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THE INVESTIGATION OF ANCIENT POTTERY
Application of thermal analysis

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Ancient ceramic samples (single fragments and different parts of pots, unbroken and repaired; total about 180 samples) dated from the transitional period of late Bronze to early Iron Age (VIII-VI centuries BC) and early Iron Age (VII-IV centuries BC) were investigated by thermal analysis, X-ray powder diffraction, petrography, and scanning electron microscopy equipped with the energy-dispersive X-ray analyzer. In addition to that, to identify the clay sources for the ceramic manufacturing, about 15 samples of clays and soils found near archeological digs and taken from the mineralogical museum were investigated. We found out that the calcite content of ceramics is a very informative parameter for the identification of the clay source for the pottery manufactured at low technological level (low-temperature firing).

Keywords: *ancient ceramics, calcite, clay, pottery, thermogravimetry*

Introduction

Thermal analysis is an adequate tool for checking quality in the manufacture of ceramics. It allows one to control the processes at firing and to analyze the starting materials and products. Traditional approach to the interpretation of thermoanalytical results is based on several postulates, which can be readily checked experimentally. For example, a thermal transformation in a constituent mineral of clay is considered irreversible if a gas escapes from the sample. When a product of the ceramic manufacture is analyzed again, i.e., at the second heating, exothermic reactions or/and those with a gas release are supposed to occur only at temperatures higher than the temperature of the first heating.

This consideration is the base for the investigation of ancient ceramics and pottery in many publications [1–7]. The investigations are aimed at the reconstruction of manufacturing operations and identification of raw clay sources. Comparing the ceramics from different regions, clays from various localities, and specific features of pottery manufacturing and burning in a kiln, the archaeologists make conclusions about the technological level of ancient pottery-makers and trading relations among various regions.

Recently, following this tradition, a careful and thorough examination of chemical composition and phase constituent of Etruscan-Padan type pottery from the Veneto region was accompanied by the experiments on firing clay samples from areas surrounding the archaeological sites [8]. The temperature of firing ranged from 400 to 1100°C. The freshly prepared products after the firing were compared with the ancient pottery, to reconstruct the firing temperatures. As for the source areas of the raw materials used in ceramic production, the conclusion was made that these cannot be identified.

The situation when attempts to identify the source of raw materials used in ceramic production using the traditional interpretation of the experimental data obtained by thermoanalytical techniques is rather common. In our own investigations of the ancient pottery manufactured at a very primitive technological level, we realized that a new approach to the interpretation of the experimental results was needed. Our objective therefore became to examine the conventional base for the thermoanalytical investigation of ancient pottery, to identify the controversial points, and to

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suggest an alternative approach, which could help to solve the problems remaining unsolved otherwise. We used our own thermoanalytical data, for those published are not complete for a complete analysis.

Experimental

Samples

We investigated the samples of ancient ceramics dated from the transitional period of late Bronze to early Iron Age (Chicha and Linjovo of Novosibirsk region, VIII-VI centuries BC) and early Iron Age (Glazovka, Zhelty Yar, Poltse, Bulochka, and Amursky Sanatory of Russian Far East, VII-IV centuries BC). About 180 samples total were investigated by thermal analysis (TG, TMA, DSC). In searching for the clay sources for the ceramics manufacturing, we investigated 15 samples of clays and soils found near the archeological digs and taken from the Mineralogical Museum of the United Institute of Geology, Geophysics and Mineralogy of SB Russian Academy of Sciences (UIGGM SB RAS). In the present paper, we describe the results obtained for several selected samples only, which are very representative. When describing the results of the experiments, we shall refer to them as follows:

Sample 1: The clay from an abode N17 of Linjovo. A lump of red clay as if prepared for the production of a ceramic vessel, was found during the archeological dig. The sample was analyzed ‘as found’.

Sample 2: The clay from a nearest clay deposit, near a lake, 2 km far from the place of archeological dig in Chicha-1.

Sample 3: The clay loam from Chicha-1. The sample was taken right at the place where the abode was.

Sample 4: The clay from the Angren bentonite deposit (Uzbekistan), taken from the collection of the Mineralogical museum of UIGGM SB RAS.

Sample 5: The sherd of Linjovo. A piece of the bottom part of a pot.

Sample 6: The sherd Ch18-02, Late Irmen´ Culture. Single fragment.

Sample 7: The sherd Ch24-02, Late Irmen´ Culture. Single fragment.

Sample 8: The sherd from Zhelty Yar, N38. A piece of pot N4.

Analytical techniques

The samples were investigated by thermogravimetry (TG-50 Mettler and TG-209 Netzsch), thermomechanical analysis (TMA-40 Mettler) and differential scanning calorimetry (DSC-30 Mettler). TG was found to be the most informative technique. To make the comparison between investigated samples as accurate as possible, most of the experiments were carried out under identical conditions: TG-209, heating from 22 to 850°C at the heating rate of 20°C min^{-1}, flow of high-purity Ar of 25 mL min^{-1}, open golden crucible of 546.8 mg, sample mass 47.00±0.15 mg.

X-ray powder diffraction patterns were measured using diffractometer D8-GADDS (Bruker) with CuK_α radiation. The experiments were carried out both with static position of a sample and with rotating sample holder.

