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The mass-loss diagram for the ancient ceramics

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Cultural Heritage Special Chapter

Abstract The procedure for the visualization of thermogravimetric results for ancient ceramics is described and justified. Two main parameters for the analysis are dehydration and dehydroxylation, which are derived from the experiment as the values of mass loss at temperature interval from room temperature to 350 °C and from 350 to 600 °C. Three examples show how to use the mass-loss diagram for (1) the analysis of the material of a single pot; (2) comparison between different pots from the same archeological site, and (3) search for the source of clay for the manufacturing ancient ceramics.

Keywords Ancient ceramics · Dehydration · Dehydroxylation · Thermogravimetry

Introduction

Thermal analysis is used for the characterization of ceramics for several decades. In contemporary ceramic industry, thermal analysis allows one to investigate the quality of row materials (clays, minerals, and organic fillers) and the products. In archeology, thermal analysis is widely used for the investigation of ancient ceramics. From the very start, it seemed reasonable to apply the experience of the ceramic industry, with its experimental procedures and algorithms of interpretation, to the samples produced several thousands years ago. In following this way, one can see that the ancient ceramics differ evidently from contemporary samples.

Figure 1 shows the results of thermogravimetric measurements of two samples, a sherd of the pot produced about three thousands years ago and a sherd of a cup produced recently. Present-day sample was fired at very high temperature. The components of starting ceramic paste have transformed completely into a glass not sorbing water, and, therefore, showing no mass loss (here, 0.2–0.3%). The ancient ceramics was fired at relatively low temperature of about 700 °C and then stored below ground (weathering conditions) for a long time. Made of clay, fired, and stored, it has converted again into the clay. It is evident from the comparison with pure clay, also shown in Fig. 1. The TG results for ancient ceramics and clay are very similar.

Again, Fig. 1 shows clearly that the thermoanalytical results differ significantly from the ceramics of today. However, in archeological study, it is necessary to compare a particular ancient sample not with a today's sample, but with another ancient sample. The difference in thermoanalytical results among various samples of ancient ceramics is too often not so evident as compared with today's samples.

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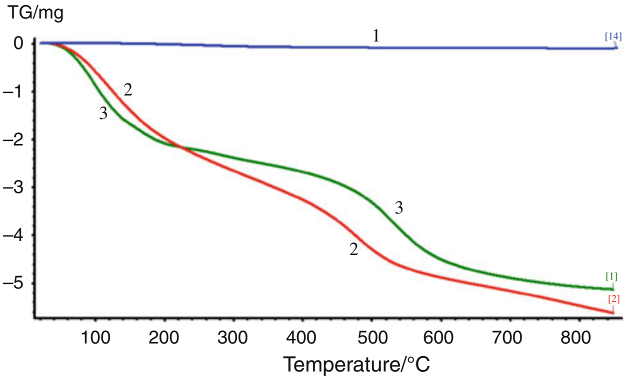

Fig. 1 Thermogravimetric results: *1* today's ceramics, *2* ancient ceramics, *3* unfired ceramic paste

The objective of this work is to show how to detect the difference among thermogravimetric data for various samples of ancient ceramics and how to use them in archeological interpretation.

