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CHEMICAL AND PETROGRAPHICAL CHARACTERISTICS OF POTTERY FRAGMENTS FROM THE NEOLITHIC AND CHALCOLITHIC SITE BULGARCHEVO, BLAGOEVGRAD REGION

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ABSTRACT. The prehistoric settlement Bulgarchevo was excavated in 1967 by archaeologist Dimka Serafimova. During 1977-1986 the renewed investigations were led by Liliana Pernicheva from the National Institute of Archaeology and Museum in Sofia and with the participation of the archaeologists I. Kulov and M. Grebska-Kulova from the Regional Historical Museum in Blagoevgrad. 48 sherds from the Early, Middle and Late Neolithic and from the Chalcolithic period were studied. The chemical and petrographic characterization of these fragments has been carried out.

Introduction

The sherds found during archaeological excavations, is one of the first evidence for the ancient culture of the Neolithic and Chalcolithic people. The prehistoric settlement Bulgarchevo was found in 1967 by archaeologist Dimka Serafimova and during 1977-1986 it has been excavated. It is situated on the fluvial terrace of the Struma river valley at about 10 km to the North of Blagoevgrad. A large quantity of sherds is found at the site. They are dated to the Neolithic and the Chalcolithic period and are in safe-keeping in the Regional Historical Museum of Blagoevgrad.

On the basis of the complex chemical, mineralogical and microstructural investigations of 48 sherds, a general characterisation of the pottery from the Early, Middle and Late Neolithic and the Chalcolithic in this region is carried out. An attempt is made with the help of mineralogical methods of study to give an answer to a number of questions: composition of the clay, used for the pottery and surface slips (with chemical and mineralogical analyses), content of calciferous inclusions, potassium content in the clay, the kind of plastics and non-plastics components in the clay, sort and size of the non-plastics, firing conditions and comparison of the pottery from different periods.

Methods of investigations

In order to answer the questions and to determine the microstructure and kind of the minerals (non-plastics) in the tiles and slips numerous of optico-microscopic (transmitting and reflection type) and X-ray powder diffraction analyses have been carried out. The chemical composition of the initial clays is indirectly determined by the composition study of the ceramic tile and slips of the sherds by using microprobe analyses, performed with Phillips-400 and AES ICP chemical analysis of the part of the sherds from the Late Neolithic.

Composition of the initial clays

A direct answer about the composition of the initial clays is impossible. Information about it can be found in the numerous indirect evidence: chemical composition of the sherds, sort and quantity of the residual clastic minerals (non-plastics), microstructure and colour characteristics of the ceramic tile and slip (Fig. 1).

Chemical composition of the sherds

Variations in the chemical composition of the sherds from the Neolithic and Chalcolithic are shown in Table 1. In order to compare the chemical composition of the clays, used for pottery in different periods of the Neolithic and Chalcolithic the content of silica, iron and calcium oxides in the sherds are accepted as main criteria.

Based on the chemical compositions of some fragments from the Early and Middle Neolithic a similarity in the chemical compositions of the pottery can be established. This is indicative for the use of the same clay materials from local deposits in both periods.

The content of the main oxides varies in the following margins: SiO_2 55.17-65.60%, and Al_2O_3 15.92-22.99%. The silica comes from clays, quartz, feldspars, micas and less – from pyroxenes and amphiboles. A relatively higher content of iron oxides (5.76-15.08%) has been established. The iron oxides are related to biotite (lepidomelan) and ore iron oxides (magnetite, hematite). The calcite oxide varies from 1.17 up to 8.82%, and the magnesium one – from 1.28 up to 4.86%. The alkaliferous oxides are related mainly to the carbonate minerals calcite and dolomite. Among the alkaline oxides K_2O predominate over Na_2O, as K_2O changes from 2.13 up to 6.91% and Na_2O – from 0.00 up to 2.90%.

