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THERMAL AND MINERALOGICAL CONTRIBUTION TO THE ANCIENT CERAMICS AND NATURAL CLAYS CHARACTERIZATION

D. N. Papadopoulou[1], *Maria Lalia-Kantouri*[2*], *N. Kantiranis*[3] *and J. A. Stratis*[1]

[1]Laboratory of Analytical Chemistry, Department of Chemistry, Faculty of Sciences, Aristotle University, Thessaloniki 54 124, Greece
[2]Laboratory of Inorganic Chemistry, P. O. Box 135, Department of Chemistry, Aristotle University, Thessaloniki 54 124, Greece
[3]Department of Mineralogy-Petrology-Economic Geology, Faculty of Sciences, Thessaloniki 54 124, Greece

In the present work 39 ancient ceramic sherds from the archaeological excavation of Abdera, North-Eastern Greece, dating to 7th century B.C., and 11 local raw clay bricks, fired at temperatures ranging from 500 to 1000°C, were characterized by ICP-AES, powder X-ray diffraction (PXRD) and thermal analysis (TG-DTA) techniques. It has been found that the mineralogical composition of the most studied sherds is quartz, feldspars and micas, which is in agreement with the composition of the local bricks. Chlorite is also present in a few samples, while there is one completely different sherd, which belongs to the Ca-rich clays. From the simultaneous TG/DTG and DTA data, under nitrogen atmosphere in the temperature ranges ambient to 1000°C, we comment on the possible firing temperature and distinguish between samples of different origin. The existence of muscovite or illite in most of the samples denotes that the firing temperature was lower than 950°C, while the existence of chlorite means that the firing process in these samples stopped before 700°C. A very different thermogram gave the Ca-rich ceramic sherd, due to the existence of calcite, denoting that the firing temperature was about 700°C.

Keywords: *ancient ceramics, chemical characterization (ICP-AES), local raw clays, mineralogical composition (XRD), thermal properties (TG/DTG-DTA)*

Introduction

An integrated characterization of ancient ceramics includes most often the description of their mineralogical, chemical and thermal properties. These data can be supplied in an interdisciplinary approach using a variety of instrumental techniques. The interpretation of the analytical results in conjunction with relevant archaeological information, may lead to significant conclusions in provenance and ancient technology studies [1–3].

The mineral constituents of ceramics contain information about the firing conditions of raw materials. During firing, minerals undergo phase transitions that are characteristic of their firing temperatures [4–6]. Thermal analysis in conjunction with powder X-ray diffraction (PXRD) provides information for the estimation of the original firing temperature of the ancient ceramics [7–9]. The chemical composition (ICP-AES) of ancient ceramics on the other hand, is related to the raw materials and can be successfully used for the classification of ceramics into groups of similar composition [10, 11]. Among the numerous analytical techniques used for the determination of the chemical content of ancient ceramics (ICP-AES, XRF, PIXE, NAA), the ICP-AES (inductively coupled plasma-atomic emission spectrometry) presents some excellent analytical characteristics, such as low detection limits, large linear dynamic range and low matrix effects and is therefore a very popular technique in archaeometric studies [11].

Finally, PXRD is a well established technique for the determination of the mineral content of ancient ceramics and is widely used [12]. Concerning the analysis of cultural objects, the combination of thermal, mineral and chemical analysis is most often found in studies of historical mortars [13] than ancient ceramics [8].

In the present work thirty-nine ancient ceramic sherds from Abdera (birth place of the ancient Greek philosopher Demokritos) and a local raw clay sample were analyzed by ICP-AES, TG/DTG-DTA and PXRD techniques. The aim of this work is firstly to characterize the ancient ceramics in terms of their mineralogical and chemical content, secondly to study their thermal behavior and determine their firing temperature and finally to distinguish groups of samples with similar properties.

Experimental

Samples preparation

Thirty-nine ancient sherds excavated from the archaeological place of Abdera (North-Eastern Greece, Thrace

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[*] Author for correspondence: lalia@chem.auth.gr

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Akadémiai Kiadó, Budapest, Hungary
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Perfecture) were studied in the present work. Most of the samples dating back to the 7th century B.C., were used for cooking or food conservation. The samples were dried overnight at 105°C prior to analysis. Sub-samples were cut off and finely powdered in an agate mortar. For the ICP-AES analysis, the decomposition was performed in a microwave oven in closed pressurized vessels. In particular, 0.1 g of each powdered sample was placed in Teflon PFA digestion vessel and a mixture of 5 mL HF 40 mass/mass% and 5 mL HNO_3 69.5 mass/mass% was added. The exact decomposition procedure has been described previously [14]. Multi-element, matrix matched standards were used for the quantitative determinations in 0.5 mol L^{-1} HNO_3.