Shortcomings of conventional archeological interpretation

In starting our thermoanalytical work on the investigation of ancient ceramics of Siberia and Russian Far East, we were in the mood to follow the conventional procedures. Unfortunately, we failed to find the detailed description of the procedures. First, we found many ways of experimental investigations. Ancient ceramics were investigated using derivatography, DTA, TG, TMA, X-ray diffraction, and porometry, etc. [1–6]. Possessing rather good experimental facilities, we failed to choose the optimal (for the cost-efficacy ratio) experimental procedure for the investigation of ancient ceramics. Different reports describe different experimental procedures, each time as a single and unique work, without the pros and cons in comparison with other published ways. The choice of the particular way (experimental technique) was probably based on the particular thermoanalytical device at authors' disposal. Second, we found that the main result of thermoanalytical investigations of ancient ceramics is the firing temperature. Unfortunately, we failed to find the detailed description of how to evaluate the firing temperature. Different experimental techniques yield different experimental values. These are Δm in thermogravimetry, ΔT in differential thermal analysis, ΔL in thermomechanical analysis, etc. Besides, these values change in time and temperature, forming peaks up and down, with different peaks for different values in the same run. We did not find the equations allowing us to calculate the firing temperature after the thermoanalytical measurements. No equation, no accuracy, and no metrology at all. The analytical work needs for the calibration and standardization if operates with accurate experimental values (see, for example, the element concentration in [7] or X-ray diffraction [8]), but the firing temperature does not. In fact, such a situation is rather expected.

Thermal transformations in clays during the firing are kinetic processes [9]. In contrast to the melting of metals or other substances with congruent melting, the degree of thermal transformation in clay minerals depends on temperature and time: $\alpha = f(T,t)$. In trying to derive the firing temperature of ancient ceramics from the results of thermoanalytical experiments, the authors usually search for the similarity between the products of today's experiments with the samples fired and then stored for thousands years in the ground. The main fault of this approach is never discussed: it is impossible to derive a single parameter (T) from the single value of a function of two parameters $f(T,t)$. Many authors report the firing temperature, but no one has ever reported the time of firing.

After the analysis of the practice in the investigations of ancient ceramics, we developed our own way of the measurements and interpretation.

Justification of our approach

In analyzing the product of a kinetic thermal transformation, it is impossible to derive the value of a single parameter, i.e., only temperature or only time. In comparing the degree of the thermal transformation in different samples, we can define the reliable difference in the value of the degree of the thermal transformation instead. It does not matter what was the reason why two samples differ from one another in the degree of transformation. It was time or temperature or both, we detect surely that two samples are different. On the other hand, if two samples were fired under different conditions, but result in the same degree of transformation, we cannot distinguish the firings. Thus, in paying attention to the degree of transformation in the ceramic paste instead of reconstruction of the firing, we remain on solid ground and only have to define the way of measuring the degree of thermal transformation in clay minerals.

The upper limit of temperature of firing in our approach is supposed to be about 700 °C. Only clay minerals are changed under such a mild thermal treating. Clay minerals contain aluminosilicate layers with cations, hydroxyls, and water molecules between them. Typical formulae for several smectites are:

Montmorillonite: $\mathrm{M_y^+}\left[\mathrm{Al_{2-y}Mg_ySi_4O_{10}(OH)_2}\right]^{-\mathrm{y}}\cdot n\mathrm{H_2O}$

Beidellite: $\mathrm{M_y^+}\left[\mathrm{Al_2(Si_{4-y}Al_y)O_{10}(OH)_2}\right]^{-\mathrm{y}}\cdot n\mathrm{H_2O}$

Nontronite: $\mathrm{M_y^+\left[Fe_2\left(Si_{4-y}Al_y\right)O_{10}(OH)_2\right]^{-y}\cdot}n\mathrm{H_2O}$

$$\text{Saponite: } \mathrm{M^+_{x-y}\left[\left(Mg_{3-y}Al_y\right)(Si_{4-x}Al_x)O_{10}(OH)_2\right]^{-x+y}} \cdot n\mathrm{H_2O}.$$

Here, M stands for the cations (Li, Na, K, Ca, and Mg). Such a notation is very simplified and not quite correct in valency of cations, but used here because of its simplicity. The formulae are shown only to point out that the chemical composition of smectites is not exact and we should not expect very accurate quantitative relations for the mass loss.