Table 1

Chemical composition of the sherds from the Neolithic and Chalcolithic, found in the prehistoric settlement Bulgarchevo

Oxides	Early Neolithic	Middle Neolithic	Late Neolithic	Chalcolithic
SiO_2	63.23-69.96	60.87-62.78	55.29-65.88	55.53
TiO_2	0.49-1.23	0.82-1.31	0.51-1.55	0.77
Al_2O_3	15.56-17.88	16.62-18.28	15.04-19.35	22.99
Fe_2O_3/FeO	5.76-7.68	7.37-10.84	6.05-15.08	8.30
CaO	2.07-2.46	3.14-4.15	1.17-8.82	3.04
MgO	1.96-3.34	1.28-1.54	1.64-4.86	2.86
K_2O	3.67-3.96	2.53-6.29	2.13-6.40	4.69
Na_2O	0.14-2.16	0.57-1.09	1.13-2.23	1.67

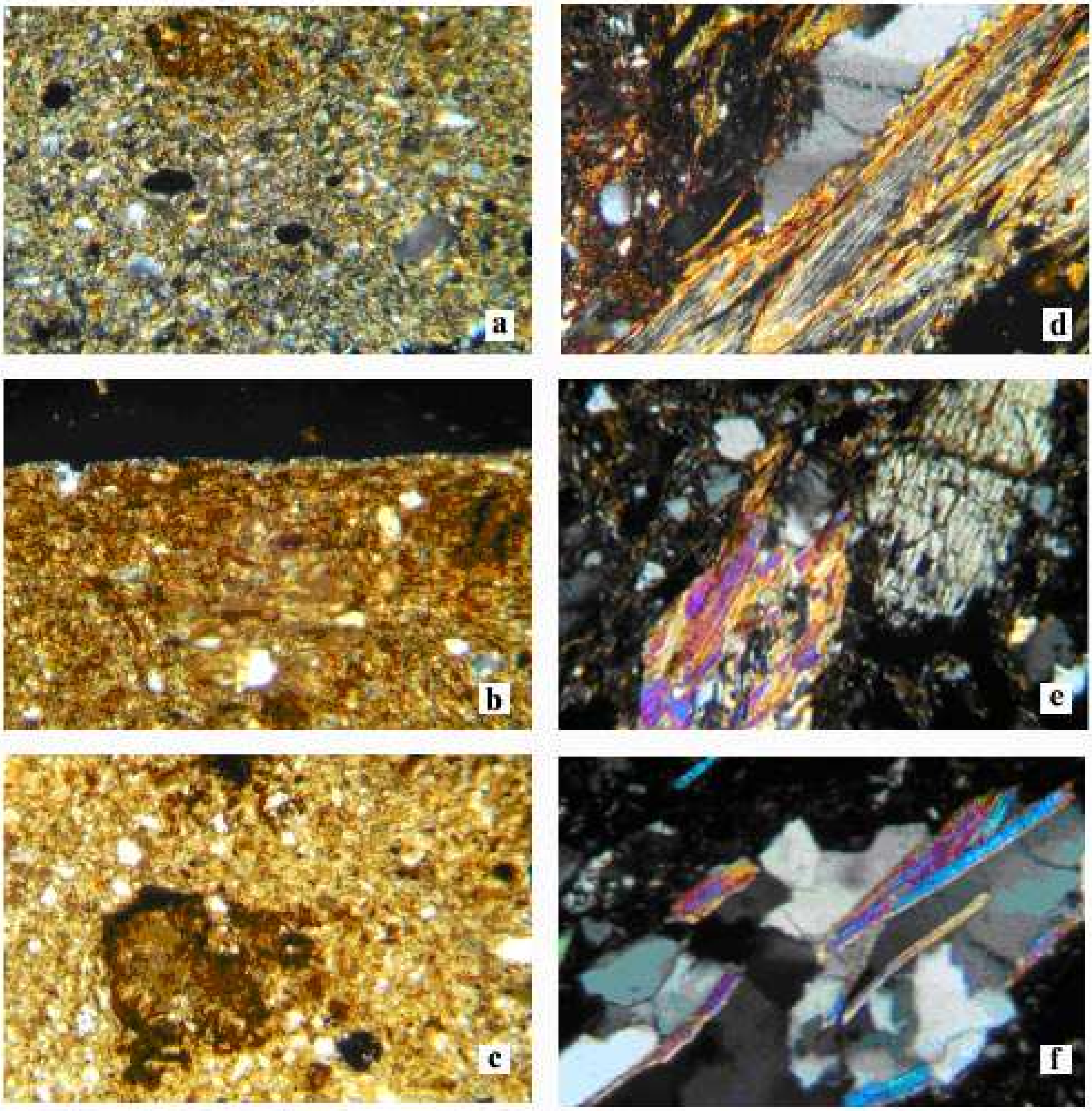

Fig. 1. Microstructure of the ceramics from the Neolithic and Chalcolithic: a – inclusion of quartz, b – microstructure of surficial layer in tobacco-brown colour, c – local fussion; d – microaggregate of quartz and mica; e – inclusion of quartz, pyroxene and mica, f – microaggregate of quartz, mica and feldspar; optical microscopy, X nicols, magnification x100

They are imported mainly with feldspar minerals (K-feldspar, albite and oligoclase) and muscovite. The titanium dioxide is with relatively constant content which is varying from 0.51 up to 1.01% and only in rare (isolated) cases up to 1.55%. Manganese oxide in insignificant amount (0.00-0.24%) was found in the sherds. Using AES ICP analyses, P_2O_5 from 0.36 up to 0.64% was identified in some of the sherds. Often it is imported by apatite. The content of SO_3<0.03% is also determined, probably imported by anhydrite ($CaSO_4$).

Following the received chemical compositions of the pottery, it can be assumed that in the clays from the Early Neolithic the amount of carbonate substance was in minor content (CaO is 2.07 up to 4.30% from the total mass) i.e. the clays were non-calcareous. Neither primary, nor secondary calcite ($CaCO_3$) is found in the initial clays. It is most likely that the clays, used in the Middle Neolithic, were enriched in carbonate substance, because of the CaO in some fragments which is 3.14 up to 4.15%. Moreover the tile in some fragments is light grey, nearly white and very well fired. This can be achieved in the presence of CaO from $CaCO_3$ (result of dissociation in temperature over 800°C) which together with iron oxide forms calcic ferrite with a grey-white colour. In the clay CaO is imported from plagioclases and ferric-calcic pyroxenes which are also determined as relict minerals in the sherds.