Petrographic analysis was carried out in the Novosibirsk Geological Survey (Expedition) according to the procedure developed specially for the ancient ceramics and described in [9].

Scanning electron microscopy was performed at the UIGGM SB RAS with SEM LEO 1430VP equipped with the energy-dispersive X-ray analyzer (EDX, spectrometer 'Oxford') with typical spot size of about 5 μm. The samples were coated with evaporated carbon.

Results

Clays

At heating, clays show significant mass loss due to (I) the dehydration (r.t. to ~200°C), (II) decomposition of hydroxyls (400 to 650°C), and (III) decomposition of carbonates, mainly calcite (700–800°C). Figure 1 shows the results of TG experiments carried out on three clay samples with three temperature intervals of the three mass loss steps indicated right at the Figure. The derivative $\mathrm{d}m/\mathrm{d}t$ shown in Fig. 2, indicates the steps more clearly. The samples lose 6.4% (1), 3.1% (2), and 3.4% (3) on dehydration and 5.2% (1), 3.8% (2), and 2.8% (3) on the decomposition of hydroxyls. As for the decomposition of carbonates, only sample 2 contains calcite and loses 1.7% additionally. Total mass loss is 14.4, 9.4, and 6.6% for samples 1, 2, and 3, respectively. Water content of clays depends on the humidity, and the mass loss of an air-dried sample ranges at the first step (up to 200°C) within the limits of 2–3%. In our measurements, experimental error in the mass loss is about 0.03% (±0.015 mg).

DSC signal is the derivative by nature and DSC curves for clays look like those of TG in Fig. 2. These are a sum of two items:

$$W = \beta\left(q\frac{\mathrm{d}m}{\mathrm{d}T} + C_\mathrm{P}m\right) \qquad (1)$$

where β is the heating rate $\frac{\mathrm{d}T}{\mathrm{d}t}$, q is the heat of dehydration (hydroxylation, decomposition of calcite), C_P

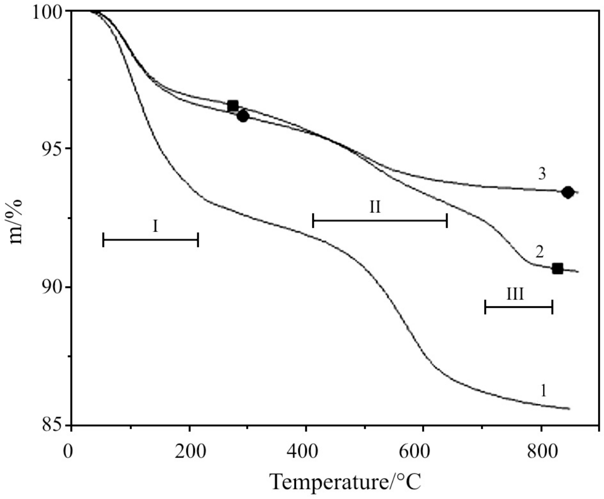

Fig. 1 Mass loss at heating of three clays: samples 1, 2, 3. Roman numerals indicate temperature intervals of dehydration (I), dehydroxylation (II), and decomposition of calcite (III)

is the heat capacity of a solid phase, and m is its mass. The first term in the right-hand part of Eq. (1) is equal to the derivative of TG signal multiplied by coefficient q, it looks like a peak. The second term is a smooth function of temperature. In comparing quantitatively the DSC results for different clays, we have either to consider the amplitude of the DSC signal (both terms together) or to integrate the peak. Experimental accuracy of DSC measurements is less than that of TG, for an experimental error of the former is the sum of the errors of (1) calibration, (2) extraction of a baseline, (3) reproducibility of kinetic conditions of dehydration (dehydroxylation, decomposition of calcite). Kinetic factors are diminished after the integration of a peak, but two first sources of the experimental error (about 3% in sum) remain:

$$\Delta H = \beta \int_{T_1}^{T_2} q \frac{\mathrm{d}m}{\mathrm{d}T} \mathrm{d}t = \bar{q}\Delta m(T_1,T_2) \qquad (2)$$

here, $\bar{q}$ is the average heat of dehydration (dehydroxylation, decomposition of calcite) over the temperature range T_1 to T_2, $\Delta m(T_1,T_2)$ is the mass loss over that range. The last value can be readily calculated after direct TG measurements with much more accuracy. As compared to TG, only one extra heat effect is measured by DSC, namely the phase transition (PT) in quartz at 573°C. Exact value of the T_{PT} in quartz was used for the comparison between natural samples [10], but there is no reliable algorithm to compare the difference in T_{PT} with other properties of a sample so far.

