

## THERMOGRAVIMETRIC INVESTIGATION OF ANCIENT CERAMICS Metrological analysis of sampling

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Sherds from restored ancient pots taken from archaeological sites of Siberian region (Late Bronze and Early Iron Age, IX–VIII to VII–VI BC) were investigated by thermogravimetry in order to define the effects of sampling. Three types of the sampling were (1) scanning through the inner surface of a pot, (2) outer surface, core, and inner surface of thick-walled sherds, and (3) random fragments of a restored pot. The results of the measurements were shown to depend on two factors, clay paste composition and firing conditions.

Redistribution between mass loss at dehydration and dehydroxylation was detected for the ancient ceramics after ‘mild’ firing. The results of the measurements are explained in terms of a temperature profile throughout the wall of a pot during the thermal treatment under firing and cooking meal.

The main conclusion of the work is that the thermogravimetric measurements will be very useful for the solution of archaeological problems only if the sampling is correct.

**Keywords:** ancient ceramics, dehydration, dehydroxylation, firing, thermogravimetry

### Introduction

Ancient ceramics was investigated by thermal analysis for a long time both by separate techniques (DTA, TMA, TG) and in various combinations (derivatography, simultaneous thermal analysis, etc.) [1–3]. The results of the measurements are usually used for the estimation of the firing temperature [4–6]. In archaeology the firing temperature is considered the characteristics of the technological level of ancient society. Such an approach was originated from the characterization of contemporary ceramic manufacturing [7].

Recently we discussed the application of thermoanalytical results for freshly prepared ceramics, fired at high temperatures, to the analysis of the results received for ancient ceramics primitively fired at relatively low temperatures and then buried in the earth for thousands years [8]. The application seems not quite adequate. Background ideas of the firing temperature investigations contradict to the well-known facts about rehydration and rehydroxylation in clay minerals in ancient pottery, discussed several times for many years ([9] and references therein).

Thermoanalytical reports dealing with the ancient pottery have little to do with metrological information. Every thermoanalytical work contains the experimental results and the firing temperature derived from these data. In our opinion, the estimation of the firing temperature has nothing to do with calculation, but with judging and reasoning. We did not find the equation for the evaluation of the temperature. In these circumstances, it does not matter how accurate is the thermoanalytical technique used for the investigation of ancient ceramics. The temperature will not be estimated more accurately even if the measurements are more precise. Contrary, it is hardly to realize how inaccurate must be the measurement as not to allow one to estimate the temperature with accuracy better than  $\pm 100^\circ\text{C}$ . And finally, how valuable is the value of the firing temperature derived from the thermoanalytical measurement if the accuracy of the measurement does not matter?

Thermoanalytical measurements of pottery are not widespread in the archaeological investigations in this situation. For example, only two of over thirty reports on the investigations of ancient pottery in Archaeometry published in 2001–2006 deal with the

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thermal analysis [10, 11]. One of them is about how to interpret the thermogravimetric curves [10].

Nevertheless, thermoanalytical investigations of ancient ceramics do provide us with the information about the technology of pottery manufacturing and use. To succeed in this work, it is necessary to pay attention to the sampling and accuracy of thermoanalytical measurements. The comparison of the results for various pots and/or different samples of one pot provide archaeologists with the information for considerations and conclusions. The conclusions, however, are of the comparative type, i.e., greater or less is one value (heat treatment, water content, temper, etc.) than the others, but not exact value (of firing temperature, for example).

This report is about the results of thermogravimetric measurements of ancient ceramics, mainly from the archaeological sites of Siberia, with special attention to the metrological aspect. The information reported was received during the multidisciplinary joint project of the Siberian Branch of Russian Academy of Sciences on the development of physical and chemical analytical techniques for the optimal investigation of ancient ceramics. Analytical team of the project was governed by academician Vladimir V. Boldyrev. As the results of the work are to be accepted by any archaeologist, not highly skilled in thermal analysis, the way of the representation was especially adapted for an appropriate level.