There is potassium found in the plastic clay. Its content in the fragments from the Early and Middle Neolithic is 2.53-6.29%. There are also alkaline oxides (K_2O and Na_2O) in the sherds from the Late Neolithic and the Chalcolithic and the content of the K_2O is 2 to 4 times higher then that of Na_2O. The content of the alkaline oxides is the lowest in the clay. In other fragments, manufactured from washed clay i.e. after coarse clastic grain elimination (mainly quartz) the content of K_2O and Na_2O is 1.5-2 times higher and in fragments from the Chalcolithic it is up to 5.90-6.91% for K_2O and 2.90% for Na_2O. The alkaline oxides are imported to the clays mainly from feldspars (potash feldspar, albite and oligoclase), from micas – muscovite and biotite (lepidomelan) and from hydromicas (illite).

The chemical composition of the clays allowed the assumption that three kinds of plastic mass are used for pottery production during the Late Neolithic and the Chalcolithic – two basic of red and grey clay and another one, probably with an addition of graphite (flakes of soot) into the red and grey clays for preparing of black products. In support of the claim that one kind of red clay was used is the presence of the same kind of the clastic material both for the surface layer and slip, and for the tile. Probably one and the same mineral deposit of red clay was exploited. The clays were sandy. The mainly used basic red clay was with content of FeO at about 8% and SiO_2 65.60% (according to its content in coarse-ware). In its natural status the red clay was used for fine ware. For fine ware the clay was additionally treated by washing in order to eliminate the coarser fractions of the clastic non-plastic material. In this way more fine-grainy material was received for thin vessels, for edges smoothing or for laying the angobe. In support of the last statement are the microprobe analyses of external parts which were smooth with more fine-grainy puddle clay. That is why the chemical composition of this surface is with lower content of SiO_2 (~55-56%) and without coarse clastic material (most often quartz-bearing).

