
Methods of Studying the Raw Material Base of the Pottery Industry

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Abstract:

The urgency of the issue is associated with the lack of a methodology for studying and identifying raw materials used for the production of non-glazed ceramics in Bolgar. The article considers the changes in the mineralogical and chemical composition of non-glazed ceramics in the process of its production. The leading method for solving this issue is the interdisciplinary approach with the use of technological experiments and physical and chemical research techniques.

As a result, changes in the petrographic and elemental composition caused by various impurities of organic, mineral and organomineral origin were investigated. The materials of the article represent the first observations of the transformations taking place in ceramic dough in the process of technological manipulation.

Keywords: *Archaeology, Non-Glazed Ceramics of Volga Bulgaria, Interdisciplinary approach, Experiment, Chemical analysis, Petrography.*

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1. Introduction

For many years, the formal typological approach has been the predominant method of studying non-glazed ceramics discovered at the sites of Volga Bulgaria. The result of long-term research was the classification of non-glazed ceramics from Volga Bulgaria suggested by Khlebnikova (1984) and further developed by Kokorina (2002). Researchers have identified 22 groups of ceramic dishware varying in terms of origin, appearance and manufacturing technology. One of the relevant problems in the study of Bolgar ceramics is the issue of industrial traditions. The most comprehensive research in this field has been carried out by I.N. Vasilieva on the basis of a historical and cultural approach by A.A. Bobrinsky (Vasilieva, 1993). In recent years, the authors of this article have studied the technological features of non-glazed ceramics from Volga Bulgaria within the framework of an interdisciplinary approach with the use of physical and chemical methods.

Analytical research demonstrated great potential in the determination of technological features of pottery products from 13th-14th century medieval Bolgar (Bakhmatova, 2012, p. 153; Khramchenkova, 2012, pp. 181-182; Bakhmatova & Kuklina, 2014, pp. 230-255; Khramchenkova, 2014, pp. 176-204). One of the relevant archeological issues of studying ancient pottery is the identification of raw materials for the determination of pottery local and foreign manufacture of ceramics. In most studies these tasks are resolved with the use of physical and chemical analysis techniques. All similar studies have been conducted based on an approach involving direct investigation of the potential raw material base and its comparison with archeological ceramics. A significant disadvantage of these studies is the lack of an established methodological comparison pattern. The comparisons of obtained results are usually highly formalized and do not consider the characteristic features of clay raw materials, the identification and characterization of raw material sampling and extraction sites, or the formulations of molding compounds, although all of these aspects require dedicated research with experimental verification of the results.

Thus, the primary objective of our study is the establishment of a universal method for identifying sources of raw materials for ancient pottery within the 'ceramics - source of raw materials' system. This objective can be accomplished by resolving the following tasks: the development of experimental study to order to investigate physical and chemical changes in ceramics under the influence of technological factors; the establishment of a pattern for the processing of data obtained during the analysis of experimental samples.

2. Materials and Methods

The methodological framework for the study is an interdisciplinary approach widely used in contemporary archaeological material science (Griffits, 1999; Hall & Minaev, 2002; Costa *et al.*, 2004; Gliozzo & Memmi Turbanti, 2004; Fernandez-Ruiz & G-Heras, 2007; Kreiter *et al.*, 2007; Ammerman *et al.*, 2008; Scarpelli *et al.*, 2010;

Braekman *et al.*, 2011; De Francesco *et al.*, 2011; Wever *et al.*, 2013). In our study, it is based on the principles of a historical and cultural approach to the investigation of ceramics (Bobrinsky, 1978, p. 14; 1999, pp. 20-22). The primary component of this approach is the technological experiment (Vasilieva & Salugina, 1999; Tsetlin, 2013, pp. 31-39). The chemical and mineralogical composition of experimental samples was determined with the use of physicochemical methods (petrography and emission spectral analysis). The obtained analysis results were processed in the form of numerical data using mathematical methods of comparing the ratio of numerical equivalents.

Technological experiment. The purpose of this experimental study is the identification of changes in the mineralogical and chemical composition of ceramic products under the influence of such technological factors as the firing temperature and the formulation of molding compounds. These factors were determined to have the strongest influence on the structure and composition of ceramic products (Salakhov & Salakhova, 2012, p. 297).

The experiment was conducted in accordance with the structure of the pottery technology, namely the preparatory, crafting and curing stages. In this case, we modeled the activities of a potter within the framework of a certain archaeological site. The initial plastic (clay) and non-plastic (impurities) raw materials were selected at the preparatory stage (selection, extraction and preparation of raw materials, composition of the molding mass. All raw materials were collected from a single ecosystem near Bolgar settlement (Code of sites, 2007, p. 321).

The clay was not subjected to special preparatory measures (soaking or sifting), and was only cleared of large debris and pebbles. The initial non-plastic raw materials were represented by basic impurities used in the production of ceramics in the Volga Bulgaria (crushed fragments of ceramic ware), river sand, cattle manure and crushed shells. The aforesaid impurities reflect various technological traditions of crafting various groups of ceramics (Vasilieva, 1988, p.103-150). Thus, the experiment was conducted with the use of three categories of impurities: organic, mineral and organ mineral (Bobrinsky, 1999, pp. 20-22).

Let us consider the process of preparing impurities and producing molding compounds. Organic impurities were represented by cattle manure in three different states (Group II): hand-rubbed dry manure (Subgroup II-1), wet manure (Subgroup II-2), wet manure extract (Subgroup II-3). In this case, the extract performs the functions of an organic solution obtained in the process of manual extraction of wet manure with the use of several layers of gauze fabric. Organic impurities are present in most groups of ceramics identified by T.A. Khlebnikova. Mineral impurities (Group III) in the form of river sand (Subgroup III-1) with the size of sand grains up to 0.5 mm. Deliberate introduction of the sand impurity is another widespread tradition associated with the preparation of molding compounds for ceramics discovered at the sites of Volga Bulgaria. It is most characteristic of the Bolgar Group I pottery referred to as

'juketau' (Group XIII ceramics), and also of the "Old Russian" pottery (Group XIV ceramics). The mineral impurities are constituted by Chamotte (Subgroup III-2) composed of pottery vessel fragments from the cultural layer of Bolgar settlement. The size of the chamotte grains varied from 2 to 5 mm with occasional larger fragments. The chamotte impurity is most typical for ceramic groups of Saltovo-Mayaki origin dating back to the pre-Mongol period (Group II, III, X, XI and XII ceramics).

Organo-mineral impurities are represented by impurities of various states and origins - river mollusk shells (Group IV). Snail shells and bivalves without the mollusks were collected in order to prepare the impurities. They were subdivided into two parts. One part was simply shattered with a pestle and mortar (Subgroup IV-2), and the other part was heated on coals and ground with the hands (Subgroup IV-1). The crushed shell impurity is one of the most unique and archaic types discovered in the dough of Bolgar ceramics. Ceramics with this type of impurities, generally corresponding to the Kama-Urals origins, is represented by Groups VII, VIII, XVIII. The admixtures were not specifically calibrated or sifted (Figure 1).