Instrumentation

Decomposition of the samples was performed in a mars 5 microwave oven (CEM, USA, 1200W) in closed high-pressure PTFE PFA vessels (100 mL, HP-Plus type, P_{max}=2.4 Mpa, T_{max}=210°C). The microwave power output is managed through direct feedback from temperature (EST-300 Plus) and pressure (ESP-1500 Plus) probes, providing precise control of the chemical reactions. Twenty chemical, major, minor and trace elements were determined by ICP-AES using a PerkinElmer Optima 3100XL Series spectrometer (40 MHz). Potassium and sodium were determined by faes technique due to the fact that in the available ICP instrument the polychromator range was 165–403 nm.

PXRD was performed using a Philips PW 1710 diffractometer with Ni-filtered CuK_α radiation on randomly oriented samples. The samples were scanned from 3–63° 2θ at a scanning speed of $1.2°/min^{-1}$. Semi quantitative estimates of the abundance of the mineral phases were derived from the PXRD data, using the intensity of specific reflections, the density and the mass absorption coefficients of the elements for CuK_α radiation.

The presence of amorphous phases in a sample is clearly indicated in the X-ray diffraction patterns. Using CuK_α-radiation the amorphous phases appear as one or more broad background humps approximately between 10–50° 2θ, depending on their chemical composition [15]. More often and mainly in inorganic samples the amorphous phases appear approximately between 10–18° [16]. According to Guinier [15], the appearance of more than one broad background humps in a sample is related to the presence of cores with different molecular size of the amorphous phases and consequently this molecular size variation is due to the differences in their chemical composition.

The semi-quantitative estimation of the percentage of total amorphous material was achieved by comparing the area of each broad background hump which represented the amorphous material in each sample with the analogous area of standard mixtures of minerals with different contents of natural amorphous material [15–17] scanned under the same conditions. The PXRD method is a very good, effective and useful tool for the determination of the percentage of amorphous material contained in a natural or synthetic sample [17].

The various samples, about 15 mg each in platinum crucibles, were submitted to simultaneous thermogravimetric-thermal analysis (TG/DTG-DTA) investigations, at the heating rate 10°C min^{-1}, in the temperature range ambient to 1000°C, under nitrogen atmosphere, in a Setaram Model Setsys 1200 instrument.

Results and discussion

The ceramic samples have been divided in five main categories according to their chemical, mineralogical and thermal findings as following: 1) twenty samples, 2) four samples, 3) two samples, 4) eight samples and 5) five samples.

Chemical and XRD studies

The chemical analysis of some representative per group sherds of the 7th century B.C., from the archaeological excavation of Abdera, characterized by ICP-AES, are presented in Table 1. Comparison of these data with the chemical analysis of the local raw

Table 1 Chemical analysis of some representative ancient ceramic sherds from Abdera, characterized by ICP-AES (mass/mass%)

Sample/group	SiO_2	Fe_2O_3	CaO	MgO	MnO	TiO_2	BaO	K_2O
A103/1	58.5	7.03	1.25	1.41	0.15	0.61	0.05	1.16
A91/2	58.7	7.30	0.98	1.32	0.09	0.59	0.05	1.12
A114/3	53.5	6.71	9.43	1.87	0.11	0.70	0.08	1.84
A107/4	59.3	6.47	4.34	2.41	0.09	0.90	0.05	2.36
A43/5	89.2	2.24	0.69	0.86	0.01	0.41	0.03	0.92
Raw material	53.7	5.34	0.84	1.25	0.21	0.77	0.05	2.32

Table 2 Semi-quantitative mineralogical composition (mass/mass%) of ancient ceramic sherds from Abdera

Sample	Quartz	Feldspars	Micas[1]	Chlorite[2]	Calcite	Pyroxene[3]	Amorphous
A103/1	84	11*	5	–	–	–	–
A91/2	71	20*	6	3	–	–	–
A114/3	21	35^	11	–	20	6	16
A107/4	70	20	4	–	6	–	–
A43/5	68	3#	3	–	–	–	26

