J Therm Anal Calorim (2011) 104:431–437
DOI 10.1007/s10973-010-1141-x

Thermal, chemical, and mineralogical characterization of ceramic tobacco pipes from Cyprus

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Cultural Heritage Special Chapter

Abstract This study is focused on simultaneous thermo-analytical investigations by TG/DTG-DTA technique applied for characterization of samples collected from archaeological site of Nicosia, Cyprus, dating to seventeenth century and gave new information on the firing technology. The ceramic samples derived from Ottomanic tobacco pipes were characterized by the related techniques such as X-ray powder diffraction for the mineralogical composition, and inductively coupled plasma-atomic emission spectrometry and micro-X-ray fluorescence spectroscopic analysis for the chemical content. It was found that they consisted mainly of quartz, calcite, feldspars, and micas. For the majority of the investigated ceramic samples, the thermal behavior investigation collaborates with their mineralogical findings, and resulted to the firing temperature at ~700 °C, due to the existence of calcite. Only in two samples with very high content in quartz, absence of calcite, low amounts of adsorbed water and of total mass loss, and absence of micas, the firing process resulted up to 1000 °C.

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Keywords Ceramics · Tobacco pipes · TG/DTG-DTA · PXRD · ICP-AES · μ-XRF

Introduction

The chemical, mineralogical, and thermal characterization of ancient ceramics can give information to the provenance of raw materials and the technological practice. [1–4]. The employment of various methods both destructive and non-destructive has been used for the qualitative and quantitative characterization of ancient mortars, plasters, and clay ceramics.

The Ottoman ceramic tobacco pipes were used in the daily life for both men and women from the beginning of the seventeenth century until the collapse of the Ottoman Empire. In Cyprus, the use of tobacco was very popular and imported from Turkey at about 1605 AD. Based on the written documents and museum collections from archaeological excavations in different layers, the ceramic pipes had different size, color, or composition [5, 6]. The oldest tobacco pipes were significantly small in their size, while the color of the initial clayey material varied from white to gray. At the end of the seventeenth century and during the eighteenth century, the color turned to brown, while at nineteenth century the red-brown color of clayey material predominated.

The mineral constituents of ceramics provide information about the firing conditions of raw materials. During firing, minerals undergo phase transitions that are characteristic of their firing conditions (temperatures and/or heating time) [7, 8]. Thermal analysis in conjunction with X-ray diffraction (XRD) provides information for the estimation of the original firing temperature of the ceramics [9–13]. On the other hand, the chemical composition of ceramics is related to the raw materials and can be

Fig. 1 Ceramic pipes from Nicosia, Cyprus

successfully used for the classification of ceramics into groups of similar composition [14]. The determination of the chemical content, among the numerous analytical techniques used for of ceramics studies are inductively coupled plasma-atomic emission spectrometry (ICP-AES), XRF, PIXE, and NAA. The ICP-AES technique 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 [14].

Finally, XRD is a well established technique for the determination of the mineral content of ancient ceramics and is widely used [15, 16]. Concerning the analysis of cultural objects, the combination of thermal, mineral, and chemical analysis is most often found in studies of historical mortars and plasters [17, 18] than ancient ceramics.

In this study, samples of Ottoman pipes were collected from the research excavation in Cyprus, Nicosia, road Kinyra, and they belonged to personal objects in the interior of the Ottoman buildings (Fig. 1). The samples cover all the types of tobacco pipes from the above mentioned excavation from the archaeological department team of Cyprus. These samples were analyzed by ICP-AES, thermogravimetric-differential thermal analysis (TG/DTG-DTA), PXRD, and μ-XRF techniques. The aim of this study is first to characterize the Ottoman ceramics in terms of their mineralogical and chemical content, second to study their thermal behavior and determine their firing temperature, and in final, to distinguish groups of samples with similar properties.