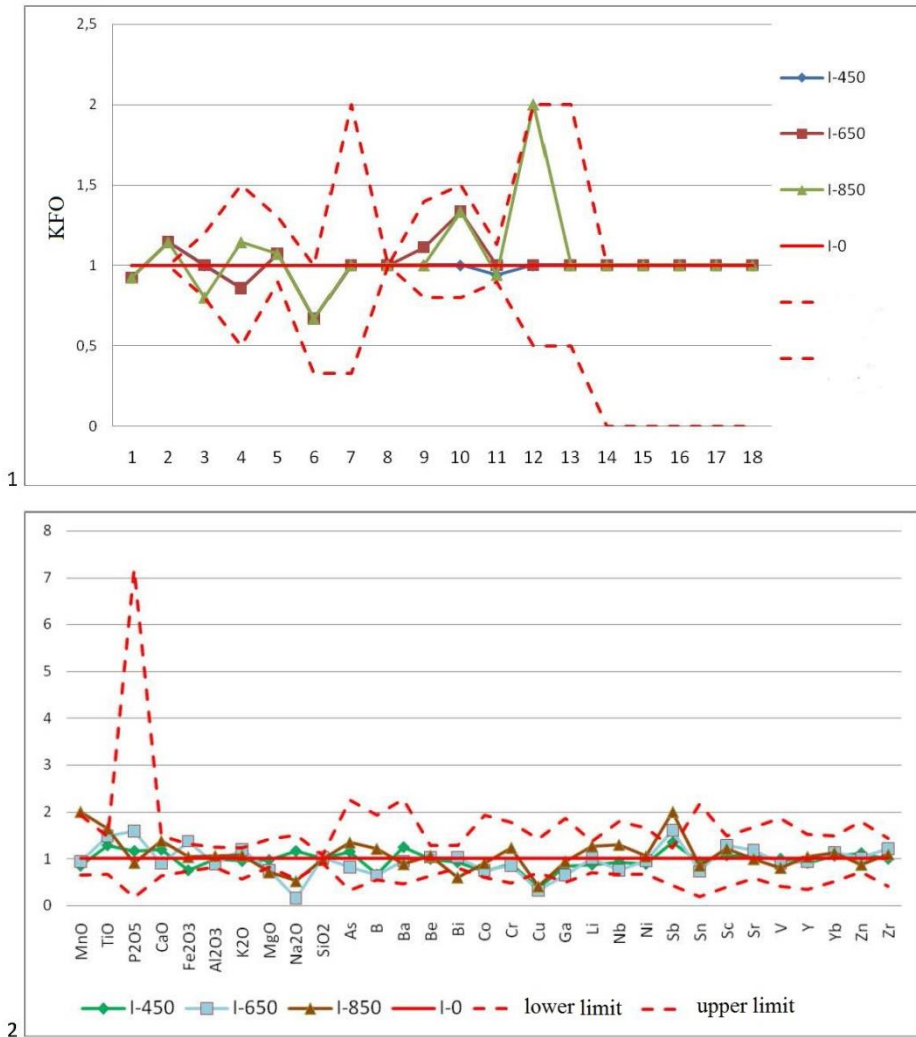
The molding compounds was prepared in accordance with principles based on the original traditions of purity, that is, the formulation comprised the initial plastic raw material (in this case it is clay) and a single type of impurities only (Tsetlin, 2012, pp. 68-70). All types of impurities were mixed with clay in a wet state with the ratios of 1:1, 1:2, 1:3, 1:7. Blocks dimensioned 10x1x1 cm were formed from the obtained compounds. Samples of pure clay with no admixtures were taken as well. All samples were marked with special codes (This technique for preparing experimental samples in order to study multicomponent molding compounds was suggested by Bobrinsky (1999)).

At the curing stage, all samples were dried in a ventilated room for the purpose of hardening. Firing of the material in an oxidizing medium was carried out in laboratory conditions in a muffle furnace with slowly rising temperature and an exposure period of an hour at 650 and 850 °C. The period of exposure to 450 °C amounted to approximately 12 hours (Fig. 1). The firing temperature was determined on the basis of experimental studies (Vasilieva & Salugina, 1999, pp. 181-198; Volkova & Tsetlin, 2015, pp. 56-62; Vasilyeva & Salugina, 2013, p. 66; Avgustinik, 1975, p. 189-196). As a result, an experimental series consisting of 108 samples was obtained (Appendix A, Table 1).

The complex of analytical methods was selected in accordance with the current task to trace the changes in the mineralogical and chemical composition of the experimental samples. A study of ceramic samples by optical spectroscopy and petrography allowed to determine their mineralogical and petrographic characteristics. A total of 110 thin sections were produced for the analysis. The analysis of the thin sections included the determination of the mineral composition, structure, and texture of the samples (The analysis was conducted by Ph.D. A.N. Kolchugin. The thin

sections were produced in the grinding workshop of FGUP TsNIIgeolnerud. The and Lithology of the Institute of Geology and Oil and Gas Technologies, Kazan Federal University, with the aid of the AxioImager.A2 polarization microscope. The results of optical microscopic investigation of the thin sections were corrected in accordance with x-ray analysis results). During the analysis, attention was paid to the amount of binding and fragmentary material, optically amorphous and thin-crystalline material, fragmentary, carbonate and other grains present in the sections, their shape, size, distribution across the area of the section, and spatial orientation.

Figure 1: Dynamics of the composition of samples consisting of pure clay without the addition of impurities (without firing I-0, firing at 450 C - I-450, firing at 650 C - I-650, firing at 850 C - I-850): 1 - mineralogical composition, 2 - chemical composition.



sections were analyzed in the lithology laboratory of the Department of Mineralogy. The following calibration scale was used in the analysis of fragmentary material - silt size 0.01-0.1 mm (fine silt 0.01-0.05 mm, coarse silt 0.05-0.1 mm); sand dimensions - 0,1-1 mm (fine sand 0,1-0,25 mm, medium sand 0.25-0.5 mm, coarse sand 0.5-1 mm); crushed stone dimensions - over 1 mm (Geological dictionary, vol. II, 1955, p. 138; Belousova & Mikhina, 1972, pp. 205-206; Betekhtin, 2007). The attribution of pore spaces is not perfectly accurate due to the specific features of the thin section production process.