[1]Mainly muscovite and/or illite $K_2Al_6Si_6O_{20}(OH,F)_4$, [2]$(Mg,Fe^{2+},Fe^{3+},Mn,Al)_{12}(Si,Al)_8(OH)_{16}$, [3]mainly diopside $Ca(Mg,Al)(Si,Al)_2(O)_6$,*mainly albite $NaAlSi_3O_8$, #mainly potassium feldspars $KAlSi_3O_8$, ^mainly anorthite $CaAl_2Si_2O_8$, quartz: SiO_2, calcite: $CaCO_3$

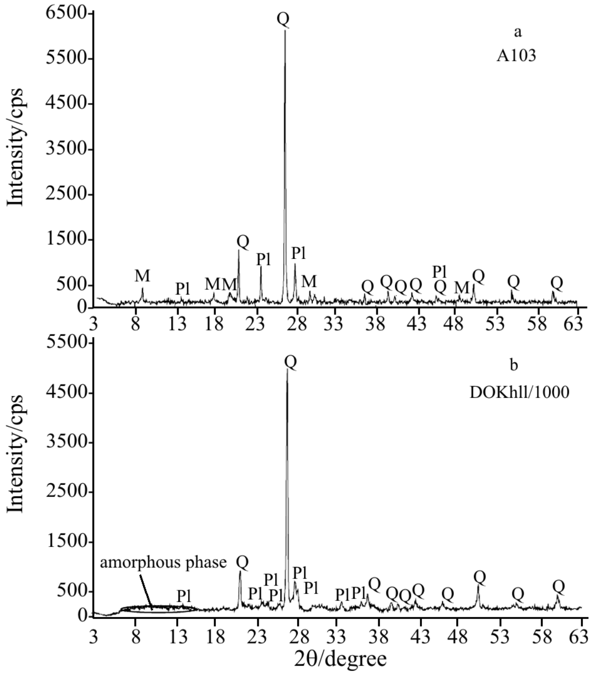

Fig. 1 Representative XRD patterns of a – the sherd samples (A103) and b – the raw clay bricks (DOKh11/1000). Q: quartz, Pl: plagioclase, M: micas

clay material (Table 1) gives evidence for the provenance of the samples.

The results of the semi-quantitative estimation of the mineralogical composition of the studied sherds are shown in Table 2, while a representative PXRD pattern is given in Fig. 1a for the sample A103. Eleven bricks have been laboratory prepared from local raw clay by firing at temperatures ranging from 500 to 1000°C under oxidizing conditions. These bricks have been gradually heated in the maximum temperature and remained there for 3 h. In Table 3 the mineralogical results of the treated bricks are given, while a representative PXRD pattern is given in Fig. 1b for the brick heated at 1000°C.

From Table 2, it can be seen that the mineralogical composition of the most studied sherds consisted mainly of quartz (68–86 mass/mass%), feldspars (3–21 mass/mass%) mostly albite and micas (3–11 mass/mass%) mostly muscovite and/or illite, which is in agreement with the composition of the local raw clay bricks (Table 3). In two samples (e.g. A91) chlorite is also present, while there is one completely different sherd (A114), which belongs to the Ca-rich clays because it consists mainly of Ca-rich feldspar

Table 3 Semi-quantitative mineralogical composition (mass/mass%) of the raw clay bricks, fired at 500–1000°C

Sample/temperature/°C	Quartz	Feldspars[1]	Micas[2]	Amorphous
DOKh1/500	74	15	11	–
DOKh2/550	74	16	10	–
DOKh3/600	73	15	12	–
DOKh4/650	75	14	11	–
DOKh5/700	73	16	11	–
DOKh6/750	75	15	10	–
DOKh7/800	76	13	11	–
DOKh8/850	78	15	7	–
DOKh9/900	77	15	8	–
DOKh10/950	80	15	5	–
DOKh11/1000	81	11	–	8

[1]Mainly albite $NaAlSi_3O_8$, [2]mainly muscovite $K_2Al_6Si_6O_{20}(OH,F)_4$, quartz: SiO_2

Table 4 Summary of thermoanalytical results (TG, DTG, DTA curves) of the ancient ceramic sherds and associate compounds to the thermal events