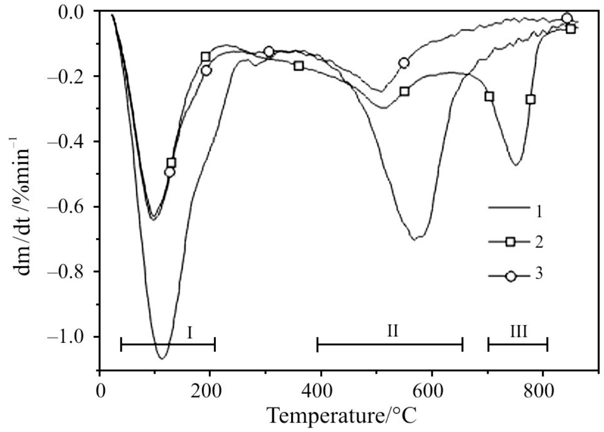

Fig. 2 The rate of mass loss. The numerals and samples are identical with those in Fig. 1

TMA signal also consists of two contributions, ordinary thermal expansion (α) and a size change due to the dehydration dL/dm. Sample length changes with temperature according to equation

$$\Delta L = L_0\alpha\Delta T + \frac{\mathrm{d}L}{\mathrm{d}m}\frac{\mathrm{d}m}{\mathrm{d}T}\Delta T \qquad (3)$$

where L_0 is the starting sample length and ΔT is the temperature increment. The first term in the right-hand part, i.e., ordinary thermal expansion, is always positive, but the second one is negative (contraction) for dehydration and positive (expansion) for dehydroxylation. The results of TMA measurements of sample 4 are shown in Fig. 3 together with those of TG. Anyway, Eq. (3) describes the experimental results not quite accurate. As clay consists of flat anisotropic particles, mechanical treatment, for example glossing or sedimentation, can change the bulk expansion of a sample along particular direction. As compared to TG, TMA reveals, like DSC, additional peak of expansion at the phase transition in quartz near 573°C.

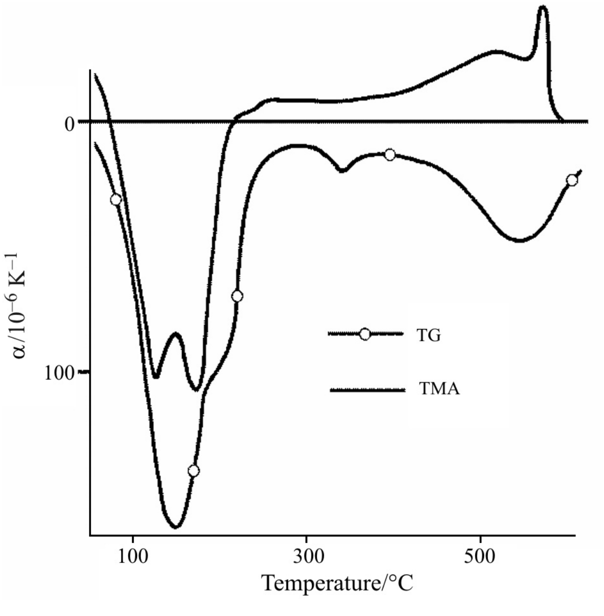

Fig. 3 Comparison of TG and TMA results of bentonite (sample 4). The sample contracts at dehydration but expands at dehydroxylation. Peak near 573°C is the phase transition of quartz

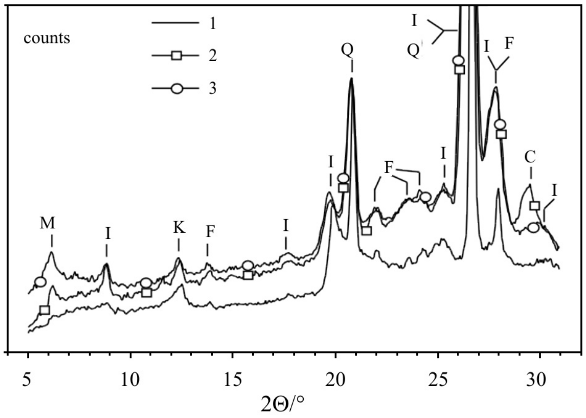

Fig. 4 X-ray powder diffraction patterns of samples 1, 2 and 3, the part for 2Θ<31°. The letters indicate the reflections of the phases: M – montmorillonite, I – illite, K – kaolinite, F – feldspar, Q – quartz, C – calcite

X-ray powder diffraction patterns of samples 1 to 3 are shown in Fig. 4. Angle range from 5 to 31° of 2Θ is used because this contains most information about clay minerals. All the samples contain kaolinite (ICDD 14-0164), quartz, and feldspar (albite-anortite). Sample 1 differs from samples 2 and 3 in the amounts of illite (26-0911) and montmorillonite (chlorite-vermiculite-montmorillonite, 39-0381). Samples 2 and 3 are very similar in mineralogical composition, except calcite. Sample 2 has the strongest reflection 104 of calcite at 29.36°. At heating, it loses mass in a temperature range of 700–800°C (Figs 1 and 2).

After heating up to 860°C, the clay minerals in the samples are destroyed. Figure 5 shows X-ray powder diffraction patterns of sample 2 before and after heating. Reflections of montmorillonite and kaolinite disappear completely, and those of illite decrease in intensity. The reflection of calcite disappears as well.

The composition of a main body of clay samples was investigated by the energy-dispersive X-ray analysis at several points for each sample. The point analyses differ from one another, but after all the results are analyzed, they allow one to consider 'average' composition of the sample. The results for the clay samples 1–3 are shown in Fig. 6. According to the X-ray powder diffraction, kaolinite is the main clay component of sample 1, but samples 2 and 3 contain mainly illite and montmorillonite. Figure 6 proves that the clay mineral in sample 1 is depleted in cations and that samples 2 and 3 are very similar in cations except Ca and P. High Ca content of the clay mineral in sample 2 agrees with the presence of calcite in the bulk clay.