The chemical composition of 107 experimental samples was determined using quantitative emission spectral analysis (The analysis was conducted by Head of the Restoration and Analysis Department of the Institute of Archaeology named after A.Kh. Khalikov of the Academy of Sciences of the Republic of Tatarstan Ph.D. Khranchenkova. The basic principle of the technique is as follows. A sample of 25 mg is burned out of a carbon electrode crater in an AC arc until complete evaporation.

The exposure time for highly volatile elements is 30 sec with a current strength of 8A, after which a portion of the diaphragm is covered, and the sample is burned at a current strength of 18A. The spectrum obtained with the DFS-458 diffraction spectrograph is recorded on PFS-03 photographic plates. The working grid of spectrograph No. 3 is 1800 pcs/mm with a resolution of 0.6 nm. The obtained spectrograms are photographed on the MF-2 spectrophotometer. The test samples are analyzed by using the traditional method of 3 standards. State reference samples SDPS-1, SCT-2, SKR-3, MSh-3 and enterprise standards were used as standards for the analysis. The analysis corresponds to the quantitative analysis with accuracy category III). The macro- and microelement composition was determined for all samples.

The statistical processing of analytical data was based on the principle of comparing the results obtained for the experimental samples with the results obtained for a pure clay control sample without the addition of impurities not subjected to firing. The analysis was carried out by means of comparing calculated numerical equivalents, which are the ratios of the value of an element or numerical petrographic characteristic in the experimental sample to the value of this element or characteristic in the control material.

The numerical equivalent reflects how many times the value of this element in an impurity sample has increased or decreased with respect to the value of this element in the pure clay sample. We referred to this numerical equivalent as the "deviation factor (DEF)" (For instance: $DEC(As, II-1 (1:7) 850) = As(II-1 (1:7) 850) / As(I-0)$, where the "deviation factor" of arsenic in a sample with an admixture of dry manure at a concentration of 1:7 is equal to the ratio of the obtained value of arsenic content in the sample with an admixture of dry manure in a concentration of 1:7 to the obtained value of arsenic in a pure clay sample with no impurities). Thus, the DEF of a pure clay sample is always equal to 1.

Most of the obtained values were greater or less than 1, in certain cases in tens of times. In this case, it is important to determine which changes are caused by errors in the analytical method, and which values exceed the specified limits. This required the introduction of the notion of 'error corridor (EC)' - a range of DEF values classified as errors in the method or the analysed collection of samples.

The 'error corridor' for the results of an optical microscopic study of thin sections was calculated using the aforesaid method of calculating DEF for a collection of samples consisting of repeating descriptions of certain experimental samples. It was discovered in the process of calculation that the only stable values in the corridor of error are those calculated for petrographic characteristics related to the silt and sand components of the samples. The appearance of larger grains or specific minerals in the experimental samples which are absent in the original source of raw material may imply certain indicators of impurities. Therefore, error calculations are only nominal for these impurities.

A total of 18 fragments were sampled from different ceramic vessels (1 fragment for a single vessel) to determine the 'error corridor' of spectral analysis results. Three samples of each fragment were taken from different parts of the fracture - from the inside of the vessel, from the outside of the vessel, and from the middle section of the fracture. These weighed samples were selected due to the different functional purposes of the vessels, which can account for different results of surface and inner layer analysis. The chemical composition of all samples was determined. When the results were compared, the values of elements from middle fractions were used as reference units. The DEF was calculated for the 'error corridor' of each element of the chemical composition and each petrographic characteristic of quantitative significance. After the completion of all calculations, maximum and minimum polar values were selected, which were referred to as 'upper and lower limits'. The unit and limit values were the primary components in the assessment of the dynamics of changes in the chemical and mineralogical compositions of the studied experimental samples.

3. Results

All samples were photographed and inspected after firing. As a result of the inspection, all experimental samples can be characterized as ceramic products with various impurities, that is, they have acquired strength and chemical resistance to the aqueous medium (they did not dissolve in water as a result of the residual plasticity test. The residual plasticity test was carried out in accordance with the procedure proposed by A.A. Bobrinsky (1999, pp. 20-22). All samples, regardless of the firing temperature, have acquired an auburn colour. Samples with shell impurities in all concentrations fired at 850 °C have acquired a drop-shaped transparent glassy stains on the surface (Fig. 2). Subsequently, samples with shell impurities fired at 850 and 650 °C collapsed, and some of them turned to powder (This case partially repeats the experiment with shell impurities conducted by Salugina (2006, pp. 379-381). Samples

fired at 450 °C with all concentrations and shell conditions have retained their shape and mechanical hardness.

As mentioned above, the assessment of the dynamics of the chemical and mineralogical composition of the experimental samples was carried out depending on the temperature conditions (non-fired samples, 450, 650 and 820 °C) and the types of impurities contained in the samples. The comparison was conducted in accordance with the general petrographic characteristics. (Appendix B, Table 2) An important feature of the series of experimental samples is their large petrographic similarity, which greatly complicates their classification.

According to the mineralogical composition, all samples can be subdivided into two large groups. Petrographic characteristics of these groups can be described on 2 diagrams (Figure 3). They are very similar in their general structure. Group 1 is naturally distinguished by the presence of detritus with a carbonate composition, which is represented by crushed shells. Group 2 comprises samples with organic and mineral impurities. An analysis of the colour characteristics of the clay binder contained in the polished section has not yielded any results. The colour varies from yellow and auburn to grey. It is not dependent on firing or type of impurity. It has a homogeneous base with an almost equal percentage of optically amorphous material in all samples. The qualitative composition of the primary binder can only be determined for the samples of group 1, which has a hydro-micaceous composition. An assessment of changes in the chemical composition was conducted in accordance with the macro- and micro-elemental composition with the consideration of an entire range of elements. Information on statistical processing results is given below.

Group I (pure clay samples). First, let us consider the mineralogical composition of pure clay samples without the addition of impurities, which have been fired at different temperatures. In this case, information has been obtained on how the firing temperature affects the mineralogical and elemental composition of the clay. Minor changes in the mineral composition take place during heating, but all of them are accounted for by the calculated 'error corridor'. The most significant changes occurred in the ratio of the primary binder amount and the general fragmentary component. This can be associated with an increase in the volume of quartz grains, which is caused by considerable heating of the grains. This circumstance is also confirmed by certain fluctuations in the average grain size across all size groups, which an increase of the firing temperature from 650 °C (Fig. 4). There is no significant dynamics in the chemical composition either. There are changes in the distribution of Na₂O, and the Cu content is rather low, which directly correlates with the firing temperature increase (Fig. 2).