At heating, the first thermal transformation in a clay mineral is the dehydration. Each formula of the minerals above contains *n* water molecules. Equilibrium *n* value for a particular clay mineral depends on temperature and humidity, and these relationships are also different for different minerals. Dehydration usually comes to an end below 250 °C. The second thermal transformation is the dehydroxylation according to reaction

$$2\mathrm{OH^-} = \mathrm{H_2O} + \mathrm{O^{--}}.$$

It usually takes place in a temperature range from 400 to 600 °C, depending on the experimental conditions and clay mineral species. Having the measured mass loss of a sample of ancient ceramics and comparing it with the mass loss for native clay, we can estimate the degree of thermal transformations in the sample. This is the main idea of the new approach, rather trivial. The only task is to develop a simple visual way of how to derive the degree of thermal transformation from mass-loss data. This problem is solved by means of the mass-loss diagram. It is shown below how to plot this diagram.

Tempering

Change in the mass loss of a ceramic sample can arise not only because of the thermal treatment, but also because of the variations in the dilution of ceramic paste with other minerals not losing their mass at heating (tempering). The mass-loss curves for three samples (A, B, and C) of ceramic paste with different tempering are shown in Fig. 2. Sample A is pure clay, without additives of tempering minerals (quartz, feldspar, and carbonates, etc.). Sample B contains 1/3 fillers and 2/3 clay minerals (by weight), and sample C contains 2/3 fillers and 1/3 clay minerals. These three samples lose mass after dehydration ($m_{1\mathrm{A}}$, $m_{1\mathrm{B}}$, and $m_{1\mathrm{C}}$) and dehydroxylation ($m_{2\mathrm{A}}$, $m_{2\mathrm{B}}$, and $m_{2\mathrm{C}}$). It is obvious that the mass loss at every stage is proportional to the clay content of ceramic paste:

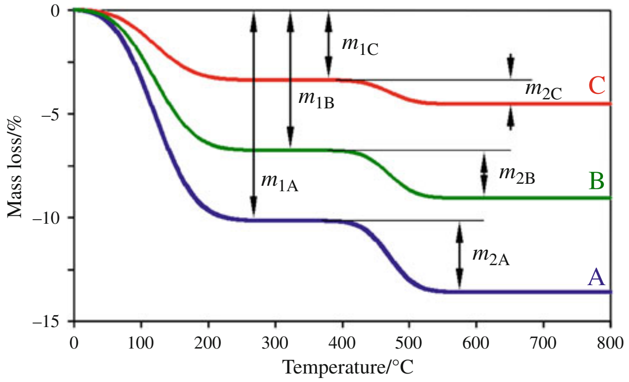

Fig. 2 Thermogravimetric results for ceramic pastes ranging in the tempering: *A* pure clay, *B* 2/3 clay + 1/3 temper, *C* 1/3 clay + 2/3 temper. Mass loss: m_1 at dehydration and m_2 at dehydroxylation

$$m_{1\mathrm{B}} = 2/3m_{1\mathrm{A}} \text{ and } m_{1\mathrm{C}} = 1/3m_{1\mathrm{A}};$$

$$m_{2\mathrm{B}} = 2/3m_{2\mathrm{A}} \text{ and } m_{2\mathrm{C}} = 1/3m_{2\mathrm{A}}.$$

The $m_{2\mathrm{i}}$:$m_{1\mathrm{i}}$ ratio is constant for any sample prepared with tempering. In analytical chemistry, this is the conventional way to receive the calibration curve, where the measured value (here, mass loss at the particular temperature range, m_1 or m_2) is proportional to the quantity of the detected substance in a mixture with other substances, not active in the signal measured. We will create not the calibration curve (mass loss vs. content), but the diagram of the mass loss at dehydroxylation vs. mass loss at dehydration. Points A, B, and C in Fig. 3 are plotted using the measured values of dehydration (m_1) and dehydroxylation (m_2). In the experiments, we define them as the mass loss from room temperature to 350 °C and from 350 to 600 °C, respectively.