Experimental

Samples preparation

Nine Ottoman ceramic pipes, excavated from the archaeological place of Nicosia, Cyprus were studied in this study. All the samples dating to the seventeenth century were used in daily life as traditional entertainment. The samples were dried overnight at 105 °C before 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% (m/m) and 5 mL HNO_3 69.5% (m/m) was added. The exact decomposition procedure has been described previously [19]. 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, 1200 W) 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). Sodium was determined by AAS technique because of the fact that in the available ICP instrument the polychromator range was 165–403 nm.

XRD was performed using a Philips PW 1710 diffractometer with Ni-filtered CuKα radiation on randomly oriented samples (X-ray powder diffraction, PXRD). The samples were scanned from 3 to 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 XRPD data, using the intensity of specific reflections, the density and the mass absorption coefficients of the elements for CuKα radiation for the minerals present. Corrections of the mineralogical composition were made using external standard mixtures of pure minerals. The detection limit of the method was ±2% m/m.

About 15 mg of each sample were placed in platinum crucibles, and submitted to simultaneous TG/DTG-DTA investigations, at the heating rate 20 °C min^{-1}, in the temperature range ambient to 1000 °C, under nitrogen atmosphere, in a Setaram, Model Setsys 1200 instrument. An ARTAX 400 XRF, Bruker was used for the determination of some elements (Table 3).

Results and discussion

The ceramic samples have been divided in two main categories according to their chemical, mineralogical, and thermal findings as follows: group-1 (pipe samples 1, 2, 4, 6, 7, and 8) and group-2 (pipe samples 3, 5, and 9).

Chemical and XRD studies

The chemical analysis of nine ceramic samples of Ottomanic pipes from the archaeological excavation of Nicosia, Cyprus, characterized by ICP-AES, is presented in Table 1 and gives evidence for the provenance of the samples. The results of the semi-quantitative estimation of the mineralogical composition of the studied ceramic pipes are shown in Table 2, while the μ-XRF analogous in Table 3.

In the first group (group-1), the major mineral phase found is calcite ($CaCO_3$) with concentrations ranging from 21 (pipe sample 2) to 80% m/m (pipe sample 4), meaning that the raw material belongs to the Ca-rich clays. Quartz (SiO_2) is also predominant constituent ranging from 11 (pipe sample 4) to 58% m/m (pipe sample 8). Feldspars, mainly plagioclases [albite ($NaAlSi_3O_8$) and/or anorthite ($CaAl_2Si_2O_8$)] are found in minor amounts ranging from 3 (pipe sample 7) to 19% m/m (pipe sample 1). Micas [mainly muscovite, $K_2Al_6Si_6O_{20}(OH,F)_4$] are found in minor amounts in small quantities in four samples (pipe sample 1,2,4 and 8) ranging from 2 to 10% m/m, while in two samples (pipe samples 6 and 7) they contained in high amounts, 41 and 44% m/m, respectively.

In the second category (group-2), the calcite is present only in the pipe sample 3 (5% m/m), while it is absent in the other two samples (pipes 5 and 9). On the contrary, quartz is the major constituent varying between 72 (pipe sample 3) and 97% m/m (pipe sample 9). Moreover, micas are present only in the pipe sample 5 (6% m/m), while it is absent in the pipe samples 3 and 9. Representative XRPD patterns of the two groups are given in Figs. 2 and 3.

Thermal analysis

From the simultaneous thermoanalytical TG/DTG-DTA curves, the authors comment on the possible firing temperature and distinguish between samples of different origin. The summarized results of the thermal analysis of the ceramic pipes are given in Table 4. According to the authors' thermal findings, it can be deduced that there are two main categories between the nine investigated pipe samples. Two of them (pipe 1 and pipe 8) from the first class are depicted in Figs. 4 and 5, respectively.