Group II (samples with organic impurities). According to the primary petrographic characteristics, the mineralogical composition of this group is rather static. The ratio of the common binder and the general fragmentary component is changing in accordance with a characteristic pattern. Regardless of the concentration, these

deviations only constitute about 5%. The greatest deviations are observed in the content of sand-size quartz in samples with dry manure across all temperature conditions. The content of feldspar in experimental samples with a dry manure admixture has considerably increased, which is especially true for the sand fraction. Especially noteworthy is a sample featuring a wet manure admixture with a concentration of 1:3 (fired at 650 °C). In its composition features a sharply increased silt component, an average grain size and qualitative composition with the exception of quartz. This phenomenon probably has a random nature, determined by an uneven distribution of the impurity in the sample, for no such pattern is observed in other samples with this type of impurity. Among the most static petrographic features is the quantity of the aleuritic component, as well as the amount of quartz in the silt and sand components (Figure 3).

Figure 2: Dynamics of the composition of samples with organic impurities (dry manure - II-1, wet manure - II-2, manure extract - II-3): 1 - mineralogical composition, 2 - chemical composition.

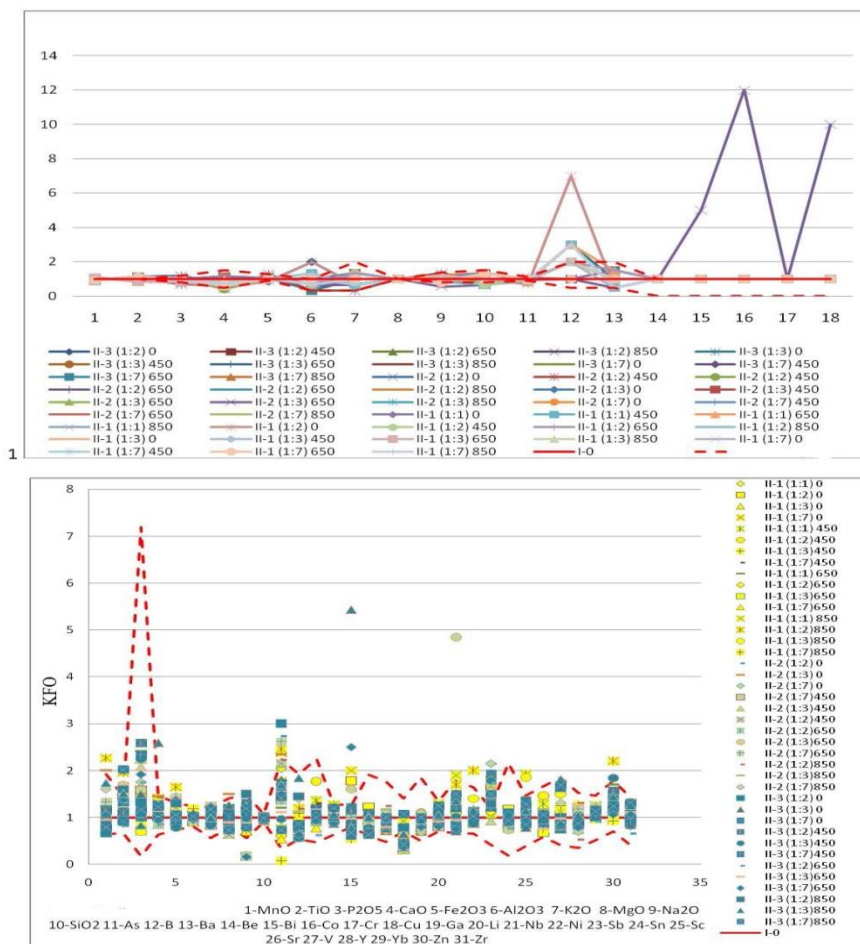


Figure 3: Dynamics of the composition of samples with mineral impurities (sand - III-1, chamotte - III-2): 1 - mineralogical composition, 2 - chemical composition.

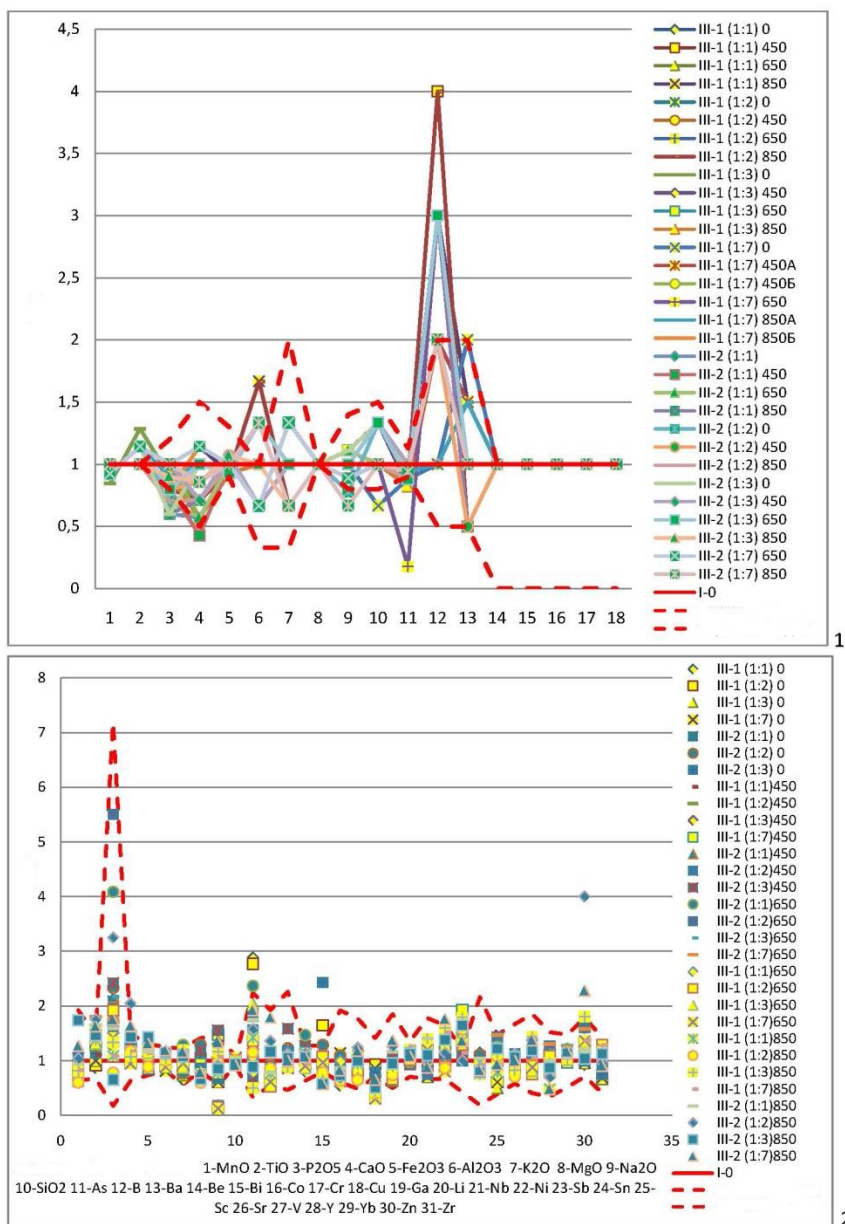
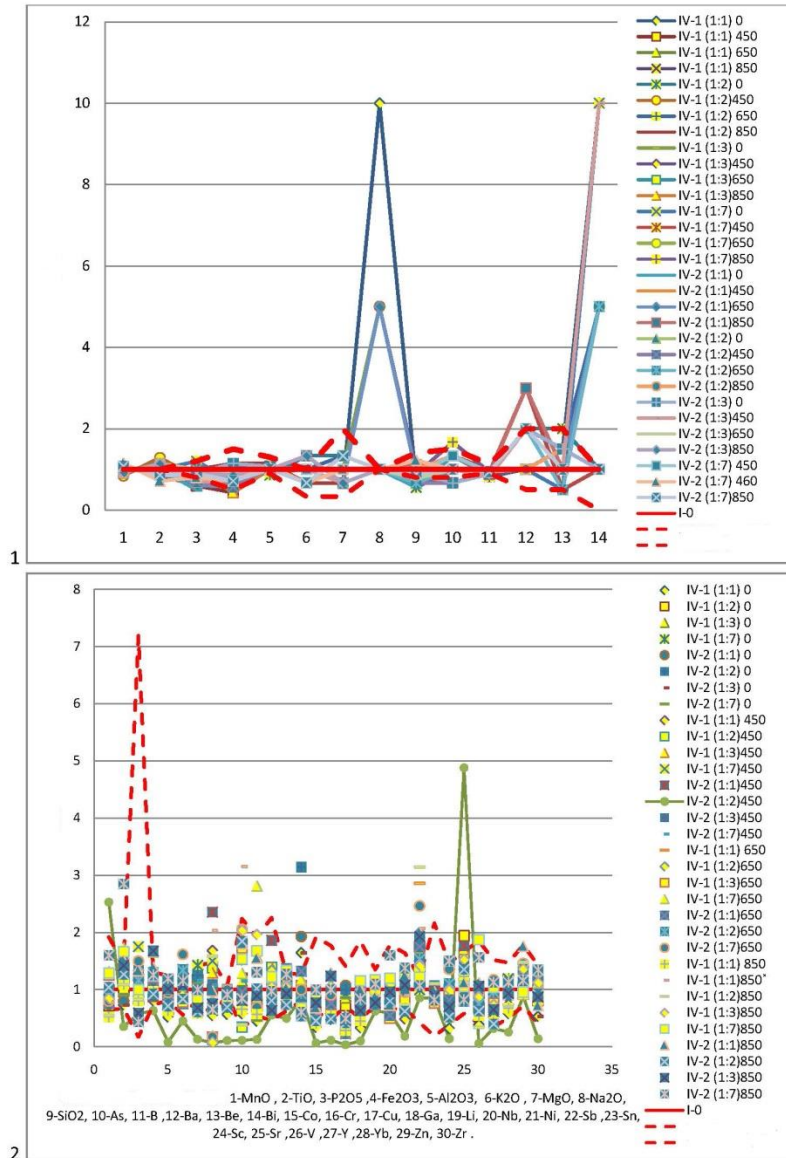