## Experimental

The samples investigated in this report are the ceramics from archaeological site Chicha-1 of transient age from Brass to Iron [12]. The site was investigated intensively by joint Russian–German expedition during 1999–2001 [13, 14]. It is located in the Novosibirsk region. Carbon analysis dated back to IX–VII BC. Three types of the experiments are reported in this work.

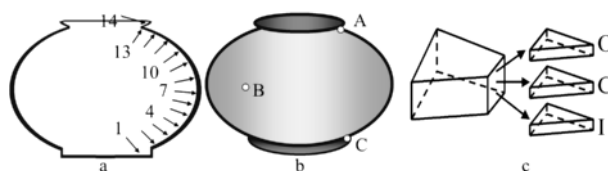
- A pot restored from sherds. The samples for the analysis were taken off from the internal surface of the pot, at an unbroken part of the sherds, not at their edge. The sherd was drilled with a special metal tube of 5 mm in diameter with the teeth at the end. The procedure grinds locally the ceramics into a powder. The powder was used in the TG measurements. The distance between the points of the drilling ranged from 1 to 2 cm. The numbering of the samples is shown in Fig. 1a, starting from the bottom and finishing at the neck.
- Sherds of restored pots. This way of the sampling was chosen especially to be sure that the sherds belonged initially to one pot, but from its different

places. The samples were taken off with nippers at the edges of the sherds. The distance between the positions of the samples was greater than 15 cm. Figure 1b shows the scheme of the sampling with the parts of the pot marked by letters. Four pots were investigated with different sets of samples: pot I – one sample from the bottom (I-1) and two others from the body (I-2 and I-3); pot II ('Sargat' culture) – three samples from different parts, i.e., body (II-1), bottom (II-2) and neck (II-3); pot III – three samples from different places of the body; pot IV – two samples from the body (IV-1 and IV-2) and one from neck (IV-3). Two samples of the second pot (II-1 and II-2) were measured twice in order to check the reproducibility of the measurements.

- Thick-walled sherds. Three samples were taken from the same place of a sherd, but from different depth inside the wall. To diminish the post-depositional alterations on the edge of a sherd, the samples were taken about 1 cm far from the edge. A fragment was cut from the sherd by two gashes directed to each other under acute angle and taken away. Then the top of this triangle fragment was divided into three samples, (1) near the outer surface of the pot, (2) near the inner surface, and (3) the core (Fig. 1c).

Thermogravimetric measurements were carried out using TG-209 Netzsch in a temperature range of 25–850°C at a heating rate of 20°C min<sup>-1</sup> in high-purity argon (25 mL min<sup>-1</sup>). Sample mass was within the limits of 46.85 to 47.15 mg in an open gold crucible (547 mg). When the samples were measured in a series, for example in the experiment with 14 samples from the inner surface of the repaired pot, the order of the sample numbers was random: 9, 3, 12, 8, etc., instead of 1, 2, 3, 4, etc.

Resolution of TG signal is 0.001 mg. The reproducibility of  $m(T)$  values for empty crucible is within the limits of  $\pm 0.02$  mg for 800°C. The difference changes with temperature and is about  $\pm 0.01$  for 500°C. For our experiments, accuracy of the total mass loss at 850°C is about 0.05%. Thus, the differ-



**Fig. 1** Taking samples of ancient ceramics for the investigations: a – scanning the inner surface of the restored pot from the bottom to the neck; b – different parts of restored pots (A – neck, B – body, C – bottom); c – different parts of thick-walled sherds (O – outer surface, I – inner surface, C – core)

ence in the mass loss between any two samples should be considered insignificant, within the limits of experimental error, if it is less than 0.1%.