Mild firing

The m_2:m_1 ratio changes in the ancient ceramics, which was exposed to firing many years ago and possessing today

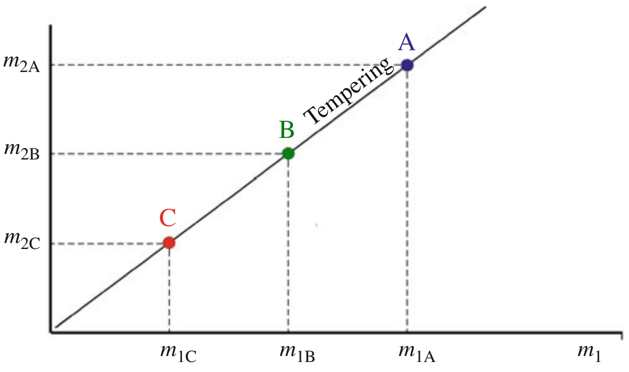

Fig. 3 The line of tempering for the mass-loss diagram. The letters (A, B, C, $m_{1\mathrm{i}}$, and $m_{2\mathrm{i}}$) stand for the values as in Fig. 2

a degree of thermal transformations since that time. The dehydroxylation in the samples of this kind is always less than that for native clay paste. It is because the sample after mild firing can readily sorb the water molecules back when exposed to the weathering conditions, but the rehydroxylation goes much more slowly [10–12]. We will not discuss here the problem of the rehydroxylation because this is very important for the reconstruction of the firing and recovering of clay minerals in the ancient ceramics, but not for the detection of the degree of thermal transformation as such. We should only emphasize that the m_2:m_1 ratio in the ancient ceramics is always less than that in native clay. Being plotted on the mass-loss diagram like Fig. 3, the points of ancient ceramics always lie below the tempering line.

One more consideration was expressed in our report [13] that the decrease in the hydroxyl content is followed by the increase in the dehydration. This fact was found in the experiments and shown in Fig. 4 (taken from [13]). This phenomenon can be explained by the expansion of the sample at dehydroxylation, which increases the internal volume of the sample available for the sorption of water. Similar changes in the water content was found and discussed early by Shoval et al. [14]. They analyzed the IR spectra of the samples heated at different temperatures and concluded "that as firing temperature increases, the amount of adsorbed water firstly increases due to the formation of amorphous matter, and later decreases due to crystallization". We agree completely with this point of view if substitute the degree of transformation for the firing temperature. The phenomenon was explained by different types of amorphous matter in the pottery [14], but we consider it as the substitution for hydroxyles with water molecules. The last stage of changes found by Shoval et al. [14], the decrease "due to crystallization", will be discussed below as the effects of strong firing.

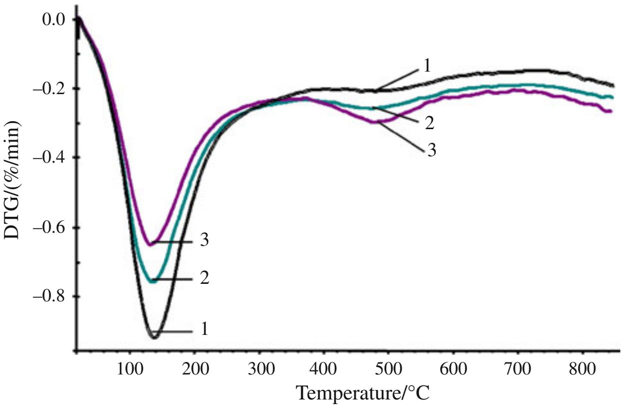

Fig. 4 Redistribution of the mass loss between dehydration and dehydroxylation after mild firing. The degree of thermal transformation is the greatest for 1 and the least for 3, with 2 in between