Figure 4: Dynamics of the composition of samples with organomineral impurities (heated shell - IV-1, 'raw' shell - IV-2): 1 - mineralogical composition, 2 - chemical composition.



The chemical composition is also rather static, except for certain elements and samples. There are virtually no deviations in the macro-elemental composition. In terms of the micro-elemental composition, there is a minor tendency towards an increased distribution of As, Bi, Sb, Nb, and reduced Cu content in samples containing all kinds of organic impurities with all concentrations and various firing temperatures.

Of special interest is a specimen containing a dry manure admixture with a concentration of 1:2, fired at a temperature of 850 °C; its composition features a slightly higher content of MnO, TiO₂, Fe₂O₃, As, Ni, Sb, Sc and Zn. Among the most static elements with their content practically unchanged under the influence of temperature and the introduction of organic impurities, are Al₂O₃, CaO, K₂O, MgO, SiO₂, Be, Co, Cr, Ga, Sn, V, Yb and Zr (Fig. 5).

Group III (samples with mineral impurities). More active dynamics is observed in the petrographic characteristics of samples with these kinds of impurities. Firstly, there is no gravel component in samples with a sand admixture (considering that sand with a grain size of 1.5-2 mm or less was used as an admixture in their production). This fact may indicate that grains of larger size and slit grains were painted when the polished section was produced.

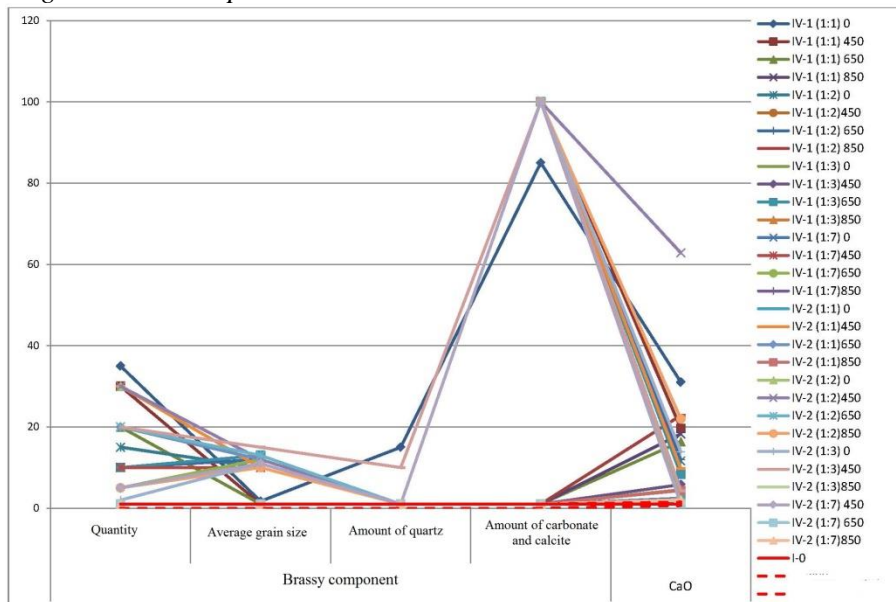
This circumstance disrupts the established pattern of the petrographic features of the sample. The ratio of cement base and fragmentary component in terms of quantity has insignificantly changed by approximately 5%. The series of characteristics intrinsic to the silt constituent of the samples is unchanged with several minor differences. The most peculiar pattern is observed in relation to sand size minerals. Changes in these characteristics directly depend on the mineral composition of the added sand and ceramics, which constitute the chamotte. In this case, the main components of these impurities are feldspars, as the content of quartz and other minerals remains within permissible ranges. The content of feldspars increased several times in the silt and sand component. The most stable characteristics are the content of quartz in aleuritic and sand dimensions, the total amount of aleuritic and sandy material, as well as the presence and content of single minerals and rocks, which account to no more than 5% of the total volume of the section (Fig. 6).