Special procedure of petrographic analysis for ceramics provided us with the information about quantitative volume composition of minerals. This information is very important for the analysis of which minerals were added to the clay during the production of ceramics and in what amount.

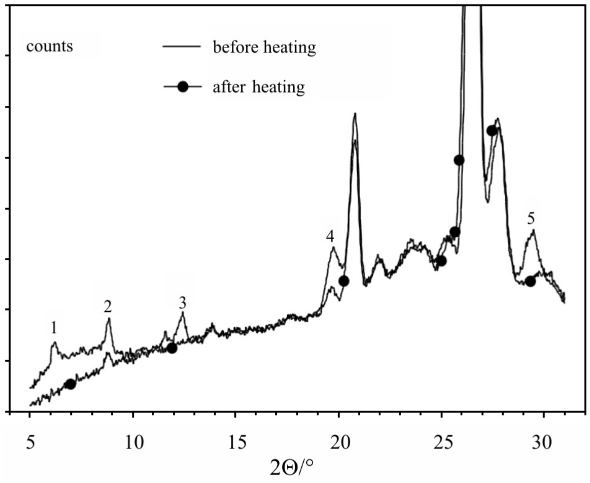

Fig. 5 X-ray powder diffraction patterns of sample 2 before and after heating to 860°C, the part for 2Θ<31°. Reflections 1, 3, and 5 vanished, 2 and 4 decreased

Ceramics

The results of thermogravimetric measurements of three samples (5, 6 and 7) of ancient ceramics are shown in Fig 7. These samples differ from one another in the same way as the samples of clays (1, 2 and 3) differ in Fig. 1. They also lose mass due to dehydration (4.2, 3.0 and 2.0%) and dehydroxylation (2.0, 1.5 and 1.4%). As for the decomposition of carbonates, only sample 6 contains calcite and loses 0.8% additionally. Total mass loss is 9.4, 7.4 and 5.1% for samples 5, 6 and 7, respectively. Figure 8 shows the rate of mass loss of these samples. As compared to the clays in Fig. 2, the peak of dehydroxylation is evidently less for ceramics than for clays. Nevertheless, the dehydroxylation does occur at heating of ancient ceramics.

X-ray powder diffraction patterns of ancient ceramic samples are similar to those of fired clays but with additional reflections from mineral fillers (feldspar, quartz, etc.). For the range of 2Θ<21°, the patterns from ceramic samples are very similar to each other and differ only for 2Θ>21°.

Petrography of ancient ceramics provided us with the information about mineral fillers, their variety and concentration, and fire cracks. Unfortunately, this was of little use for the solving the problem of what was the source of clay for the ceramics production. More informative is the scanning microscopy equipped with the energy-dispersive X-ray analysis.

Figure 9 shows the picture of sample 5 from the SEM. The crosses indicate the spots where the chemical composition was determined. All the analyses are very similar to one another and to the analysis shown in Fig. 10a except the spot indicated by the arrow. The latter turned out to be the quartz crystal.

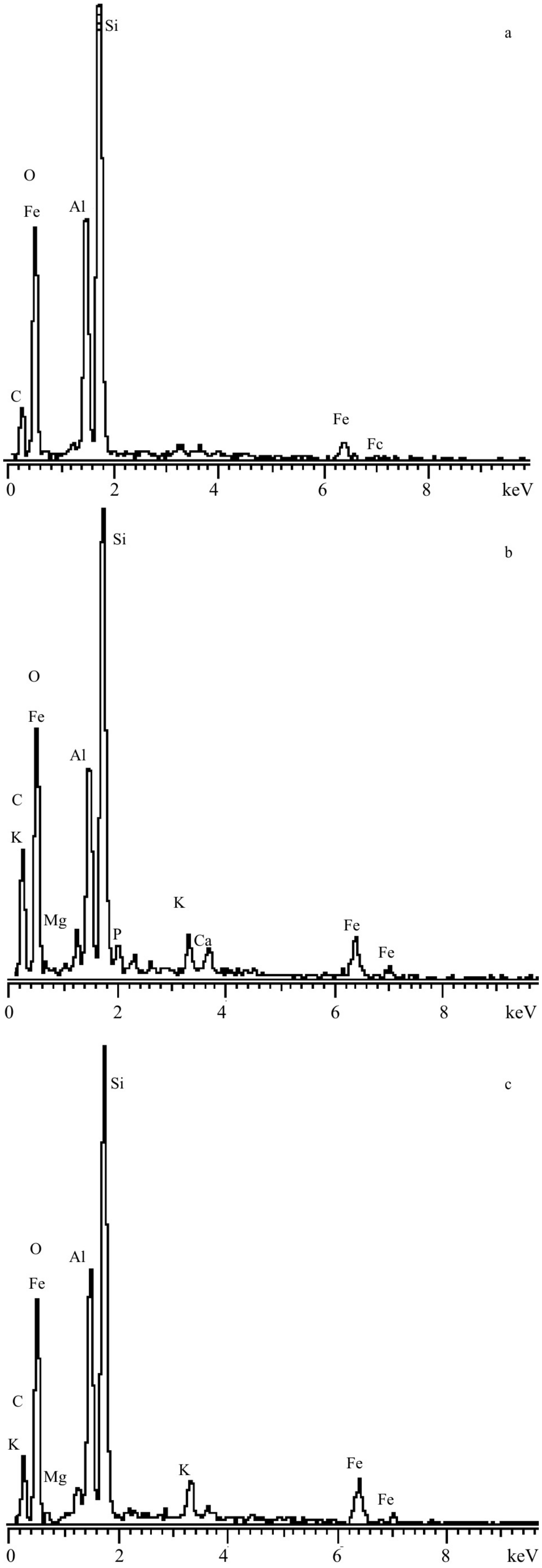

Fig. 6 Energy-dispersive X-ray analysis of a – sample 1, b – sample 2, c – sample 3