**Results and discussion**

*Internal surface of the restored pot*

Sample mass as a function of temperature  $m(T)$  for the samples taken from the internal surface of the restored pot are shown in Fig. 2. Total mass loss for all samples ranges from 5 to 7%. The difference of  $\pm 1\%$  exceeds certainly the experimental error of thermogravimetric measurements, which is about 0.1%. The reliable difference can result from (i) the differences in the temper content of the starting clay and (ii) the different ratio between the mass loss due to the dehydration and dehydroxylation. Let us consider the phase composition of the ceramics as a sum of two components, clay minerals (c) and temper (t). Total mass of the sample will be the sum of the masses of the components:

$$m = xm_c + (1-x)m_t \tag{1}$$

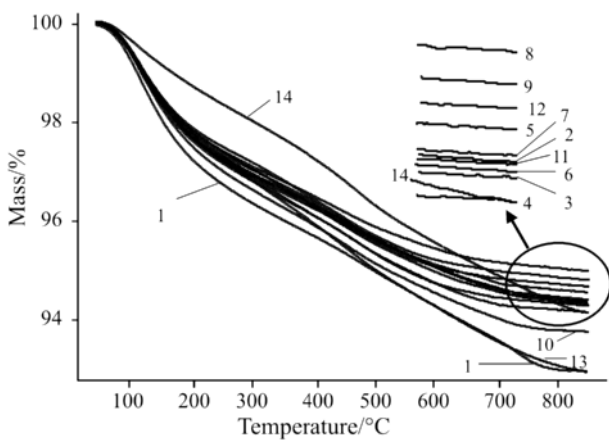
where  $x$  is the fraction of the clay minerals. Only clay minerals lose the mass at heating, and the loss of the ceramics is a fraction of the mass loss of pure clay:

$$\Delta m(T) = x\Delta m_c(T) \tag{2}$$

For two ceramics ( $i$  and  $j$ ) with identical clay minerals but different temper-to-clay ratio (different  $x$  values), the difference in the mass loss is

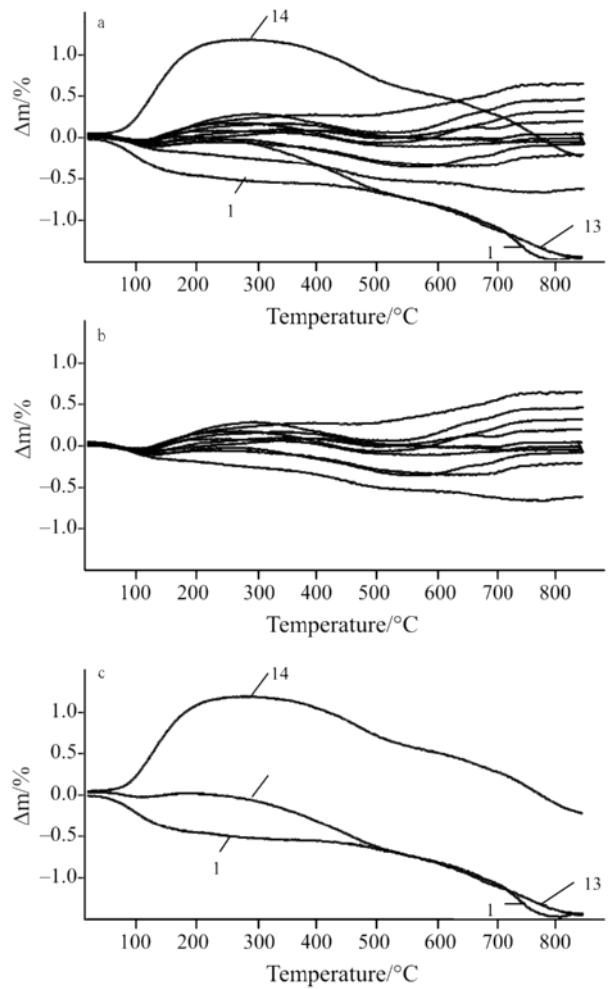
$$\Delta m_i(T) - \Delta m_j(T) = (x_i - x_j)\Delta m_c(T) \tag{3}$$

increasing with temperature according to the stages in the mass loss of pure clay (dehydration, dehydroxylation, decomposition of carbonates). If clay miner-