The macroelemental composition of samples with mineral impurities remains stable, although there is a certain tendency towards a decrease in the content of Na₂O. The content of As, Bi and Zn in the microelemental composition of the group of samples increased. In most samples, the Sb content is increased, and the Cu content is decreased. The most stable components are Al₂O₃, Si₂O₃, Ba, Ga, Li, Sn, Sr, V, Yb and Zr (Fig.6).

Group IV (organomineral impurities). The crushed shell impurity is fairly accurately identified by microscopic examination of ceramics using a binocular microscope. The presence of these impurities in experimental samples was also determined in the description of thin sections, but certain peculiarities can be distinguished in terms of changes in the mineralogical composition. The change in the ratio of the basic binding substance and the amount of fragmentary material is within 5%. The characteristics associated with the silt component are rather stable, except for the content of carbonate minerals and calcite. Almost the same pattern is observed with respect to the characteristics of sand material, which features a slightly increased content of feldspar grains. However, this trend is not typical of all samples, for several the samples

demonstrate high dynamics in the composition and amount of raw material. The content of quartz grains has significantly changed in two samples only. None of the samples contain shell inclusions larger than 1.5 mm, although the shell impurity was not individually calibrated. The increase in the number of feldspar grains of sand size and quartz grains of silt size probably has a random nature for certain samples. These grains could have appeared into the molding composition of this material together with the shell fragments collected in a coastal river area. Among the most static indicators is the amount of quartz in the silt and sand fractions.

Figure 5: Diagram for the distribution of the slit component and CaO in samples with organomineral impurities.



The addition of crushed shells affected the distribution of most elements of the chemical composition. These regular changes take place both in the form of increasing and decreasing in terms of the distribution of a single element. There is also a significant increase in the distribution of Na_2O , Bi, Sb and Sr for certain samples. For half of the samples, there is a tendency towards a decrease in the content of Al_2O_3 , SiO_2 , Co, Cu and Ga. The content of such elements as Sn, Li, V, Zn, Zr and Cr is almost unchanged.

The chamotte component and cloddy clay aggregates of the petrographic composition.

In the context of the analysis of this group of experimental samples, cloddy clay aggregates represent a natural component of the initial plastic raw material. These inclusions of different sizes and amounts are present in most experimental samples. Of most significance in this regard in the analysis of the chamotte grain dimensions in thin sections. The maximum value is defined as 1.5 mm, which also implies painting of larger grains during the preparation of the polished section (Appendix C, Table 3).

4. Discussion

Authors of this study attempted to answer the following two primary questions: how the composition of ceramic products varies depending on the formulation of the moulding composition, and how these changes depend on the firing temperature.

Ambiguous results were obtained after studying the changes in the mineralogical composition of experimental samples on the basis of optical microscopic examination of thin sections. The firing temperature in the oxidizing medium within the range of 450-850 °C selected by researchers had no significant effect on the mineralogical composition of the samples in question with any types of impurities and different concentrations. Initial strong fluctuations in the values of petrographic characteristics are observed and the temperature of 850 °C, but even these values are within the calculated 'error corridor'.

As a result of research, it was discovered that during the production of the thin section, large grains of hard minerals starting with 0.1 mm in size and larger chipped from its surface. This circumstance disrupts the overall pattern of the mineralogical composition of the sample for the majority of petrographic characteristics: the overall ratio of the binder and the amount of the fragmentary component, the content and dimensions of the grains of the sand and gravel component. Despite these circumstances, information on changes occurring in the material of the aleuritic dimension was obtained. The study of these indicators led to the conclusion that when impurities are added to the molding composition, most of the characteristics of the silt component remain unchanged. The strongest changes were observed in samples with the addition of organ mineral impurities, but these changes have an unstable nature and require further investigation (Appendix D, Table 4a).

The circumstances of the formation of cloddy clay aggregates and their relationship with the addition of chamotte to the molding composition raise many questions. It was impossible to determine regular changes in the ratio of the components of the mineralogical composition as a function of the concentration for the aforesaid reasons (chipping of large fractions during the preparation of the section). In the course of processing petrographic data, a conclusion was made regarding the cautious use of the petrographic method in order to elucidate certain technological features of the manufacture of ceramics, such as the molding formulation and the grain size of artificial leaners. However, this method is very promising in terms of characterizing the features of the initial plastic raw materials and its microscopic components.

Results of the study of changes in the chemical composition were also obtained. In the evaluation of changes in the chemical composition associated with the firing temperature in samples composed of pure clay, the greatest changes are observed in the distribution of the trace element composition - a decrease in the Cu content and an increase in the Sb content, although these changes are also observed in samples with various concentrations of all types of impurities. The macro-elemental composition

remained practically unchanged, especially in terms of the Al₂O₃ and SiO₂ content. The only exceptions are samples with crushed shell admixtures. All other changes in the chemical composition to a greater extent depend on the type of added impurity than on the temperature. However, at a temperature of 650 °C, visible changes in the chemical composition occur. A group of trace elements was also distinguished, the content of which did not change either with the addition of the impurity or with changes in the firing temperature - Cr, Li, Sn, Yb and Zr (Appendix E, Table 4b).

5. Conclusions

Thus, as a result of conducted research, the authors were able to identify certain patterns in changes of the composition of non-glazed ceramics, depending on certain technological factors - the firing temperature and the manual introduction of several kinds of impurities. The acquired observation results allowed to formulate the principle of identifying raw sources of ancient pottery on the basis of a statistical analysis of the results of physical and chemical studies of raw material and ceramic samples, caused by a change in the chemical and mineralogical composition of ceramic products during experimental firing. The completed experimental and analytical work can only be considered as the initial stage of scientific research.

Experimental studies in this field are not conclusive, but only determine promising research directions. In order to obtain a complete picture of the transformations that occur in the clay on its way to a finished ceramic product, it is necessary to study the influence of a number of technological factors, such as the type of firing (bugle, fire, hearth), medium and duration of firing (oxidative, reducing, combined), mixed recipes of molding compositions, and others.

The obtained results concerning the changes in the composition of ceramics depending on the type of impurity and firing in an oxidizing medium at different temperatures have revealed the necessity of taking these technological factors into account when analyzing the data of natural and scientific methods within the framework of non-glazed ceramics research. Probably, another important factor affecting the composition of ceramic vessels is the thickness of the vessel walls themselves. The results of the studies additionally confirmed the need for an integrated interdisciplinary approach to the study of ancient ceramics.