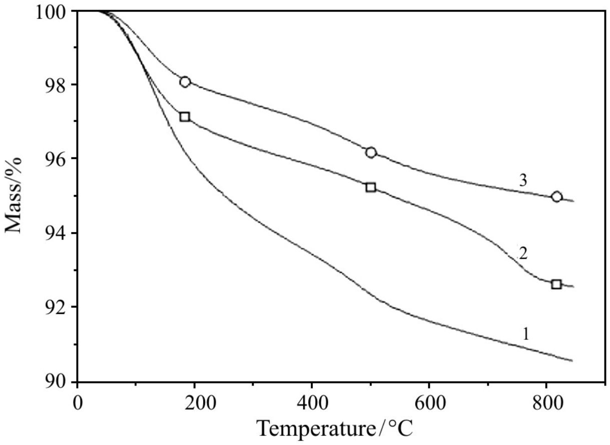

Fig. 7 TG curves (mass loss) of three sherds: 1 – sample 5, 2 – sample 6, 3 – sample 7

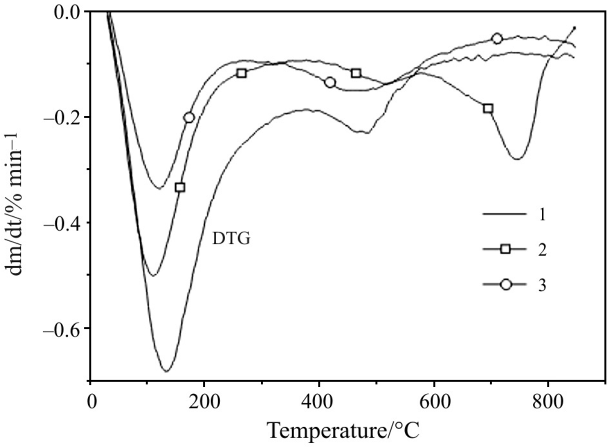

Fig. 8 The rate of mass loss of three sherds: 1 – sample 5, 2 – sample 6, 3 – sample 7

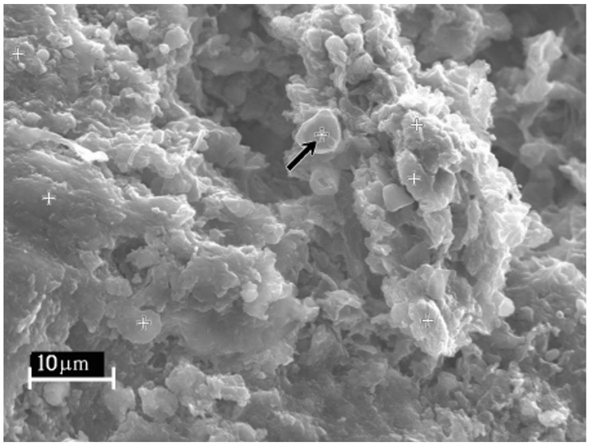

Fig. 9 Scanning electron microscopy of sample 5

Typical results of chemical composition analysis for ceramic samples are shown in Fig. 10. The clay component of ceramics is very similar for all these three samples. Probably, phosphorus has appeared in sample 5 due to the bones used as mineral fillers. We found in the sample 5 a section of the surface with a very high P content. X-ray powder diffraction pattern of this sample does not show feldspar in amounts other than those in the starting clay (sample 1).

Discussion

After an investigation of clays and ancient ceramics, one should try to solve the problem of how to identify which clay was used for the production of particular ceramics. It is not quite correct to compare directly the properties of a ceramic sample with those of clays, because firing destroys kaolinite and montmorillonite. Some part of clay minerals preserves its crystalline structure but in general X-ray powder diffraction patterns of natural and fired clay differ from one another.

A conventional way to search for the clay is based on the comparison of properties of the ancient ceramics with those of clays fired at various temperatures. This is often assumed to allow one to define at once both source for the ceramic production and the firing temperature. We consider this approach to be incorrect for two reasons. Firstly, freshly fired clay differs from a clay fired 3000 years before, and then stored under ambient conditions in the earth, in direct contact with various minerals, water, gases. Second, a low-temperature firing of ancient ceramics resulted not in a phase transition, but in several solid-state chemical reactions, and for a chemical reaction the very concept of a 'reaction temperature' cannot be introduced. The firing temperature cannot be reconstructed precisely, in principle, since the course of a solid-state reaction and, as a consequence, – the composition of products formed can be influenced upon by a variety of factors, including not only the reaction temperature, but, for example, the size of the particles in the starting sample, their pre-treatment (e.g. grinding), the presence of impurities, etc. [11].