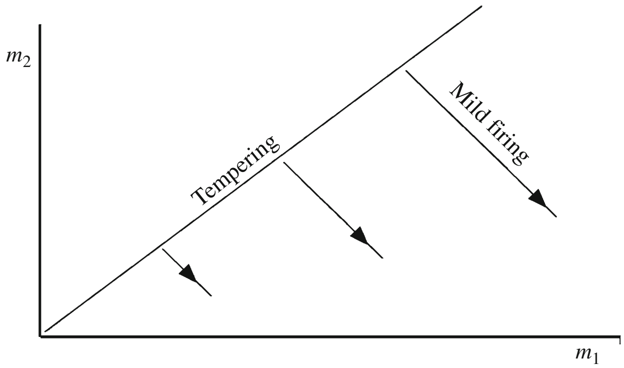

Fig. 5 The lines of mild firing, which start from various points of tempering. The arrows indicate the increase in the degree of thermal transformation

For mild firing, we may consider the simplest relationship between changes in mass loss at dehydroxylation and dehydration as if their sum is constant: $m_2 + m_1 = \text{const}$. Mass loss is redistributed between dehydration and dehydroxylation. The lesser the mass loss at dehydration, the greater the mass loss at dehydroxylation. The arrow on line "mild firing" in Fig. 5 shows the progress in the changes caused by the mild firing. Such a line starts from the point of the ceramic paste used for the pottery production. Three parallel lines with arrows start from the three points of the tempering line shown in Fig. 3.

Strong firing

Lines of mild firing go not to axis m_1, but to a new line indicating the constant ratio of m_2:m_1. After complete dehydroxylation, the sample does not show the peak of mass loss near 500 °C (see Fig. 6 and compare it with Fig. 4), but still contain the water sorbed. The mass loss in the temperature range of 350–600 °C for the sample after strong fire is not because of dehydroxylation, but because

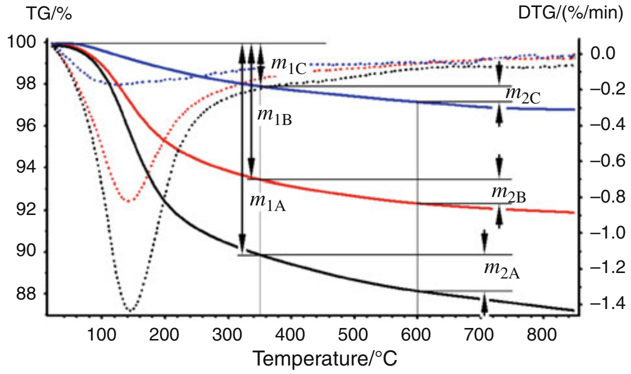

Fig. 6 Thermogravimetric results for the ancient ceramics after strong firing. The samples differ from one another in the sorbent content (the greatest for A and the least for C). There is no peak of dehydroxylation near 500 °C

of physical desorption. The greater the amount of the sorbent, the greater the mass loss at heating. Different samples with different amount of the sorbent lose different mass at heating. The mass loss in a fixed temperature range is proportional to the amount of the sorbent, and we deal again with the constant ratio of m_2:m_1, but now with another value of the constant. Here, we deal with another type of thermal transformations in the ceramic paste as compared with mild firing. At mild firing, the transformations are in the water and hydroxyl sites in the structure of clay minerals, inside and between the aluminosilicate layers constituting the structure of clay minerals. At strong firing, the transformations are in the amorphization of clay minerals, in the destruction of their structure.

Line of strong firing goes through the point of origin in the mass-loss diagram (Fig. 7). In fact, it directs to the point of origin because the strong firing leads to the sintering of grains of clay minerals after the completion of their amorphization and is finished with the transformation of a sample into a glass. The glass does not sorb water and shows very small mass loss at heating. This is the case of contemporary ceramics shown in Fig. 1. The transition from the sorbent shown in Fig. 6 to the glass shown in Fig. 1 is the gradual degradation and depends on the degree of thermal transformation. The greater the degree of transformation at strong firing, the lesser the internal volume of a sorbent and mass loss at heating.