Probably in order to achieve red colour of the slips the ruddle ochre was added to the red clay. The ruddle ochre is a fine powdered mass consisting of iron oxides and hydroxides. The higher content of iron oxide (up to 15.08% FeO) in red slips of some fragments can be explained by this.

Part of the pottery from the Late Neolithic, as well as the imported pottery type “Acropotamos”, are manufactured from red clay with 3-4 times higher content of CaO (8.82%) and MgO (4.86%) in comparison with other fragments. This is calcareous clay. The presence of enriched in carbonate minerals parts in the deposit is not impossible. The lighter colour of the tile is a result of higher content of CaO and MgO in the red clays with FeO about 8% – the calcic ferrites are formed.

Grey clay was also used. The preservation of the grey colour on the sherds is possibly a result of the lower temperature of firing. Less products were manufactured from this clay.

On the basis of microstructure and mineral composition of the clastic material can be assumed that other type of clay was used for a fragment from the Chalcolithic (without chemical analysis) and for some undated fragments. These fragments are referred to the dark brown almost black pottery. They differ from other fragments with coarse micrograiny structure and with scaly microaggregates of muscovite, mica with quartz, quartz with potash feldspar (Fig. 1d-f).

Possibly the black pottery is manufactured from red and grey clay with high content of bituminous in combination with graphite (flakes of soot). These vessels were fired in low temperatures.

Mineral composition of the non-plastics

On the basis of the optico-microscopic investigations the main non-plastics in the clay are quartz and potash feldspar. The geological setting of the prehistoric settlement “Bulgarchevo” (on the middle-high fluvial terrace among gravel-proluvial-deluvial depositions) suggests presence of the non-plastic minerals as clastic material in the composition of the initial clay. In this case the clay can be characterized as polyphase with aleurolite-pelitic micro-structure. The clastic fractions are 0.001 up to 0.01 mm in size. The coarser psammite fractions (0.01-0.1 mm) are rare and mainly in coarse-grainy ceramics. The feldspars grains in size about 1-2 mm and more than 1 mm are observed visually. In the sherds from the Early and Middle Neolithic their size is up to 5 mm.

The mineral composition of the non-plastics in sherds from the Late Neolithic and the Chalcolithic is the same clastic material presented mainly by quartz, feldspar (potash feldspar and acid plagioclase), grains of microaggregates of quartz with feldspars, mica (muscovite, biotite), in less content pyroxene, amphibole, rarely apatite, ore and other minerals. All these clastic minerals with relict origin are well observed microscopically. Quartz, K-feldspar, plagioclase, hematite and muscovite are studied also by X-ray powder diffraction.

For part of the sherds the dominant non-plastic is quartz with some feldspar (potash feldspar and acid plagioclase), while for others it is potash feldspar. Using X-ray powder diffraction analyses of coarse-grainy sherds from the Early Neolithic the free silica (quartz) is established as the main clastic mineral both in the tile and in the angobe. The content of quartz is usually more in the tile. On the basis of the same method, the predominant clastic mineral in fragments from the Early and Middle Neolithic in the tile and slip is the potash feldspar.

During the firing process potash feldspar and other minerals were not in complete interaction with generating cryptocrystalline clay mass and with the melting potash feldspar. Because of this they are preserved in all studied fragments. The potash feldspar is predominant mineral in the pottery, together with microcline and some plagioclase (albite type with polysynthetic twins). The potash feldspar is the melter. The clastic minerals in the clays, mainly potash feldspar, acid plagioclase (albite type) and hydromicas are relatively easy to melt. The melting of feldspars depends on admixtures and mainly onf the quartz content. The relatively pure feldspar (albite type) is fireproof at about 1118°C and potash feldspar – at 1150°C. The mixed K-Na feldspars are characterized with low fire-resistance – at about 1150°C, because of the formation of eutectics. In case of low content of quartz the alkaline melting influence is stronger and without any free quartz in the clays their temperature of sintering is lower than 1000°C. It is well known that the type of viscose of the potash feldspar melt is higher than those of the other minerals and this is very important for pottery. On the other hand in the melt of potash feldspar the admixtures of iron are easily soluble and are responsible for the brown or black colour. In the fragments from the Early and Middle Neolithic the micas are studied microscopically and with X-ray powder diffraction analyses. The muscovite is observed visually as fine flakes with pearl lustre.