Repeatability of thermal transformations

Traditional approach

The information about thermal transformations in clays is derived from experiments. These are the experiments that show the irreproducibility of some thermal transformations at repeated heating. Thus, one conventional statement says: if the sample is heated for the second time, only reproducible thermal transformations will be detected. Irreproducible transformations will be detected only at temperatures higher than the upper temperature limit of the first heating.

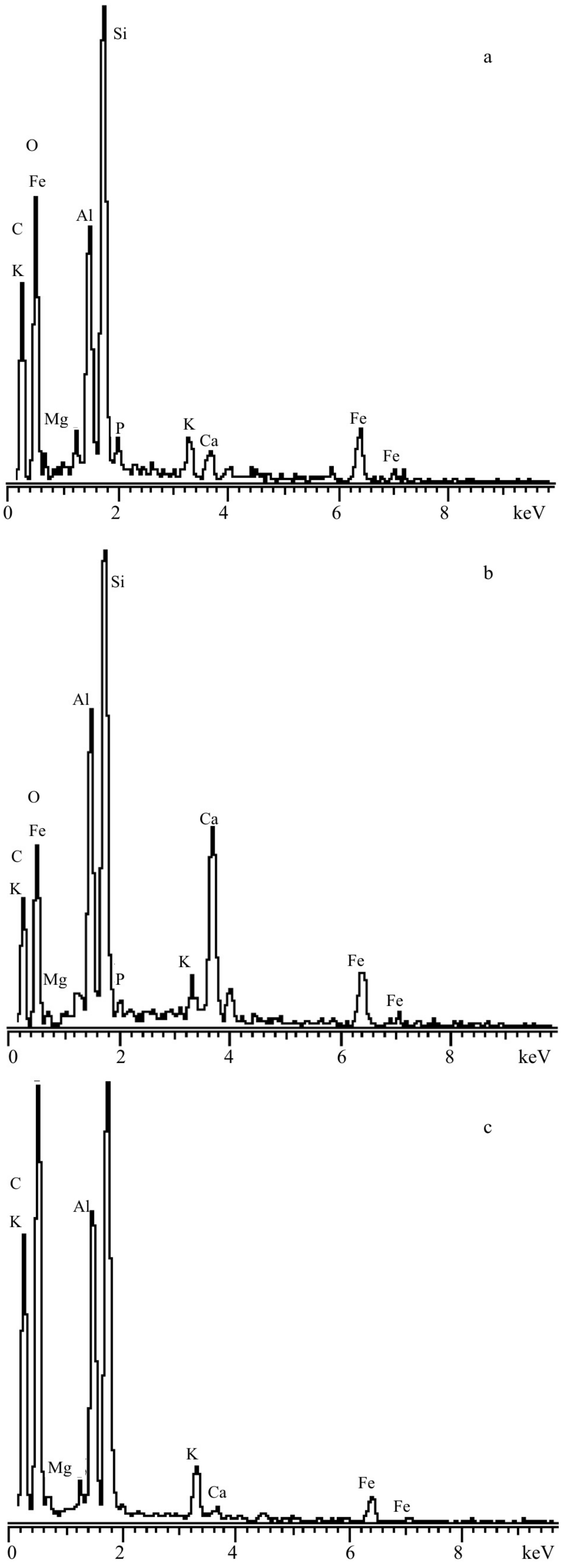

Fig. 10 Energy-dispersive X-ray analysis of three sherds: a – sample 5, b – sample 6, c – sample 7

Arguments against the traditional approach

The irreproducibility of thermal transformations in clay is the result of heat-induced changes in its chemical composition and phase constitution. The higher is the temperature of firing, the more considerable are the changes. When fired above 1100°C, clay paste transforms into a glass-like substance containing the grains of refractories. Such a product has little to do with its starting material. But for a low-temperature firing without melting, the changes in properties are minor and, in the long run, reversible. This is exemplified most clearly by the thermoluminescence of minerals [10]. The phenomenon is used for dating the ancient pottery shreds [12].

Incomplete reversibility of a thermal transformation in ceramics was shown to exist in freshly fired samples. Similarly, the relation between temperatures of irreversible thermal transformations and the temperature of firing is valid with certainty for the freshly fired samples. But the longer is the time between the first and the second heating, the weaker is the relation. This also can be easily checked by direct experiment. If ancient pottery is heated up to 300°C, it loses mass starting from 25°C due to the dehydration. Immediately heated for the second time, the sample does not lose mass below 300°C. The results of the experiments are shown in Fig. 11 (sample 8). The experiment proves that the results of the second heating depend on the temperature of the first heating. In our opinion, it will be wrong to conclude after this experiment that the sample of ancient pottery was never heated above ambient temperature. It contains carbonized organic material inside and smoked surface, showing that 3000 years ago it was treated by fire. Nevertheless, traditional approach suggests that the specimens of this kind were produced after '... much more primitive methods of firing than the other specimens, perhaps even simple sun drying...' [6]. The discrepancy arises because the time between the two runs is not considered and the results of two experiments proceeded one by one are applied to the explanation of the results received in the experiment proceeded 3000 years after the first heating (or even 7000–10000 years [6]).