Application of the mass-loss diagram

Experiment

To receive reliable data on contemporary firing of different samples of ancient ceramics, one should proceed all experiments under the same conditions. Our thermogravimetric measurements were carried out using TG-209 (Netzsch) in a gold crucible at a heating rate of 20 °C min^{-1} in the flow of argon of 25 mL min^{-1}. Temperature range from room temperature to 850 °C allows us to detect not only changes in clays, but also in carbonates (calcite). We use the thermal decomposition of calcite not for the interpretation of firing of ancient ceramics, but for the detection of the source of clay for the ceramic manufacturing [15]. Sample mass in our experiments ranges from 46.85 to 47.15 mg. Details of the sampling and sample preparation was described elsewhere [13]. The mass in blank experiments is reproduced within the limits of ±0.05% (for 47 mg) and the difference exceeding 0.1% between two samples should be considered reliable.

The thermogravimetric results are corrected for the baseline and the mass loss at the temperature ranges of 22–350 °C (m_1) and 350–600 °C (m_2) are measured. Then, these values are plotted on the mass-loss diagram. Here, we will show several examples of the results of this kind and their discussion.

Example 1: variations in a single pot

Recently, we reported on high accuracy of thermogravimetric measurements making it possible to detect the difference in the ceramic samples taken from different points of a single pot [13]. To make it clear, we used four figures with unconventional treatment and long explanations. The mass-loss diagram allows us to use only one plot. We took 14 samples of ceramics from internal surface of the restored pot starting from bottom (1) through body (2–13) and finishing at the neck (14). The results of the measurements are shown in Fig. 8. Samples 2–12 are gathered in a group, very close to one another. Samples 13 and especially 14 differ from the rest. Sample 1 is also differs, but much less. Thus, the bottom, body, and neck of the pot were in fact made from different ceramic pastes.

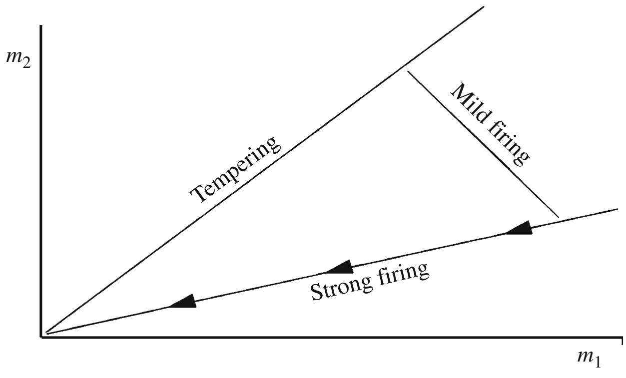

Fig. 7 The line of strong firing on the mass-loss diagram. The *arrows* indicate the increase in the degree of thermal transformation

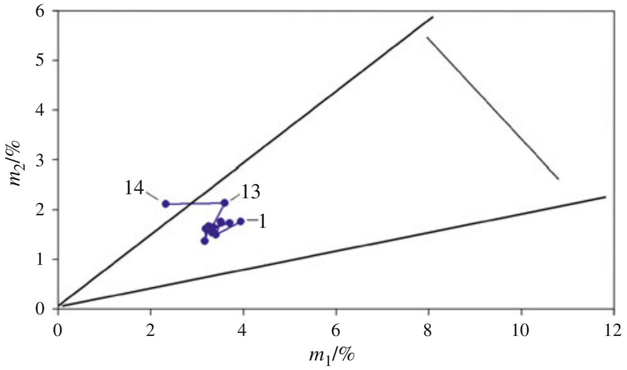

Fig. 8 The mass-loss diagram with the results for the single restored pot, total 14 points. Points 1 (*bottom*), 13, and 14 (*neck*) are surely different from the rest points. The neck (point 14) is fired to the least degree

Example 2: variations among pots

Many broken and safe pots and three portions of ceramic paste ready for the manufacturing of pots were found at archeological site Linjovo (Novosibirsk region). We investigated total 29 samples. Here, we will show the results for the pastes and three pots. The samples investigated were taken from different parts of the pots (bottom, body, and neck).

The results for clay pastes and pot 1 are shown in Fig. 9. Clay pastes fit well the tempering line. The points of the pot fit well the line of mild firing. It is interesting that the line starts near the point of clay paste 1. This pot and the clay paste were found at one place (dwelling).