Samples/group	Curve	*T*/°C ~90 (endo)	*T*/°C ~480 (endo)	*T*/°C ~573 (endo)	*T*/°C 690 (endo)	Estim. firing *T*/°C
A103/1	DTA	intense	small	sharp, small		
	TG	↓4%	↓3%	–		<950
	DTG	Peak	–	–		
	Comp.	H_2O (adsorbed)	–OH (micas) –H_2O (bound)	quartz		
A91/2	DTA	intense	small	sharp, small		
	TG	↓5%	↓3%	–		<700
	DTG	Peak	–	–		
	Comp.	H_2O (adsorbed)	–OH (micas) –OH (chlorite) –H_2O (bound)	quartz		
A114/3	DTA	medium	–	sharp, small	intense	
	TG	↓1%		–	↓4.5%	700–800
	DTG	Peak		–	Peak	
	Comp.	H_2O (adsorbed)		quartz	CO_2 (calcite)	
A107/4	DTA	intense	small	sharp, small	intense	
	TG	↓2%	↓0.4%	–	↓2.5%	700–800
	DTG	Peak	–	–	Peak	
	Comp.	H_2O (adsorbed)	–OH (micas)	quartz	CO_2 (calcite)	
A43/5	DTA	small		sharp, medium		
	TG	↓0.25%	–	–		~1000
	DTG	–	–	–		
	Comp.	H_2O (adsorbed)	–	quartz		

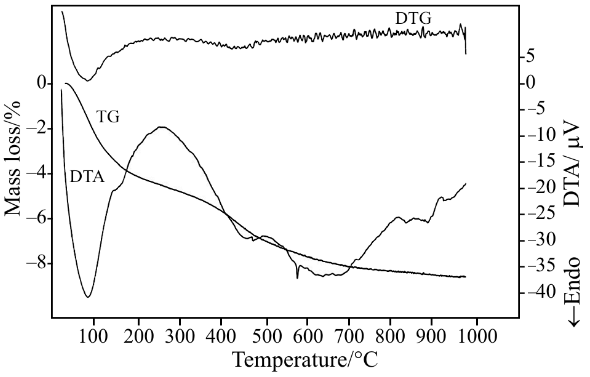

Fig. 2 Thermal curves of sample A103

(anorthite, 35 mass/mass%), calcite (20 mass/mass%) and Ca-rich pyroxene (diopside, 6 mass/mass%), while the amount of quartz is very low (21%). In a few samples (e.g. A43 and A114) amorphous phase was also determined. The amorphous phase is probably the result of the sintering of the initial constituents of the ceramic during the firing process.

Thermal analysis

From the simultaneous thermoanalytical TG/DTG-DTA curves we comment on the possible firing temperature and distinguish between samples of different origin. The summarised results of the thermal analysis of the ceramic sherds and the raw bricks are collected in Tables 4 and 5 respectively.

According to our thermal results, we can deduce that there are five main categories between the 39 investigated sherds. Two of them (A103/1 and A114/3) are representatively depicted in Figs 2 and 3 respectively.

In the first class, e.g. A103, which represents the thermal behavior of the majority of the investigated pottery sherds (Fig. 2), the TG curves showed an almost continuous mass loss with two main stages. In the first, a rapid mass loss of about 3%, accompanied by a strong endotherm below 100°C, as a result of the eliminated adsorbed water, mainly manifested by micaceous mineral. In the second, slow and smaller event between 400–500°C with endotherm peaks at about 480°C is probably due to the dehydroxylation of structural OH^- in micas, such as muscovite and/or illite, which is conventionally an irreversible process [2] or a controversial subject [9]. The mass loss

Table 5 Summary of thermoanalytical results (TG, DTG, DTA curves) of 11 raw clay bricks, fired at 500–1000°C, and associate compounds to the thermal events

Sample/temperature/°C	Curve	T/°C ~90 (endo)	T/°C ~480 (endo)	T/°C ~573 (endo)
DOKh1/500, DOKh2/550	DTA	intense	small	sharp, small
	TG	↓4.5%	↓2.5%	–
	DTG	Peak	–	–
	Comp.	H_2O (adsorbed)	–OH (Micas)	Quartz
DOKh3/600, DOKh4/650	DTA	intense	small	sharp, small
	TG	↓4.5%	↓2.5%	–
	DTG	Peak	–	–
	Comp.	H_2O (adsorbed)	–OH (Micas)	Quartz
DOKh5/700, DOKh6/750	DTA	medium	small	sharp, small
	TG	↓4%	↓2%	–
	DTG	Peak	–	–
	Comp.	H_2O (adsorbed)	–OH (Micas)	Quartz
DOKh7/800, DOKh8/850	DTA	medium	small	sharp, small
	TG	↓3%	↓1.5%	–
	DTG	Peak	–	–
	Comp.	H_2O (adsorbed)	–OH (Micas)	Quartz
DOKh9/900, DOKh10/950	DTA	small	small	sharp, medium
	TG	↓1%	↓1%	–
	DTG	Peak	–	–
	Comp.	H_2O (adsorbed)	–OH (Micas)	Quartz
DOKh11/1000	DTA	small	–	sharp, medium
	TG	↓0.25%	–	–
	DTG	–	–	–
	Comp.	H_2O (adsorbed)		Quartz