Table 2 Semi-quantitative mineralogical composition in (% m/m) by XRD of the ceramic pipes from Nicosia, Cyprus

Sample	Q	F		Am	Px	Ep	C	M	Ch
		Pl	Kf						
Pipe 1	15	19		9			47	7	3
Pipe 2	54	11					21	7	7
Pipe 3	72	15			3	2	5		3
Pipe 4	11	5					80	2	2
Pipe 5	81	13						6	
Pipe 6	27	4					25	41	3
Pipe 7	21	3				2	30	44	
Pipe 8	58	7					25	10	
Pipe 9[a]	97		3						

Q Quartz, *F* Feldspars, *Pl* Plagioclase, *Kf* Potassium feldspars, *Am* amphibole (mainly tremolite), *Px* Pyroxene (mainly diopside), *Ep* Epidote-zoisite group, *C* Calcite, *M* Micas, *Ch* Chlorite

[a] contains also traces of TiO_2 (rutile and/or anatase)

In Fig. 4, which represents the thermal profile of the majority of the investigated ceramic tobacco pipes with colors brown or red-brown, the TG/DTG curves of pipe 1 showed a total mass loss of 17% in three decomposition stages. In the first stage, a mass loss of about 3%, with $DTG_{max} \sim 80$ °C, as a result of the eliminated adsorbed water, is mainly manifested by micaceous mineral.

The second, gradually mass loss between 400 and 500 °C, is possibly because of the dehydroxylation of structural OH– in micas, such as muscovite. However, the expected DTG_{max} at 450 °C is clearly seen only in the case of pipe 8 (Fig. 5), although some of the samples contain micas or chlorite minerals. The third stage with sudden mass loss of 7–13% and DTG_{max} at ~730 °C coincides well with the decarboxylation of calcite in the Ca-rich clays, which usually decomposes at 750–850 °C [20].

Table 1 Chemical analysis of the ceramic pipes from Cyprus, characterized by ICP-AES in ppm (μg/g) or in (% m/m)* for the oxides

Sample	Al_2O_3*	CaO*	Fe_2O_3*	MgO*	Ba/μg/g	B/μg/g	Cr/μg/g	Cu/μg/g	Pb/μg/g	Mn/μg/g	Zn/μg/g	Na_2O*
1	5.84	3.83	5.09	2.11	53	200	900	150	240	700	100	0.34
2	10.68	6.28	4.39	1.96	240	150	1000	150	450	500	90	0.62
3	7.52	3.81	4.45	1.54	240	110	1100	80	250	640	80	0.69
4	4.38	7.56	3.16	1.49	40	70	1400	110	160	350	60	0.75
5	13.64	1.65	5.82	1.24	210	90	2400	300	600	550	170	0.70
6	11.15	5.72	3.92	1.71	250	100	1460	80	500	400	100	0.35
7	8.88	4.35	4.07	1.23	190	130	1400	240	330	400	100	0.45
8	10.11	5.16	3.93	1.92	200	90	2100	80	330	470	80	0.65
9	12.87	0.71	2.65	0.36	80	50	3200	600	2.47*	90	100	0.20

Table 3 Results from micro-X-ray Fluorescence spectroscopic analysis (μ-XRF) for the ceramic pipes from Cyprus in % m/m

Element/Sample	1	2	3	4	5	6	7	8
MgO	4.164067	3.04196	2.706797	2.13977	3.47407	3.165642	1.841152	2.562559
Al_2O_3	10.51681	17.83463	15.02324	7.117279	14.27685	20.37345	20.04306	15.49102
SiO_2	44.97592	48.55994	58.66157	32.56567	46.51391	48.6633	48.37644	44.77236
P	0.009428	0.022027	0.008674	0.061793	0.044991	0.036265	0.026514	0.009275
K_2O	1.181749	2.227205	1.162465	0.73701	1.134818	2.73401	2.924295	1.683514
CaO	12.00564	8.638524	5.631431	25.2077	6.630609	11.8109	10.66296	9.253627
TiO_2	0.827628	0.970286	1.47165	0.388831	2.345265	1.028318	0.568609	0.737297
V_2O_5	0.001357	0.015547	0.016943	0.003253	0.028845	0.011946	0.004752	0.013764
Cr_2O_3	0.017279	0.030072	0.045865	0.01361	0.020487	0.022521	0.021394	0.016244
MnO	0.162512	0.098626	0.107718	0.057368	0.146401	0.080443	0.082915	0.073803
Fe_2O_3	9.862649	7.956473	7.748093	4.796183	11.06596	7.722073	6.784331	5.984474
CoO	0.005668	0.004142	0.003722	0.002107	0.005211	0.003441	0.003135	0.002618
NiO	0.034114	0.085326	0.10472	0.001959	0.071258	0.0592	0.042357	0.048053
CuO	0	0	0	0	0	0	0	0
ZnO	0.016242	0.011099	0.014186	0.009695	0.025419	0.015548	0.012459	0.010306
Rb_2O	0.002408	0.010879	0.005782	0.000736	0.003327	0.016214	0.013531	0.009215
SrO	0.052267	0.031211	0.045147	0.0527	0.033775	0.040255	0.051648	0.024243
BaO	0.040602	0.061295	0.071818	0.034302	0.088972	0.059915	0.071019	0.049645
PbO	0.001117	0.004671	0.001298	0.001958	0.005799	0.003021	0.004585	0.003489