**Fig. 2** Sample mass as a function of temperature for all samples from the internal surface of the restored pot (sampling in Fig. 1a)

als in the ceramics differ in cations or mineral species, the difference in the mass loss with temperature will be irregular. The curves  $m_i(T)$  in Fig. 2 are shown again in Fig. 3, but with the results for sample N2 subtracted:  $m_i(T) - m_2(T)$ . Sample N2 was chosen because its mass as a function of temperature is typical of the most samples from the repaired pot and the total mass loss is close to the mean value (insert in Fig. 2). The large number of the curves in Fig. 3a makes it difficult to analyze them and discuss the results. The curves are separated into two types represented in Figs 3b and c. Curves corresponding with the Eq. (3) are shown in Fig. 3b. They diverge in a fan pattern starting from 120°C. After 250°C the dehydration comes to the end and the lines become nearly horizontal up to 400°C. After then the divergence starts again due to the dehydroxylation, and then to the decomposition of carbonates. All reactions with the mass loss finish near 750°C and all lines become horizontal again up to the end of the measurement. Differences in the total



**Fig. 3** Differences in sample mass  $m_i(T) - m_2(T)$ : a – all samples; b – samples with identical clay but different temper contents; c – samples with different clays

mass loss for all samples in Fig. 3b are within the limits of  $\pm 0.3\%$  at  $300^\circ\text{C}$  and  $\pm 0.6\%$  at  $800^\circ\text{C}$ .

Figure 3c with the results for samples 1, 13 and 14 looks completely different. Sample 1 loses mass by 0.5% greater than sample 2 already at  $180^\circ\text{C}$  and the difference remains unchanged up to  $500^\circ\text{C}$ . Then the difference increases linearly, reaching the value of 1.5% at  $850^\circ\text{C}$ . Mass loss at  $200^\circ\text{C}$  for sample 14 is 1% less than that for sample 2, and the difference remains constant up to  $400^\circ\text{C}$ . Then the difference in mass decreases and changes in sign. The final value at  $850^\circ\text{C}$  is  $-0.25\%$ . Sample 13 loses mass very similar to sample 2 at heating up to  $300^\circ\text{C}$ . The difference in the mass loss at the dehydration is less than 0.1%. At further heating, the difference in the mass loss forms and increases with temperature. Mass loss above  $400^\circ\text{C}$  is very similar for samples 13 and 14; their lines in Fig. 3c are nearly parallel.

One can conclude that the experiment in the tracing of the internal surface of the restored pot reveals the difference in clay between bottom, body and neck. At the same time, all the samples taken from the body of the pot turned out to be very similar.

#### *Separate samples from different parts of repaired pots*

The results of the measurements of samples from different spaced sherds of repaired pots are listed in Table 1 as the mass losses on temperature intervals of  $22\text{--}350^\circ\text{C}$  (dehydration),  $350\text{--}600^\circ\text{C}$  (dehydroxylation), and  $600\text{--}850^\circ\text{C}$  (decomposition of carbonates, mica, etc.). These values are summarized in the last column.

All pots exhibit the variations in the mass loss, both on intervals and total. The greatest differences are for pot II (sargat). The total mass loss ranges in the limits of 3%, from 5.5 to 8.5%. The variations on the temperature intervals are less: 1.3% for dehydration, 1.1% for dehydroxylation, and 0.8% above  $600^\circ\text{C}$ . The mass losses on the intervals change regularly: the larger the mass loss at dehydration, the greater is at dehydroxylation. This type of the difference between the different parts of a pot is caused by the variations in the temper content and obeys Eq. (2). The sum of the variations on the intervals ( $1.3+1.1+0.8=3.2\%$ ) is equal to the variation in the total mass loss (3%). Let us remember that three sherds of pot II were taken from bottom, body, and neck. They were produced from ceramic paste uniform in the mineral composition of clay, but with different temper content, contrary to the restored pot described above in the experiment on the tracing through the internal surface. One can conclude that pot II and the pot 'traced' were manufactured using different technologies.