There was a significant amount of iron-bearing minerals (pyrite, iron oxides and hydroxides, hydroalumosilicates, pyroxenes). Hematite and hydroxides are in fine disperse status with red, brown and yellow colour and they import their colour to the clay. These are the so called red or "coloured" clays. Depending on the kind of gaseous medium (oxidizing or reduction) during the heating the pyrite becomes decomposed and oxidizes and forms hematite, wustite or magnetite. It is most likely that the content of the iron oxides in the deposit was variable. It can be assumed that in the region of the prehistoric settlement the clays with low content of iron were present. They were bentonitic clays, dark grey in colour and were used for decoration in coarse-grainy ceramics. Some amount of organic material is found in the clays. In order to get the black colour of the tile the clays with higher content of organics were fired in oxygen deficit. This colour is a result of low oxidated forms of iron (divalent iron, included into the cryptocrystalline hosted mass after destruction of clay minerals in temperature lower than 500-600°C, into the glass-phase or as a black coloured crystal phases wustite and magnetite).

In the ancient prehistoric settlement "Bulgarchevo" the coarse-grainy ceramics from the Early Neolithic is manufactured from fusible clay enriched in hydromicas or bentonitic – with low content of the iron-bearing minerals. The kind and quantity of the coarse clastic material, remaining in the coarse-grainy fragments, suggests that the clays were aleurite-pelitic type with low quantity of coarse-grainy (psephitic and psammitic) fractions. In the composition of these clays the fine-grainy aleurite-pelitic fractions are predominant with minor content of organic material.

Microstructure of the sherds

The microstructure of the sherds is defined by the size and quantity of the clastic material, its distribution in the tile and surface slip, by the degree of its alteration during the firing process and by the degree of alteration of the clay material – its sintering and glaze, especially in the superficial slip of the pottery or in the hosted mass with local heated sections. The heavier sherds and those that are not well fired are characterised by more coarse-grainy structure of the clastic material mainly quartz (Fig. 1a-c), feldspars grains, micas aggregates, microaggregates of quartz with feldspars and mica (Fig. 1d-f). The quantity of the preserved relict clastic minerals varies in the fragments. Obviously it depends on whether the clay was preliminary cleaned from the coarse clastic material and on the temperature of firing. For example, in the surface slip, where the glassy phase is in more quantity, the content of the residual minerals (non-plastics and melters) is less than into the tile of the earthenware. In some sherd from the Early and Middle Neolithic the content of non-plastics is 5-10% from the whole mass, but in other it is about 15-20%. In the coarse-grainy ceramic fragments from the Early Neolithic the content of non-plastics is about 50%. The quantity of the coarse-grainy clastic material in the sherds from the Late Neolithic and the Chalcolithic also varies, depending on whether the used clay is in its natural state or it is additionally washed. In some sherds the quantity of the clastic material is more than 15-20%, in other – between 5-10%, and in third – at about 5% or 1-2%. Many sherds are very similar in microstructural aspect and they differ from each other only in colour of their surfaces – for example, brown surface on the cream-coloured base or they are monochromatically shaded.

The hosted ceramic mass is with semicrystalline microstructure which is characterized by presence of opticoisotropic amorphous material with inclusions from fine fractions of non-plastics, as well as from newly formed phases. In terms of heating process in temperature over 650°C the clay minerals became transformed in non-crystalline, optically isotropic material. In some ceramics the crystal microstructure of the hosted mass is fine-grained.