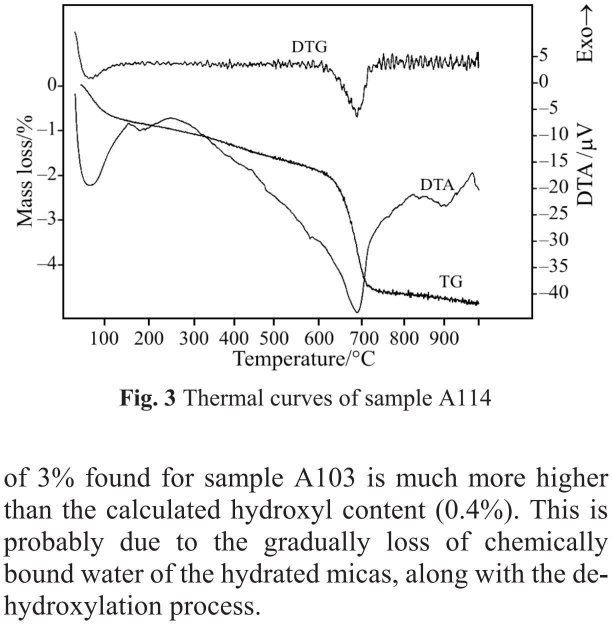

Fig. 3 Thermal curves of sample A114

of 3% found for sample A103 is much more higher than the calculated hydroxyl content (0.4%). This is probably due to the gradually loss of chemically bound water of the hydrated micas, along with the dehydroxylation process.

Mass losses between 350 and 900°C vary from 2–4%. The endotherm peak around 920 and the exotherm at 880°C in the DTA curves are associated with the destruction of illite and the formation of new crystalline phases [18, 19]. The existence of muscovite denotes that the firing temperature was lower than 950°C. This conclusion comes from the comparison of the TG-DTA results of the fired raw bricks (Table 5), as it is further discussed.

In all the samples, in the DTA curve a small sharp endotherm peak without associated mass loss has been observed at 573°C, which is related with the transformation of α-quartz to β-quartz [20]. The plagioclases, e.g. Na-feldspar like albite, are very stable and show no thermal events from 20–1200°C and for this reason they do not play a role in the determination of the firing process. The existence of chlorite (3 mass/mass%) in the second class, which represents only a few samples, e.g. A91, means that the firing process stopped before 700°C, although there is no significant difference in their thermal profile with that of the first class.

The third class contains the calcareous type (Ca-rich) ceramic sherds, e.g. A114 (Table 2), with Ca-rich feldspar (anorthite, 35 mass/mass%), quartz (21mass/mass%) and calcite (20 mass/mass%) as major phases, while amorphous phase (16 mass/mass%), micas (11 mass/mass%) and Ca-rich pyroxene (diop-