**Table 1** Mass loss in the temperature intervals for the sample from various points of the restored pots

Pot	Sample	Mass loss in the intervals/%			Total
		22– 350°C	350– 600°C	600– 850°C	
I	1 bottom	6.44	2.00	0.87	9.31
	2 body	5.84	2.19	1.14	9.17
	3 body	5.38	1.82	1.12	8.32
II	1 body	5.02	2.03	1.41	8.47
	1 body–2 <sup>nd</sup>	4.83	2.22	1.50	8.54
	2 bottom	3.70	1.12	0.71	5.54
	2 bottom–2 <sup>nd</sup>	3.65	1.11	0.71	5.48
III	3 neck	4.50	1.44	0.99	6.93
	1 body	6.32	2.93	2.11	11.36
	2 body	7.59	2.08	1.08	10.76
IV	3 body	6.74	2.63	1.78	11.15
	1 body	7.64	1.67	0.86	10.17
	2 body	6.25	1.93	1.36	9.54
	3 neck	6.31	2.38	1.34	10.03

The pattern is different for the rest three pots. The variations in the total mass loss are 1.0% for pot I and 0.6% for pots III and IV each, with values ranging from 8.32 to 9.31%, from 10.76 to 11.36% and from 9.54 to 10.17%, respectively. The variations on the intervals are greater than the total mass loss: 1.1, 0.4 and 0.3% for pot I; 1.3, 0.85, and 1% for pot III; and 1.4, 0.7 and 0.5% for pot IV. The mass losses on the intervals change irregularly, indicating that the clays in sherds range in properties. Most obvious is the variation in the sherds of pot's bodies: the larger the mass loss at dehydration, the less is at dehydroxylation. For the sherds from the bodies of pots III and IV, the redistribution of the mass loss between these two mechanisms is completely evident. The reason of the redistribution is the difference in the grade of thermal transformations in clay under firing. It was mentioned in our previous report [8], and is discussed again in the next section with the results of the investigations of thick-walled sherds.

From this part of the work one may conclude that the different parts of a pot behave differently at heating. It is not correct to conclude about thermal properties of an ancient pot after a measurement of a single sample. The differences in thermal properties can arise both from the differences in the temper content and from different firing of different parts of the pot.

#### *Thick-walled sherds*

The results of the measurements of samples from different layers of thick-walled sherds are listed in

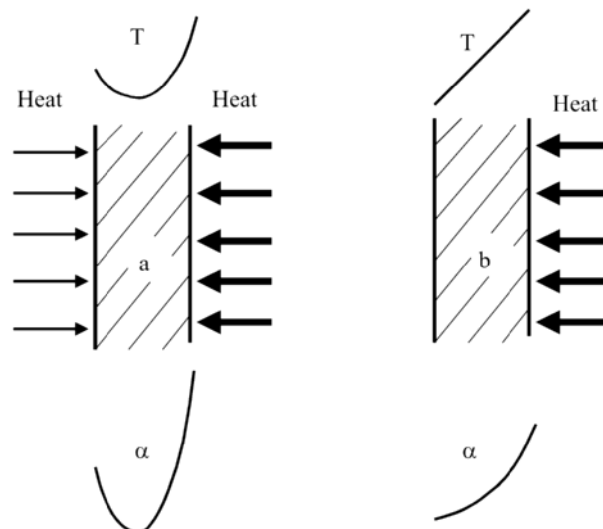
**Table 2** Mass loss in the temperature intervals for the samples of thick-walled sherds

Sample (thickness)	Mass loss in the intervals/%			Total
	22–350°C	350–600°C	600–850°C	
<b>1 (13 mm)</b>				
Inner	7.79	2.76	0.15	10.70
Core	6.85	3.47	1.85	12.17
Outer	6.56	1.74	0.26	8.56
<b>2 (12 mm)</b>				
Inner	4.40	1.29	0.46	6.15
Core	3.92	1.32	0.52	5.76
Outer	4.41	0.95	0.21	5.57
<b>3 (12 mm)</b>				
Inner	4.81	2.46	2.03	9.30
Core	5.57	2.22	1.73	9.52
Outer	6.30	1.72	1.21	9.23
<b>4 (17 mm)</b>				
Inner	3.07	1.61	1.18	5.86
Core	3.45	1.62	1.02	6.09
Outer	3.49	1.26	0.26	5.01
<b>5 (10 mm)</b>				
Inner	4.30	1.70	0.97	6.97
Core	4.07	2.08	1.62	7.77
Outer	4.05	3.56	2.20	9.81
<b>6 (10 mm)</b>				
Inner	3.68	1.50	0.82	6.00
Core	4.11	1.48	0.58	6.17
Outer	4.31	1.30	0.27	5.88