P in ppm (μg/g)

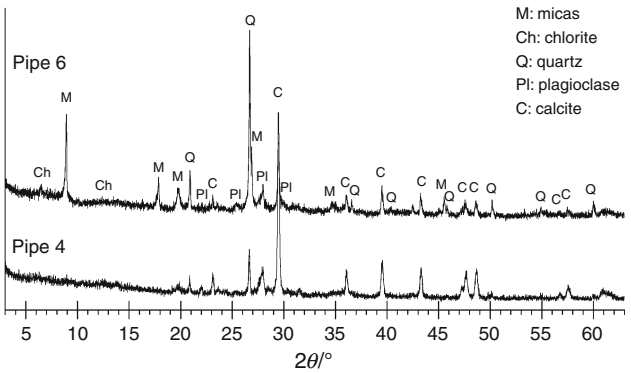

Fig. 2 Representative XRD patterns of the first group of ceramic pipes

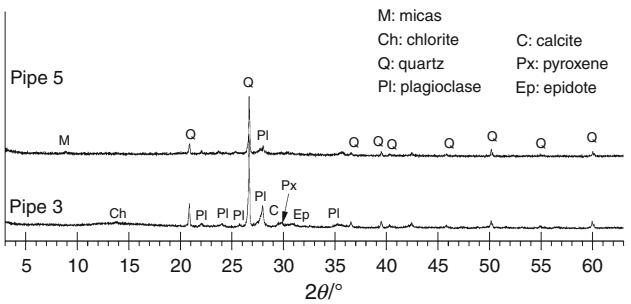

Fig. 3 Representative XRD patterns of the second group of ceramic pipes

From the thermal analysis results, the authors can estimate that the firing temperature for the first category of the investigated Ottomanic ceramic pipes is 700–800 °C for the majority of the samples, while for pipes 2 and 8 (which have red-brown color) is estimated at ~700 °C.

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 [21]. The plagioclases, e.g., Na-feldspar like albite, are very stable and show no thermal events from 20 to 1200 °C and for this reason they do not play a role in the determination of the firing process.

In the second class, the thermal profile of pipes 5 and 9 is identical to each other (a representative one is given in Fig. 6 for pipe 5), where the adsorbed water is ~1%, the total mass loss until 1000 °C is only 3.7%, with the DTG curve being almost horizontal and only the quartz transformation peak on the DTA curve is obvious at 573 °C. 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 material is in very large amount (81 and 97% m/m, respectively).

The sample of pipe 3 has two different colors (brown and black), but there is no archaeological information about its origin. Although the quartz material is also in large amount (72% m/m) this sample gave different thermogram from samples of pipe 5 and 9 (which have black color), as it can be seen in Fig. 7. Along with the adsorbed

Table 4 Summary of thermoanalytical results (TG/DTG-DTA curves) of the ceramic tobacco pipes from Cyprus and associate compounds to the thermal events