The results for pot 2 from the same dwelling are shown in Fig. 10. The points also fit to the line of mild firing, but the starting ceramic paste was evidently tempered.

The results for pot 3 from another dwelling are shown in Fig. 11. Now the points are scattered and the bottom was made of the ceramic paste different from that used for neck and body. The tempering minerals are detected with X-ray powder diffraction, but this theme is beyond the scope of this report.

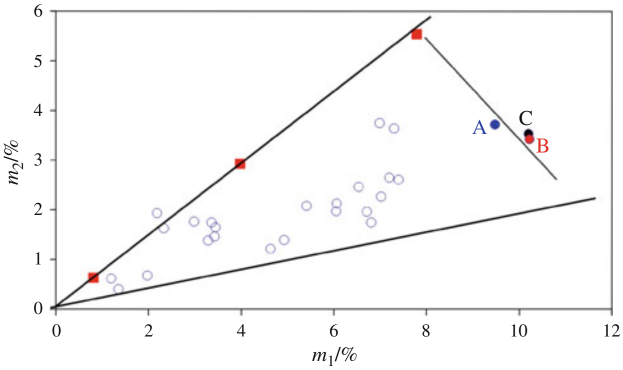

Fig. 9 The points of pot 1 (Linjovo site) on the mass-loss diagram: *A* neck, *B* body, *C* bottom

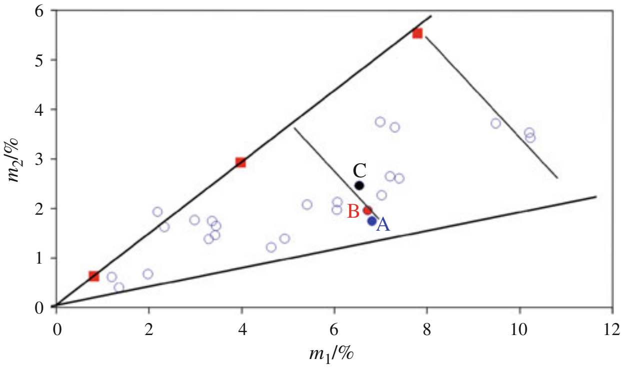

Fig. 10 The points of pot 2 (Linjovo site) on the mass-loss diagram: *A* neck, *B* body, *C* bottom

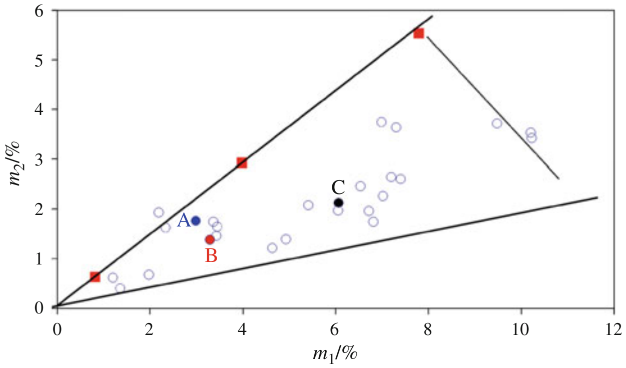

Fig. 11 The points of pot 3 (Linjovo site) on the mass-loss diagram: *A* neck, *B* body, *C* bottom

Example 3: variations in the clay

Archeological site Chicha-1 is multicultural, with wide variations in artifacts. It was very interesting to recognize whether the clay used for the manufacturing of ancient ceramics was obtained from different sources. We found out that a part of sherds was with the significant impurity of calcite and the rest was without calcite at all [15]. The nearest clay deposit was found 2 km far from the place of archeological dig, on the shore of a lake. The mass-loss diagram for the samples of Chicha-1 is shown in Fig. 12. The sherds with calcite, actually, can be made of the clay from the deposit near the lake. They are located in the region where the tempering ceramics manufactured from the clay must fall. The point of the clay itself is marked with filled square. Many sherds without traces of calcite are located in the area (right and up) where the sherds made from the clay with calcite cannot be. These are evidently were made from another clay.