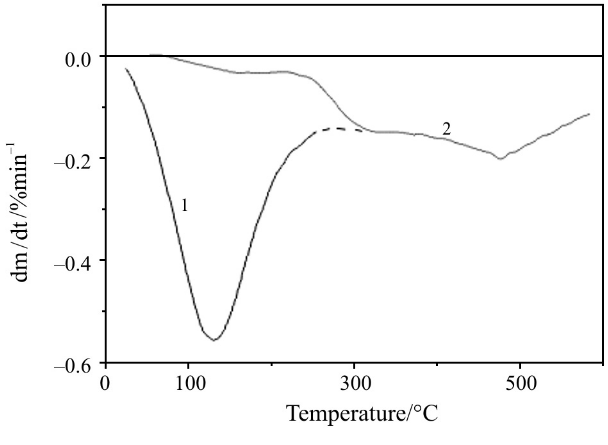

Fig. 11 Rate of mass loss experiments on the reversibility of thermal processes in ancient pottery: 1 – the first heating of a sherd (sample 8); 2 – the second heating of the same sample

On the irreversibility of the decomposition reactions in ceramics

Traditional approach

Three reactions produce the main part of mass loss at firing ceramics. These are (*i*) clay dehydration (ambient temperature –250°C), (*ii*) decomposition of hydroxyls (400–650°C) $2OH^- \rightarrow O^{2-} + H_2O\uparrow$, and (*iii*) decomposition of calcite (700–800°C) $CaCO_3 \rightarrow CaO + CO_2\uparrow$. Temperature intervals ascribed to the reactions are indicated approximately. More correct values depend on the particular mineral species in the clay (for dehydration and decomposition of hydroxyls) and conditions of heating (firing), namely, sample mass, crystalline state, atmosphere, temperature program, etc. Dehydration of clay minerals looks irreversible in 'express' experiments (Fig. 11) but is evidently reversible in the long run. Decomposition of hydroxyls is a controversial subject. Decomposition of calcite is considered irreversible and the calcite impurity in ancient ceramics is used as a marker for the reconstruction of firing conditions. Thus, the other conventional statement says: if the sample contains calcite, the firing temperature was below 800°C.

The arguments against the irreversibility of the decomposition reactions

First, we have doubts concerning the correctness of firing temperature determination in principle. All reports dealing with the reconstruction of ancient pottery technique operate solely with temperature of firing, ignoring the time of the heat treatment. But everyone concerned with thermal analysis or chemical reactions knows that the degree of conversion in a reaction can be enlarged by increasing either temperature or time. These are complementary variables. Lower firing temperatures need more time to get the same conversion degree than higher ones. Temperature characterizes only isothermal phase transitions, i.e., melting. In the reactions with the decomposition of phases and without traces of melting, the temperature of a heat treatment cannot be determined with precision.

Second, we know that the decomposition of calcite is reversible. Lime, CaO, is the product of calcite decomposition. At high temperatures, CaO in contact with clay minerals can give silicates and aluminosilicates, which can then, on storage in contact with water and CO_2, decompose and produce again $CaCO_3$. Sherds of ancient ceramics are stored in the earth for thousands years under ambient conditions and are then excavated by archaeologists. No one ever stated that lime after the firing of pottery and decomposition of calcite will be stored unchanged. We also did not find in the literature information that lime was found in ancient ceramics (actually, it would be strange, if it were ever found).

The irreversibility of thermal transformations in clay minerals is a much more difficult problem. Chemical composition of clay minerals is described by formula $(\Sigma M^{+})_x(\Sigma M^{2+})_y[Al_{x+2y-z}Si_{1-x-2y}O_2](OH)_z{\cdot}nH_2O$. Water content of clay depends on temperature and humidity, and thermal dehydration is completely reversible. Mass loss due to the decomposition of hydroxyls is considered irreversible because aluminosilicate framework of a mineral fired becomes amorphous for X-ray powder diffraction. After a long storage (several months) of amorphous sample under ambient conditions its mass remains unchanged and crystal structure does not recover.

Most samples of ancient ceramics contain clay minerals losing hydroxyls at heating to 550°C. If we follow the concept that only reversible thermal transformations are detected at the second heating, we have to choose between two alternative cases: either the firing temperature of ancient ceramics was less than 550°C or the decomposition of hydroxyls is reversible. In fact, as the low-temperature firing of a clay paste produces the pottery containing amorphous product of clay minerals, a very long storage of ancient ceramics under ambient conditions results in the recovery of clay minerals back to the initial state, with hydroxyls and water molecules. This idea was discussed in [13], but is not used in the interpretation of thermoanalytical results of studies of ancient ceramics.

Alternative approach

Background

Since the conventional way of the interpretation of thermoanalytical results of investigation of ancient ceramics does not allow one to solve several important problems (the origin of clay used for the production of ceramics being among the most important of them), we suggest an alternative approach. This is based on two points. First, at heating of a sample of ancient ceramics, thermal transformations similar to those proceeded 3000 years ago at firing starting clay paste are detected. Among the transformations, are the reactions of dehydration and the decomposition of hydroxyls and calcite. Second, chemical composition and phase constitution of ancient ceramics after such a long storage in the earth become again similar to those of the initial clay paste.