Table 2 as the mass losses on temperature intervals of 22–350°C (dehydration), 350–600°C (dehydroxylation), and 600–850°C (decomposition of carbonates, mica, etc.). These values are summarized in the last column.

Three samples of every sherd range in the mass loss, with the least value of 0.3% for N3 and N6 and 3.6% for N1 in total mass loss. In discussing the variations in the mass loss for different sherds of repaired pots and different places of the internal surface of the pot, we considered two probable reasons, namely the temper content and heat treatment. Here, only the heat treatment affects the mass loss, because the decrease in the dehydration is always accompanied with the increase in the dehydroxylation. This can be explained in terms of the thermal decomposition of clay minerals under firing.

Ancient ceramic pots were exposed to two types of thermal treatment. First, the firing of a fresh pot transforms soft wet clay into hard dry ceramics. Sec-



**Fig. 4** Two types of thermal treatment of ceramics: a – firing of a freshly prepared pot; b – heat treatment during the cooking meal. Temperature profiles (upper,  $T$ ) are different, producing the difference in the degree of thermal transformations in clay minerals (bottom,  $\alpha$ )

ond, the pot is used for cooking meal and heated in a bonfire. The difference in the heat treatment conditions between these two types is shown in Fig. 4.

During the firing of the manufactured pot the heat affects the clay paste simultaneously from both outside and inside, but the heating is somewhat greater from outside, and the temperature near the outer surface is greater than that near internal one. Besides, the thermal transformations in the clay paste release water at dehydration and dehydroxylation. Water vapor escapes more readily from the outside surface of the pot than from the inside surface. The temperature profile through the wall of the pot for the firing is shown in Fig. 4a. Temperature is maximal at the outer surface, decreases along the wall depth, reaching a minimal value inside the wall, and then starts to increase again. The degree of the thermal transformation of clay is maximal near the outer surface of the wall and minimal inside.

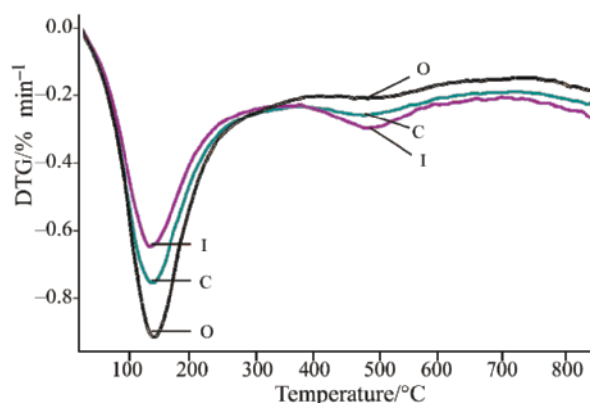
When the pot is used for cooking, its outer surface is exposed to the heat of a bonfire, as it was during the firing. But the internal surface of the pot is at low temperature, depending on the meal under cooking: less than 100°C if water is used and 200–250°C in case of a fat. Temperature profile is different as compared with that at firing. It is shown schematically in Fig. 4b. The greatest temperature is again at the outer surface of the wall, but the least value is at the inner one.