The proposed scheme of statistical data processing based on comparison of numerical equivalents as early as at this stage can be suitable for the analysis of ceramics and raw materials in the 'ceramics - source of raw materials' identification system. However, further research is required in order to identify a series of reliable mandatory characteristics for comparative analysis, especially in terms of the petrographic and mineralogical characteristics. The indisputable advantage of this approach is that the statistical processing of the results of each method can be performed independently. The next stage in the development of the method is the extrapolation of the results of the presented study to specific archaeological and raw material.

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°With firing	admixtures	II Organic impurities			III Mineral impurities		IV Organomineral impurities		I Clean clay with no added impurities
	concentration	II-1 Dry manure	II-2 Wet manure	II-3 Manure extract (organic solution)	III-1 River sand	III-2 Chamotte (crushed fragments of ceramic ware)	IV-1 Coal-heated crushed shells of river mollusks	IV-2 'Crude' crushed shells of river molluscs	
without firing	1:1	II-1(1:1)0			III-1(1:1)0	III-2(1:1)0	IV-1(1:1)0	IV-2(1:1)0	I-0
	1:2	II-1(1:2)0	II-2(1:2)0	II-3(1:2)0	III-1(1:2)0	III-2(1:2)0	IV-1(1:2)0	IV-2(1:2)0	
	1:3	II-1(1:3)0	II-2(1:3)0	II-3(1:3)0	III-1(1:3)0	III-2(1:3)0	IV-1(1:3)0	IV-2(1:3)0	
	1:7	II-1(1:7)0	II-2(1:7)0	II-3(1:7)0	III-1(1:7)0	III-2(1:7)0	IV-1(1:7)0	IV-2(1:7)0	
450 °C	1:1	II-1(1:1)450			III-1(1:1)450	III-2(1:1)450	IV-1(1:1)450	IV-2(1:1)450	I-450
	1:2	II-1(1:2)450	II-2(1:2)450	II-3(1:2)450	III-1(1:2)450	III-2(1:2)450	IV-1(1:2)450	IV-2(1:2)450	
	1:3	II-1(1:3)450	II-2(1:3)450	II-3(1:3)450	III-1(1:3)450	III-2(1:3)450	IV-1(1:3)450	IV-2(1:3)450	
	1:7	II-1(1:7)450	II-2(1:7)450	II-3(1:7)450	III-1(1:7)450	III-2(1:7)450	IV-1(1:7)450	IV-2(1:7)450	
650 °C	1:1	II-1(1:1)650			III-1(1:1)650	III-2(1:1)650	IV-1(1:1)650	IV-2(1:1)650	I-650
	1:2	II-1(1:2)650	II-2(1:2)650	II-3(1:2)650	III-1(1:2)650	III-2(1:2)650	IV-1(1:2)650	IV-2(1:2)650	
	1:3	II-1(1:3)650	II-2(1:3)650	II-3(1:3)650	III-1(1:3)650	III-2(1:3)650	IV-1(1:3)650	IV-2(1:3)650	
	1:7	II-1(1:7)650	II-2(1:7)650	II-3(1:7)650	III-1(1:7)650	III-2(1:7)650	IV-1(1:7)650	IV-2(1:7)650	
850 °C	1:1	II-1(1:1)850			III-1(1:1)850	III-2(1:1)850	IV-1(1:1)850	IV-2(1:1)850	I-850
	1:2	II-1(1:2)850	II-2(1:2)850	II-3(1:2)850	III-1(1:2)850	III-2(1:2)850	IV-1(1:2)850	IV-2(1:2)850	
	1:3	II-1(1:3)850	II-2(1:3)850	II-3(1:3)850	III-1(1:3)850	III-2(1:3)850	IV-1(1:3)850	IV-2(1:3)850	

	1:7	II-1(1:7)850	II-2(1:7)850	II-3(1:7)850	III-1(1:7)850	III-2(1:7)850	IV-1(1:7)850	IV-2(1:7)850	
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Appendix A. Table 1. List of an experimental sample series with codes.

Appendix B. Table 2. Primary petrographic characteristics of a series of experimental samples

No.	Primary petrographic characteristics of thin sections of a series of experimental samples
1	Primary binder (optically amorphous substance).
2	General fragmentary portion.
3	Amount of the silt component (grain size 0.01-0.1 mm).
4	Average grain size of the aleuritic component.
5	Amount of quartz of the aleuritic dimension.
6	Amount of feldspars of the aleuritic dimension.
7	Amount of siliceous rock fragments of the aleuritic dimension.
8	Amount of other minerals of the aleuritic dimension (calcite, carbonate).
9	Amount of sandy components (grain size 0.1-1 mm).
10	Average size of grains in the sandy component.
11	Amount of quartz of the sandy dimension.
12	Amount of feldspars of the sand dimension.
13	Amount of siliceous rock fragments of the sandy dimension.
14	Amount of other minerals and rocks of the sandy dimension (calcite, carbonate).
15	Amount of the silt component (grain size of 1 mm and larger).
16	Average size of grains of the silt component.
17	Content of quartz of the silt dimension.
18	Content of other minerals and rocks of the silt dimension (calcite, carbonate).

Appendix C. Table 3. Composition of cloddy clay aggregates and chamotte in the sections of the experimental samples.