The first point is based on the assumption, that the sample after a very long storage under ambient conditions is in the thermodynamic equilibrium with the environment, not in an unstable state controlled by the kinetics of the irreversible reactions. The arguments for the point are as follows. Initial clay paste was prepared using natural components, except the organic ingredients. Natural components were taken as such and in equilibrium with the environment under ambient conditions. The paste was treated by low-temperature firing, without melting, and then cooled down back to ambient temperature and humidity. All structural and chemical changes in the ceramics at the firing are, in fact, the deviations from equilibrium. The rate of recovery reactions at ambient temperature is much less than that of the decomposition reactions at firing temperature. Nevertheless, the reverse reactions will take place on storage. For example, the reaction $2OH^{-} \leftrightarrow O^{2-}+H_2O$ is known to be reversible under high pressure of water vapor, for example in autoclave [14]. Under ambient conditions, natural powder amorphous silicates (volcanic ash) crystallize completely into zeolites and clay minerals for thousands years [15].

The second point was proved after the investigations of a clay paste prepared by ancient pottery-maker for the production of ceramics but not used. Several samples were found during the archeological dig in Linjovo. These results are shown here for samples 1 and 5. X-ray powder diffraction patterns of ceramics are very similar to those of the clay paste except for the kaolinite content. Crystal structure of kaolinite and montmorillonite is not recovered. Nevertheless, chemical composition of the main body of the ceramics turned out to be very similar to that of the ceramics from Chicha-I site, i.e., the composition of montmorillonite and kaolinite (compare Figs 6 and 10).

Application of the alternative approach

Difference between the traditional and our alternative approach is illustrated by the following example.

Consider the sherds from the Chicha-I site (Novosibirsk region, Zdvinsk district). The sherds from the site belong to various pottery artifacts differing in shape and size (jars, pots) and in additives to the clay paste (mineral species, grain size and concentration). All the sherds are divided into several groups and attributed to several ancient cultures. Having such a numerous artifacts, we have to recognize what differences are the results of the changes in culture (pottery technique) and to distinct them from the changes in clay sources.

According to X-ray powder diffraction data, samples 6 and 7 contain the same set of minerals: quartz, feldspar, and clay minerals. The only difference is calcite. Several sherds from Chicha-I contain calcite, but others do not. The calcite content was not defined exactly but the estimate is <5%. High-temperature minerals (mullite, sillimanite, diopside) were not found. No traces of melting were seen under a microscope.

According to the traditional interpretation, we have to conclude that sample 6 was not heated above 700°C, for calcite decomposition started below 700°C and finished above 800°C. Similarly, we suppose that sample 7 was probably fired at temperature above 800°C. The progress in the pottery manufacture correlates in part with the firing temperature: the higher is the temperature, the more advanced is the technique. Finally, after traditional approach we conclude that sample 7 belongs to the culture of a higher technological level than sample 6.

In firing clays from the nearest sources (samples 2 and 3) at 600°C and 800°C, we found out that neither product is similar to the sherds investigated, for the clay minerals (montmorillonite) become amorphous and dry (no mass loss at all below 600°C). The rest minerals differ in content from the sherds due to the mineral filler. Thus, in following the traditional approach, we cannot indicate the clay source for the pottery manufacture.

According to our own interpretation, we have to search for the clay sources differing one from another in calcite content. The nearest source of high-quality clay is 2 km far from the abode where the sherds were found. According to TG results, it contains calcite of about 6% (in various samples the content ranges from 4.5 to 7.5%). Calcite is a common impurity to natural clays and its content can be as high as 40% [16]. Calcite content of clay (6%) agrees well with that of sample 6 (2%) for clay in the paste is usually mixed with the sand of hard minerals (feldspar, quartz) decreasing the calcite content of the paste. Clay sources without calcite were not found in the neighborhood of the Chicha-I site. Low-quality raw materials for pottery manufacture were found right at the site. This is the clay loam, the earth at the place where the abode was. This contains less clay minerals than the high-quality clay with calcite, but enough to produce low-quality pottery. Thus, our approach yields the conclusion that sample 7 was produced using low-quality raw materials found right near the abode of ancient pottery-maker. Sample 6 was produced using a high-quality clay from a source relatively far from the abode. Thus, our alternative approach argues in favor of the conclusion, contrary to that after the traditional approach, that sample 6 was produced on a higher technological level than sample 7. Besides, the problem of finding the source of clay for the pottery is solved.

Conclusions

Ancient pottery produced on a very primitive technological level (i.e., with firing at low temperature) is capable of restoring back to the starting chemical composition and phase constituent after a long storage in the earth. Traditional approach to the interpretation of thermoanalytical results is evidently not working when applied to the investigation of such pottery. In our experiments, we got experimental confirmation, that phase constitution and chemical composition of the sherds are similar to those of a clay paste used by an ancient potter for the making of ceramics. These results are in a good agreement with the assumption, that the phase transitions and reactions taking place during the firing of a fresh clay paste can take place again at the heating of the sherds several thousands years after the pottery was produced. The facts supporting this assumption are known from geochemistry and solid-state chemistry of clay minerals, but were not taken previously into consideration when interpreting the results of the thermoanalytical studies of ancient ceramics.

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