This interpretation is used below for the discussion of the TG results for thick-walled samples. The greatest degree of conversion of clay means the lowest value of the mass loss at dehydroxylation, because

the dehydroxylation takes place after dehydration but before the recrystallization of the amorphous product of clay's thermal decomposition. If the dehydroxylation is detected in our TG experiments, the step of recrystallization was achieved in neither firing nor cooking. We should pay attention to the mass loss in the temperature range from 350 to 600°C. For three samples of pot 1, the values of the mass loss obey the sequence predicted by the model of the firing and shown in Fig. 4a. The ceramics from the outer surface has the least mass loss in the interval from 350 to 600°C, and that from the core of the wall has the greatest value. For three samples of pot 3, the values of the mass loss agree with the sequence predicted by the model of the cooking and shown in Fig. 4b. The greatest mass loss in the interval from 350 to 600°C is for the inner surface, and the least value is for the outer one again. Thermal transformations in clay during the cooking exceed those during the initial firing. For sherds 2, 4 and 6, the mass loss due to dehydroxylation is the least for outer surface, but those for inner surface and core are equal within the limits of total experimental errors, due to the variations in the temper content and instrumental accuracy. One can suppose that these pots were fired and then used for cooking several times, each time increasing the degree of transformation in the clay inside the wall, but the final value of the degree does not exceed that at the inner surface of the pots. Profile of the degree of the transformation throughout the wall changes gradually from variant 4a to 4b after the sequence of the cooking.

The results of the measurements of sherd 5 turned out to be unexpected for us. Mass loss at dehydroxylation was found to be greater near outer surface than near inner one or in the core. We have investigated this sherd carefully and found out that it was probably used especially for the keeping the fire inside. The pot is layered, and outer surface was additionally covered with a clay past after its initial firing, but the detail results of the investigation are beyond the scope of this report.

We pay attention once more to the fact that the difference in the firing of sherds with identical clay paste leads to the difference in the degree of thermal conversion in the clay and manifests itself in the redistribution of the mass loss between dehydration and dehydroxylation during thermogravimetric measurements of ancient ceramics. Figure 5 illustrates this assertion. The derivatives of the mass loss are shown for three samples from thick-walled sherd 3. The greater the peak of dehydration near 140°C, the less the peak of dehydroxylation near 480°C. In the previous report we have shown from the comparison between the results of TG and TMA that pure clay contracts at dehy-



**Fig. 5** Redistribution of the mass loss between dehydration and dehydroxylation after different thermal treating of outer surface (O), core (C), and internal surface (I) of thick-walled sherd 3

dration but expands at dehydroxylation. The expansion is caused by the sites with non-compensated electrostatic charges near tetrahedra  $AlO_4$ , formed during the decomposition of two hydroxyls in different places of aluminosilicate layers. In aluminosilicates, the alumina tetrahedra do not contact with one another, only with  $SiO_4$  tetrahedra. These charged sites, defects in other words, make the stress in the aluminosilicate layer, distorting the plain of the aluminosilicate layer and increasing the total volume of a clay mineral. The sites become additional centers for the hydration of polar water molecules, increasing the water content of mildly fired clay.

The main conclusion that can be derived from the results of TG measurements of thick-walled sherds is the relation between the mass losses at dehydration and dehydroxylation. This allows one to recognize the difference in the degree of thermal transformations in clay, revealing the peculiarities of the thermal history of a sherd or total pot. This advantage is the sequence of high accuracy of contemporary thermogravimetric technique, and can be very useful in the interpretation of archaeological artifacts.

## Conclusions

Thermogravimetry was used for the measurement of mass loss by the samples of ancient ceramics, with special attention to the stages of dehydration and dehydroxylation.

Measurements of the samples (1) from different points of the internal surface of the restored pot, (2) from different layers of thick-walled sherds, and (3) from different sherds of restored pots revealed evident differences in the results. These accurate thermogravimetric analyses provided us with the information about (1) variations in the clay paste used

for the manufacturing of the ceramics, (2) changes in the degree of thermal transformations in clay under firing and using, and (3) the combination of the changes in the starting clay paste and its degree of firing.

It is not quite informative to make a single analysis of the mass loss of a sample, not attributed to a particular part of the pot, because the analyses repeated with the sample from the same pot, but taken from another place, will give another value of the mass loss. One should define in advance what do we want to know about the ceramics, and then should plan the sampling for the experiment.

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