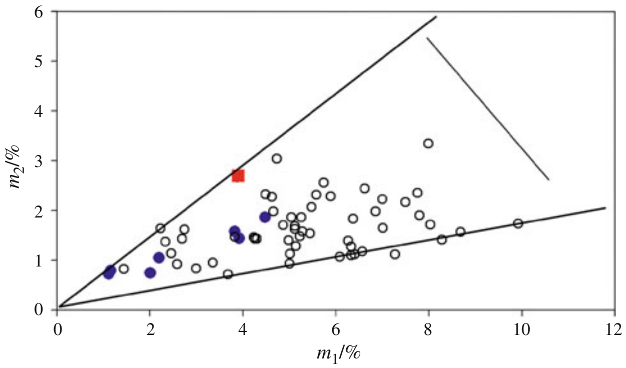

Fig. 12 The mass-loss diagram for the sherds of site Chicha-1. *Open circles* sherds without calcite, *filled circles* sherds with calcite, *filled square* clay with calcite from the deposit near the lake

Weak points of the mass-loss diagram

The mass-loss diagram is the simplest way to visualize our thermogravimetric results of the investigations of ancient ceramics. In applying this widely, we faced several points that must be taken into considerations.

First, it is necessary to be sure that the effects measured in the thermogravimetric experiment do belong to the thermal transformations in ancient ceramics (dehydration, dehydroxylation, and decomposition of calcite). There were several cases when the results were corrupted with impurities (glue for the restoration of pots, a flake of gunpowder). The mass loss at heating can be used for the diagram only if the DTG curve looks like those typical of ancient ceramics (peak of dehydration with the maximum near 100–150 °C; peak of dehydroxylation with the maximum near 450–550 °C; peak of calcite decomposition with the maximum above 650 °C). The sample should be investigated carefully with a wide set of experimental techniques if there are unusual DTG peaks. In other words, the mass-loss diagram is for the routine analysis of typical samples. We have measured a total of over 550 samples from tens of archeological sites.

Second, one should be careful about the measurement of mass loss at dehydroxylation for pure clays with very large mass loss (above 12–15%). In several cases, the mass loss was so large and the temperature of dehydroxylation was so high that the process lasted too long and the last part of dehydroxylation was above 600 °C. In this case, we extracted the area of the dehydroxylation peak from the derivative curve (DTG) according to the procedures conventional in DSC (constructing baseline).

Third, it is necessary to remember that the lines of tempering, mild and strong firing on the diagram are only eye-guides, not accurate mathematical expressions. The variations in the composition of clay minerals are responsible for the wide variations in the m_2:m_1 ratio, and, for instance, the points of pure clay with different chemical composition may be both above and below the tempering line.

Forth, one should keep in mind that the procedure of thermogravimetric analysis described above is inaccurate fundamentally. We measure the mass loss at dehydration for the samples with variable water content. In making accurate analysis of such samples, we should keep the samples under constant humidity for a particular time before the experiment. Unfortunately, such a complication increases the cost of the analysis, not improving significantly the results.

Conclusions

The procedure for the analysis of thermogravimetric results for ancient ceramics was developed that visualizes the variations in the tempering and degree of thermal transformations. The procedure is very simple, clear for understanding, and rather inexpensive. It does not imply the model experiments for the reconstruction of the firing of ancient ceramics.

The justification of the procedure is based on the fundamental processes taking place at the clay minerals. Nevertheless, the procedure should not be considered exact knowledge, but rather the source of most probable version for the conclusion about the ancient ceramics investigated.

Three examples show how the mass-loss diagram can be used for the analysis of the variations: (i) in the ceramic material of one pot, (ii) among several pots, and (iii) starting material (clay) for the fabrication of ancient ceramics.

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