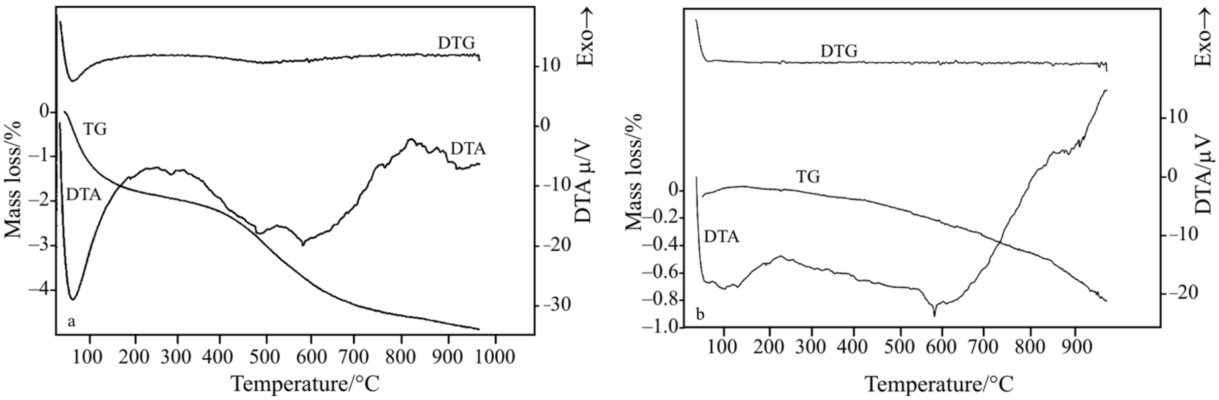

Fig. 4 TG/DTG-DTA curves of raw clay brick fired a – at 500°C and b – at 1000°C

side, 6 mass/mass%) contained in minor amounts. This sample has different color than the other sherds, but there is no archaeological information about its origin. This class gave a different thermogram, as it can be seen in Fig. 3. The adsorbed water is about 1%, but there is a rapid mass loss of about 4.5% with DTG_{max} at 690°C. At the same temperature, a strong endotherm peak is associated with the decarboxylation of calcite, which usually decomposes at 750–850°C [21]. According to Kantiranis [22] the thermal decomposition of calcite may be started at approximately 750°C depending on the mineralogical and chemical composition of a sample. The decrease in decarboxylation temperature has been related to the presence of soluble salts [23] and/or organic impurities of the sample [24].

The fourth class, e.g. sample A107, gave interested TG-DTA curves. The DTA curve showed clearly the characteristic peaks due to adsorbed water, dehydroxylation of muscovite or illite, the quartz transformation and the calcite decomposition at 690°C. The total mass loss was 5.0% with DTG_{max} at 420 and 690°C. So, we can say that this class is an intermediate category between the first and the third class.

Finally, there is another fifth class, e.g. sample A43, which gave a thermogram where the adsorbed water is only 0.25%. The DTG curve is horizontal and only the quartz transformation peak on the DTA curve is obvious at 573°C. This profile resembles a lot with that of the raw material DOKh11/1000 (Tables 4 and 5). It can be assumed that the firing temperature reached to 1000°C and this is enhanced from the mineralogical composition (Table 2), where the quartz and amorphous material are in large amount (68 and 22–26 mass/mass%) respectively.

Comparison with the raw clays fired at 500–1000°C (eleven bricks)

The results derived from mineralogical and thermal studies of the ancient pottery sherds were compared with those formed for the eleven laboratory prepared bricks of the local raw clay, baked at 500–1000°C in oxidizing atmosphere. The TG-DTA curves of the ten samples, baked at temperatures 500–950°C with intervals of 50°C, showed practically identical profiles, with features indicative of the presence of adsorbed water at ~90°C, dehydroxylation and dehydration of muscovite or illite at 490°C and its polymorphic transformation at 920°C [25].

Figure 4a gives the thermoanalytical curves (TG-DTA) of a brick sample, fired at 500°C. Small endotherm peaks at 300 and 575°C can be attributed to α and β cristoballite and quartz phase transitions, respectively [20], although the small endotherm at 300°C, can be also attributed to the partial loss of bound water of micaceous minerals [19], or to a poorly crystallized goethite [25]. Figure 4b however, illustrates the TG-DTA curves of the brick fired at 1000°C. The difference in the thermoanalytical profiles is obvious. The total mass loss is only 0.6%. Usually, ceramic pieces with lesser total mass losses are suspected of having been fired at higher temperatures. The DTG curve is horizontal and the DTA curve does not give the endotherms at 480 and 920°C of the micaceous mineral. Only the peak of the quartz transformation is evidence at 575°C. This is in agreement with the XRD findings, which gave 81% quartz, 11% albite and 8% amorphous material. The assumption is, that only in the firing temperature up to 1000°C, as it was expected, the crystal lattice of micas is destroyed and this can be used for comparison of the firing process.

Conclusions

- The studied ancient ceramic pottery sherds consisted mainly of quartz, feldspars and micas, which is in great agreement with the composition of the raw clay bricks, denoting their local origin. This composition was enhanced from the chemical results by ICP-AES.

- For the majority of the investigated sherds, the thermal behavior (TG-DTA) collaborates with their mineralogical findings and resulted to the firing temperature <950.
- The existence of calcite in some samples resulted that the firing temperature stopped before 700°C.
- The low amount of adsorbed water, the absence of micas and the existence of amorphous phase in some samples resulted in firing process up to 1000°C.

Acknowledgements

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