The microstructural peculiarities, the nature of the surface slip and the transition between slip and tile of the pottery are indicative for the use of one and the same clay. The following cases are defined in the studied pottery:

- a part of the sherds have gradual diffusion as transition between external surface (or angobe) and ceramic tile;
- in some fragments from the Late Neolithic and Chalcolithic the contact between the angobe (grey or black) and the ceramic tile is sharply outlined;
- as a result of low temperature superficial heating in some fragments from the Chalcolithic a smooth surface is obtained (it can be relatively easy separated from the tile; these are the most often observed surfaces of the dark brown coloured sherds).

Clays, used for manufacturing of pottery from the Neolithic and Chalcolithic settlement "Bulgarchevo"

On the basis of the chemical composition of the ceramics and slips, as well as the mineral composition of the clastic material and microstructural peculiarities of the studied fragments from the Neolithic and Chalcolithic an analysis of the clays composition compared to the abilities and skills of the ancient people in manufacturing various pottery shapes can be carreid out.

Comparing the data from chemical analyses of the sherds it can be established that during the Neolithic and Chalcolithic sandy clays were used. They were with similar chemical (SiO_2 at about 65%) and mineral composition, granulometric characteristics and high content of the iron oxides. These are the so called mottled or red clays. The red clay in its natural state was used for coarse ware. In order to manufacture fine ware maybe the clays were additionally washed. In this way the coarse-grainy fractions (the clastic non-plastic material) were eliminated.

Considerably low content of Al_2O_3, high content of FeO/Fe_2O_3 and K_2O defined the clays as low fusible i.e. the temperature of sintering is about 1050-1150°C. Most probably the plastic component in the clays is hydromica – illite, montmorilonite (bentonitic clay). In favour of this assumption are the wider diffraction reflexes at 9.90-5.00, 2.45, 2.12, 1.48 and 1.38 Å. These are characteristic features for illite, preserved as relict grains which have not completely reacted in the firing process. The non-plastics in the ceramics are: clastic minerals and rock pieces in sort of quartz, quartz microaggregates, feldspars (potash feldspar and plagioclases), micas (muscovite, lepidomelan), microparticles of pegmatite, composed of potash feldspar, quartz, mica, relicts of pyroxene, amphibole, chlorite, zoisite, garnet, apatite and other minerals. The characteristic feature of the deposit is its unsteady composition as regards non-plastic components.

The clays, used for red angobes are with high content of iron oxides – up to 9.20-10.84% Fe_2O_3 in fragments from the Middle Neolithic and up to 15.08% FeO in the sherds from the Late Neolithic. Probably in order to produce more brightly red coloured vessels in the Late Neolithic more ochre ruddle was added in comparison to the Middle Neolithic.

The chemical and petrographic analyses of 23 sherds from the Early and Middle Neolithic suggest that the clays, used for the tiles of various wares were from one and the same deposit. These clays are nearly identical in their chemical and mineral composition, granulometric features and in most cases they were red clays. During the Late Neolithic and mainly during the Chalcolithic more frequently the clay wares were manufactured in a sort of black pottery. In order to achieve this result probably flakes of soot (graphite) were added to the red clays. In favour of this assumption is the large quantity of black tiles among the investigated 25 fragments (from the Late Neolithic and the Chalcolithic). A large quantity of organic (humus) material in these clays can also be supposed. Because of the low temperature of firing and deoxidization, the humus defines the black colour of the tile.

The nature of the decorative effects in number of fragments (three-coloured or mixture) suggested that the ancient people were using flakes of soot (graphite) to get dark (black) colours. In support of this assertion is the homogeneous microstructure of the black surface slips in some sherds.

Obviously the ancient people from the area of the prehistoric settlement Bulgarchevo in the Blagoevgrad region as far back as the Early and Middle Neolithic became well acquainted with plastic characteristics of the clays and possibilities of manufacturing wares with different functional purposes. By means of firing the clay wares in different furnaces with limited or free access of oxygen (oxidation or reduction) they produced different kind of pottery. These people knew very well the local available sources of raw materials. They created a number of objects with various surface decorative effects.

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