding the study and narrowing the options for interpretation is to collect samples of artifacts related to production, such as crucibles, tools, and sources of raw materials used to produce pottery and glazes within the borders of the Bohai State.

Table 5
Comparison of the results of the glaze composition of three-colored Sancai ceramics from the Bohai Kraskino walled town, obtained by pXRF and SEM-EDS methods.

Area, #	Method	Sample color	Chemical Elements, wt%																	
			Si	Al	Fe	Ti	Pb	Cu	Zn	Mg	Sb	Sn	P	Zr	Hf	Bi	V	Ca	Na	K
7.1–G	pXRF	Brown/green	17,35	4,59	2,05	0,59	73,03	0,72	–	–	0,22	–	1,42	0,03	–	–	–	–	–	–
	SEM-EDS	Green	18,3– 26,9	3,3– 5,3	0,4–1,3	0,18–0,32	60,1–67,1	1,4–1,6	∼ 0,1	0,2–0,59	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0,71–0,86	0,43–0,77	0,54–0,76
	SEM-EDS	Brown	16,3–32,3	4,9–7,3	0,78–0,91	0,19–0,29	57,1–63,2	0,23–0,36	n.d.	0,2–0,31	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0,29–0,35	0,52–0,6	0,51–0,6
8.1–G	pXRF	Brown/green	40,14	3,22	1,05	0,22	54,56	–	–	–	0,24	–	0,53	0,04	–	–	–	–	–	–
	SEM-EDS	Brown	32,3–38,3	0,4–5,3	2,1–2,8	0,1–0,22	52,02–54,03	0,08–0,09	n.d.	∼0,2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	∼0,4	∼0,4	∼0,5
12.1–G	pXRF	Green	18,43	4,15	1,04	0,25	74,75	0,85	–	–	0,22	–	0,31	–	–	–	–	–	–	–
	SEM-EDS	Green	23,0–25,3	6,0–6,3	0,4–0,63	0,1–0,16	64,1–69,5	1,3–1,6	n.d.	0,19–0,24	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	∼0,5	∼0,5	0,49–0,56
	SEM-EDS	Brown	14,8–29,7	21,00–25,7	7,1–8,2	1,0–1,7	45,2–50,2	∼0,1	n.d.	0,26–0,31	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	∼0,7	∼0,7	∼0,3
21.1–G	pXRF	Brown	42,21	3,33	3,49	–	49,91	–	–	–	0,31	–	0,72	0,03	–	–	–	–	–	–
	SEM-EDS	Brown	45,9–50,3	4,1–5,4	1,9–2,5	0,12	40,60	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	∼0,4	<0,1	0,19–0,24
23.1–G	pXRF	Brown	36,67	4,40	3,12	0,39	53,77	–	–	–	0,42	0,16	0,41	0,11	0,55	–	–	–	–	–
	SEM-EDS	Brown	41,1–57	5,1–5,5	1,9–2,6	0,14–2,21	33,8–38,4	0,07–0,09	n.d.	0,43	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	∼0,5	∼0,3	∼0,3
20.1–C/G	pXRF	Brown	42,59	26,07	6,25	3,25	11,33	–	–	–	–	–	10,01	0,36	–	–	0,14	–	–	–
	SEM-EDS	Brown	14,3–16,1	23,4–25,4	8,1–9,3	1,3–1,5	23,1–25,4	0,07–0,11	n.d.	∼0,3	n.d.	n.d.	21,8–23,3	n.d.	n.d.	n.d.	n.d.	∼0,3	0,51–0,55	0,35–0,44
17.2–C/G	pXRF	Green	38,10	15,28	6,80	1,33	35,27	0,48	–	–	0,37	–	1,64	0,26	–	0,34	0,13	–	–	–
	SEM-EDS	Green	23,0–24,8	4,3–4,8	0,85–1,1	0,14–0,24	59,9–67,4	0,45–0,75	n.d.	∼0,2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0,2–0,29	∼0,4	∼0,3
	SEM-EDS	Brown	52,5–55,1	10–12,3	2,7–3,1	0,35–0,5	25,9–28,6	0,51–0,81	n.d.	∼0,4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	∼1,4	0,29–0,36	<0,1