Samples	Curve	Temperature/ °C ↓/mass loss%	Temperature/ °C	Temperature/ °C	Estim. firing temperature/ °C
Pipes 1/6	TG	25–180	–	620–800	700–800
	DTG_{max}	80, ↓ 3%	–	740, ↓ 13%	
	DTA	60–280 (v.broad, endo)	573 (endo, sharp, v.small)	740 (endo, sharp, intense)	
	Comp	H_2O (adsorbed)	Quartz	CO_2 (calcite)	
Pipe 2	TG	25–180	–	590–750	~700
	DTG_{max}	80, ↓ 2%	–	740, ↓ 7%	
	DTA	60–280 (v.broad, endo)	573 (endo, sharp, v.small)	700 (endo, sharp, small)	
	Comp	H_2O (adsorbed)	Quartz	CO_2 (calcite)	
Pipe 3	TG	30–130	–	580–700	<700
	DTG_{max}	100, ↓ 0.25%	–	650, ↓ 1.1%	
	DTA, DTA	100 (endo, sharp), 60–280 (v.broad, endo)	573 (endo, sharp, v.small)	650 (endo, small)	
	Comp	H_2O (crystal)	Quartz	CO_2(calcite)	
Pipe 4	TG	25–180	–	600–800	700–800
	DTG_{max}	80, ↓ 2.5%	–	750, ↓ 20%	
	DTA	60–280 (v.broad, endo)	573 (endo, sharp)	750 (endo, sharp, intense)	
	Comp	H_2O (adsorbed)	Quartz	CO_2 (calcite)	
Pipes 5/9	TG	25–180	–	Until 1000	~1000
	DTG_{max}	80, ↓ 1%	–	↓ Total mass Loss 3.7%	
	DTA	60–280 (v.broad, endo)	573 (endo, sharp, v.small)		
	Comp	H_2O (adsorbed)	Quartz		
Pipe 7	TG	25–180	–	620–800	700–800
	DTG_{max}	90, ↓ 3%	–	730, ↓ 10%	
	DTA	60–280 (v.broad, endo)	573 (endo, sharp, v.small)	730 (endo, sharp, intense)	
	Comp	H_2O (adsorbed)	Quartz	CO_2 (calcite)	
Pipe 8	TG	25–180	–	600–750	~700
	DTG_{max}	90, ↓ 3%	–	720, ↓ 7%	
	DTA	60–280 (v.broad, endo)	573 (endo, sharp, v.small)	720 (endo, sharp, small)	
	Comp	H_2O (adsorbed)	Quartz	CO_2 (calcite)	