admixture	Sample code	Ag	CFD	Pb	CFD	admixture	Sample code	Ag	CFD	Pb	CFD	admixture	Sample code	Ag	CFD	Pb	CFD	admixture	Sample code	Ag	CFD	Pb	CFD
pure clay	I-0	0.2	1	0.8	1	wet manure	II-2(1:2)0	0.01	0.05	0.87	1.0875	sand	III-1(1:1)0	0.01	0.05	0.65	0.8125	crushed sink preheated on coals	IV-1(1:1)0	0.02	0.1	12	15
	I-450	0.1	0.5	0.95	1.1875		II-2(1:2)450	0.24	1.2	1.2	1.5		III-1(1:1)450	0.04	0.2	1.1	1.375		IV-1(1:1)450	0.03	0.15	160	200
	I-650	2.2	11	0.94	1.175		II-2(1:2)850	1.4	7	1.3	1.625		III-1(1:1)650	0.04	0.2	1.5	1.875		IV-1(1:1)650	0.02	0.1	29.4	36.75
	I-850	1.1	5.5	1.1	1.375		II-2(1:3)0	0.02	0.1	0.91	1.1375		III-1(1:1)850	0.07	0.35	1	1.25		IV-1(1:1)850	0.23	1.15	73	91.25
dry manure	II-1(1:1)850	0.9	4.5	1.4	1.75	II-2(1:3)450	0.19	0.95	1.3	1.625	III-1(1:2)0	0.03	0.15	0.94	1.175	IV-1(1:1)850	0.1	0.5	134	167.5			
	II-1(1:1)0	0.03	0.15	1	1.25	II-2(1:3)650	0.015	0.075	1.325	1.65625	III-1(1:2)450	0.03	0.15	1	1.25	IV-1(1:2)0	0.02	0.1	12	15			
	II-1(1:1)450	0.02	0.1	1.1	1.375	II-2(1:3)850	0.1	0.5	1.4	1.75	III-1(1:2)650	0.025	0.125	1.16	1.45	IV-1(1:2)450	0.02	0.1	30	37.5			
	II-1(1:1)650	0.4	2	1.35	1.6875	II-2(1:7)0	0.02	0.1	0.9	1.125	III-1(1:2)850	0.04	0.2	0.77	0.9625	IV-1(1:2)650	0.01	0.05	2.5	3.125			
	II-1(1:2)0	0.02	0.1	1.1	1.375	II-2(1:7)450	0.27	1.35	1.1	1.375	III-1(1:3)0	0.02	0.1	1.2	1.5	IV-1(1:2)850	1.6	8	118	147.5			
	II-1(1:2)450	0.19	0.95	1	1.25	II-2(1:7)650	1	5	1.4	1.75	III-1(1:3)450	0.02	0.1	0.9	1.125	IV-1(1:3)0	0.02	0.1	25	31.25			
	II-1(1:2)650	0.045	0.225	1.55	1.9375	II-2(1:7)850	26	130	1.4	1.75	III-1(1:3)650	0.02	0.1	1.55	1.9375	IV-1(1:3)450	0.02	0.1	7.6	9.5			
	II-1(1:2)850	0.95	4.75	2	2.5	II-3(1:2)450	0.35	1.75	1.3	1.625	III-1(1:3)850	0.34	1.7	1.8	2.25	IV-1(1:3)650	0.015	0.075	2.7	3.375			
	II-1(1:3)0	0.02	0.1	0.8	1	II-3(1:3)450	0.06	0.3	1.1	1.375	III-1(1:7)0	0.02	0.1	1.1	1.375	IV-1(1:3)850	1.8	9	38	47.5			
	II-1(1:3)450	0.02	0.1	1.1	1.375	II-3(1:7)450	0.04	0.2	1.2	1.5	III-1(1:7)450	0.05	0.25	0.83	1.0375	IV-1(1:7)0	0.02	0.1	2.4	3			
	II-1(1:3)650	0.7	3.5	1.2	1.5	II-3(1:2)0	0.03	0.15	0.83	1.0375	III-1(1:7)650	0.02	0.1	1.3	1.625	IV-1(1:7)450	0.02	0.1	6.1	7.625			
	II-1(1:3)850	0.2	1	1.3	1.625	II-3(1:2)650	0.02	0.1	1.1	1.375	III-1(1:7)850	0.04	0.2	1.3	1.625	IV-1(1:7)650	0.015	0.075	7.4	9.25			
	II-1(1:7)0	0.02	0.1	0.79	0.9875	II-3(1:2)850	6.6	33	1.2	1.5	III-2(1:1)450	0.02	0.1	1.4	1.75	IV-1(1:7)850	14	70	31	38.75			
	II-1(1:7)450	0.02	0.1	1.3	1.625	II-3(1:3)0	0.02	0.1	1.3	1.625	III-2(1:1)0	0.02	0.1	1.9	2.375	IV-2(1:1)0	0.02	0.1	0.77	0.9625			
	II-1(1:7)650	0.02	0.1	1.2	1.5	II-3(1:3)650	0.02	0.1	1.2	1.5	III-2(1:1)650	0.02	0.1	2.05	2.5625	IV-2(1:1)650	0.02	0.1	0.945	1.18125			
	II-1(1:7)850	1.1	5.5	1	1.25	II-3(1:3)850	0.75	3.75	1.3	1.625	III-2(1:1)850	3.2	16	1.6	2	IV-2(1:1)450	0.06	0.3	0.8	1			
lower limit		CFD 0.05		CFD 0.56		II-3(1:7)0	0.02	0.1	0.76	0.95	III-2(1:2)0	0.03	0.15	1.7	2.125	IV-2(1:1)850	210	1050	1.2	1.5			
upper limit		CFD 12		CFD 2.13		II-3(1:7)650	0.025	0.125	0.98	1.225	III-2(1:2)450	0.02	0.1	1.3	1.625	IV-2(1:2)0	0.01	0.05	1	1.25			
						II-3(1:7)850	0.95	4.75	1.1	1.375	III-2(1:2)650	0.015	0.075	1.65	2.0625	IV-2(1:2)450	0.01	0.05	0.35	0.4375			
						II-3(1:2)650	1.2	6	1.4	1.75	III-2(1:2)850	0.37	1.85	1.4	1.75	IV-2(1:2)650	0.4	2	1.195	1.49375			
						lower limit		CFD 0.05		CFD 0.56		III-2(1:3)0	0.03	0.15	1.3	1.625	IV-2(1:2)850	120	600	1.4	1.75		

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						upper limit	CFD 12	CFD 2.13	III-2(1:3)450	0.45	2.25	1.4	1.75		IV-2(1:3)0	0.02	0.1	0.85	1.0625
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Appendix D. Table 4a. Petrographic characteristics, in terms of which the dynamics were traced after the addition of impurities and firing.

Petrographic characteristics	Organic impurities	Mineral impurities	Organomineral impurities	Pure clay with no impurities
Primary bonding material (OAB)	"+" "-"	"-"	"+" "-"	"-"
General fragmentary portion	"+" "-"	"+"	"+" "-"	"+"
Composition (A)	"0"			"0"
Average size of silt grains				
Quartz (A)	"0"	"0"	"0"	"0"
Feldspars (A)	"+"	"+"	"+"	
Fragments of siliceous rocks (A)			"0"	"0"
Other minerals (A)	"0"	"0"	"+"	
Composition (P)				"0"
Average size of sand grains				
Quartz (P)	"0"	"0"	"0"	"0"
Feldspars (P)	"+"	"+"	"+"	
Fragments of siliceous rocks (P)				"0"
Other minerals and rocks (P)	"0"	"0"	"+"	"0"
Composition (E)		"0"	"+"	a"0"
Average grain size (D)		"0"	"+"	"0"
Quartz (D)	"0"	"0"		"0"
Other minerals and rocks (carbonate, calcite) (D)		"0"	"+"	"0"
Chamotte		"+"		
Average size of chamotte grains		"+"		
GKA	"+" "-"	"+" "-"	"+" "-"	"+" "-"
Average size of GKA grains	"+" "-"	"+" "-"	"+" "-"	"+" "-"

Legend:			
Positive dynamics	"+"	Aleuritic component	(A)
Values have not changed	"0"	Sand component	(P)
Negative dynamics	"-"	Silt component	(E)
Optically amorphous substance	(OAB)	Cloddy clay aggregates	GKA