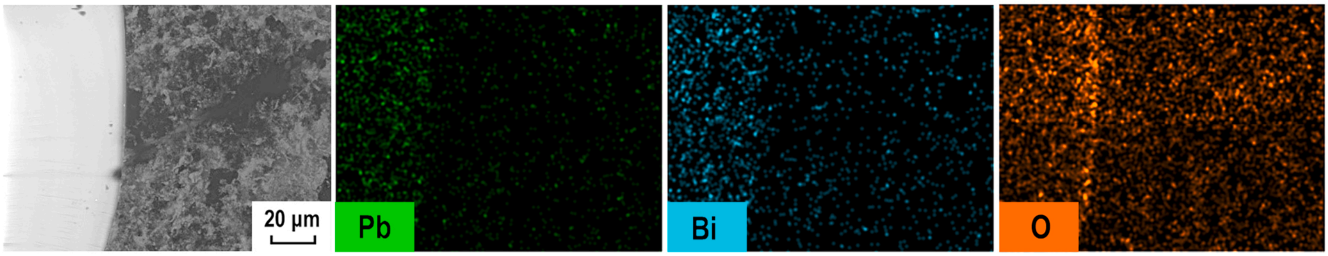

Fig. 8. Bi, Pb, and O distributions over the surface of sample No. 13.

5. Conclusions

The study of ceramics with monochrome and polychrome lead glazes collected during excavations at the Bohai sites of Kraskino and Gorbatka walled towns, and the Chernyatino-2 settlement (Russian Far East, Primorye Region) are presented. The fragments of the studied ceramic shards have no apparent similarity of technological composition (resulting from physical, chemical, and technological effects), which indicates their origin from different workshops or practicing different approaches to production. The cumulative effect of a set of technological traditions combined with the technological features of the workshops and individual masters refutes the possibility of the products belonging to a single batch or series in the final quality of the product. Glazes on the analyzed artifacts differ significantly from each other in thickness, density, and color saturation, as well as in the concentration of lead oxide. In the overall statistical sample this is characterized by a very high degree of dispersion of concentration values in the range of 36–79 wt%. Such significant differences in concentrations of lead oxide have a significant impact on the alteration of physical (fluidity, viscosity), adhesion (adhesion to the ceramic base, penetration, diffusion), and coloristic (color variety, tone, saturation, brightness) properties of the glaze under thermal treatment, changing from sample to sample the optimal firing temperature, affecting the quality of the glaze coating, leading to a wide variety of surface quality indicators. Defects in the nature of the glazes exhibits a low probability of peak firing approaches as demonstrated by the surface of samples coated in the state of the tension phase of the glaze mirror, good filling, and surface gloss. Based on the significant difference in thickness of the glaze layers on the inside and outside of the vessels, the multi-layered glaze is evident, achieved by repeated immersion and brushing. The formation of the color of the glaze is provided by a continuum of simultaneously present compositions of copper and iron compounds formed as a result of firing. The parameters and environments of which for the analyzed ceramic shards are different from sample to sample. Since most of the shards considered in this paper ~~are~~ were collected from layers II–V of the Kraskino ancient site, it is fair to argue that this variety of glazed products accumulated in the past by a process that collected them from various sources. This appears most likely. Or they may have accumulated by the continuous experimentation of local pottery workshop. However, there is no evidence of this.

The results of this study of ancient vessels with lead monochrome and polychrome glazes from Bohai sites in Primorye confirms their significant differences from Chinese Sancai. Lesser quality raw materials were used to produce these ceramics, which affected the characteristics of the glaze. The use of lead glazes for covering tiles and architectural decorations in the capital cities of the Bohai State may indirectly indicate that kilns for their production were located nearby. Glazed pottery could have been produced there as well. It is not excluded that the production of Sancai could have been established in other places as well, as potters from Kraskino produced unglazed grayish-white slip ceramics and ceramics with a grayish-white body. However, no direct evidence of glazed pottery manufacture on the site has yet been found. This study has compared ceramic samples collected from the Primorye territory to analogs found in China. It should be noted that among the visually studied samples there were no pronounced red-burning clay, as well as pure white clay, an absence of a slip layer under the glaze coating (which is not typical for Chinese analogs) and a somewhat lower brightness of glaze coatings when compared with even the dullest samples from the Tang, Japanese and Lyao kilns. In the early Bohai period, Sancai pottery was imported from China, but later it may have been produced in Bohai pottery workshops. Therefore, at this first stage of research, it has been possible to identify technological groups in the broad array of wares with lead glazes from Bohai sites located in the Promorye Region.

CRediT authorship contribution statement

I.Yu. Buravlev: Conceptualization, Project administration, Methodology, Investigation, Visualization, Writing – original draft. **E.I. Gelman:** Supervision, Validation, Resources, Writing – review & editing. **E.G. Lapo:** Investigation, Validation. **V.A. Pimenov:** Investigation. **A.V. Martynenko:** Investigation, Validation.

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