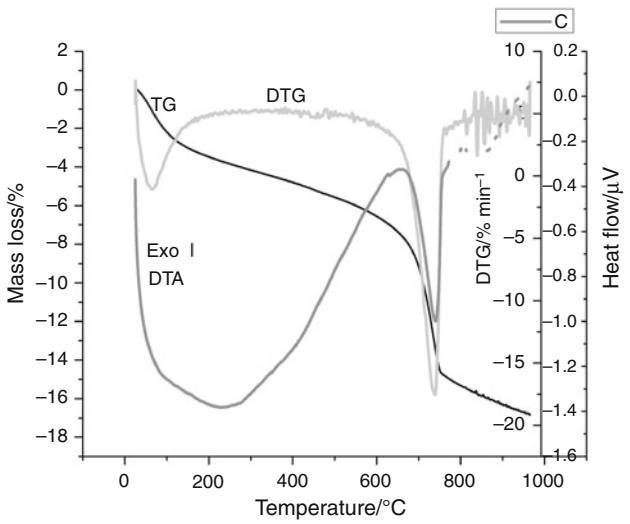

Fig. 4 TG/DTG-DTA curves of the ceramic pipe 1

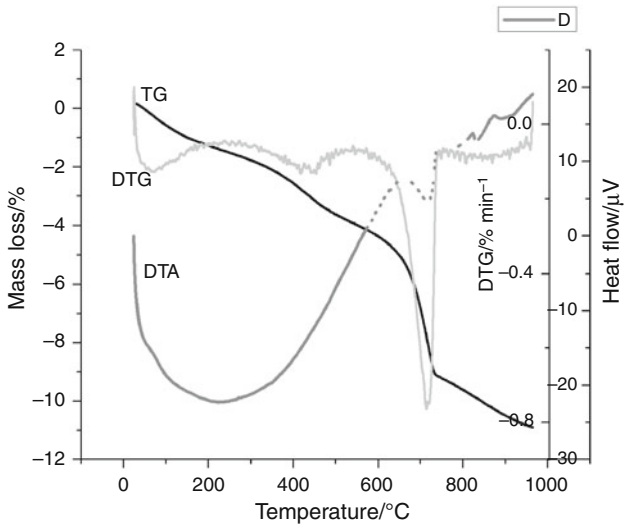

Fig. 5 TG/DTG-DTA curves of the ceramic pipe 8

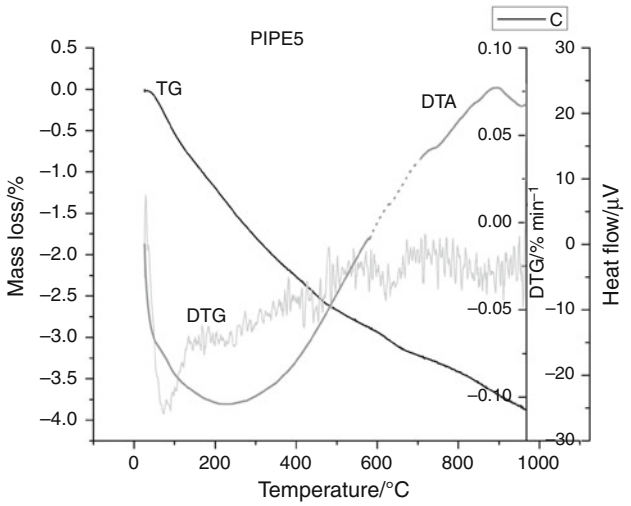

Fig. 6 TG/DTG-DTA curves of the ceramic pipe 5

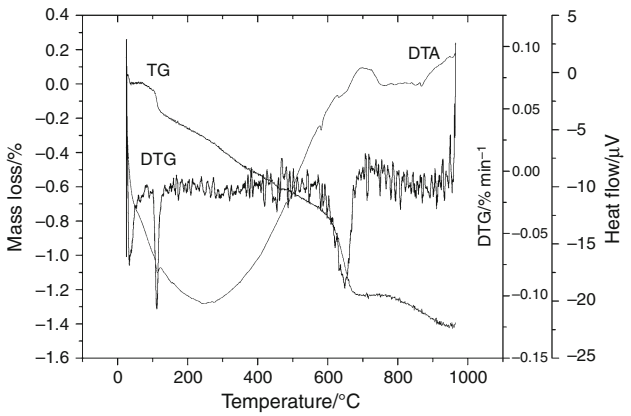

Fig. 7 TG/DTG-DTA curves of the ceramic pipe 3

water at ~50 °C, a small quantity of crystal water (0.25%) eliminated suddenly at 100 °C, as it is obvious from the DTG and DTA curves. There is also a small rapid mass loss (1.1%), with DTG_{max} at 650 °C. At the same temperature, a small endotherm peak is associated with the decarboxylation of calcite (mineralogical 5% calcite). The decrease in decarboxylation temperature has been related to the presence of soluble salts [22]. Maybe the released crystal water is an evidence for the presence of the hydrated salts in this sample. From the low decomposition temperature of calcite, it can be assumed that the firing temperature was below 700 °C.

Conclusions

• The studied ceramic tobacco pipes from Cyprus (Ottoman period) consisted, as it was deduced from XRPD studies, mainly of quartz, calcite, feldspars, and micas. This composition was enhanced from the chemical results by ICP-AES and μ-XRF.

• For the majority of the investigated ceramic samples, the thermal behavior which was derived from TG/DTG-DTA investigation collaborates with their mineralogical findings and resulted to the firing temperature at ~700 °C, due to the existence of calcite.

• Only in two samples with very high content in quartz, absence of calcite, low amounts of adsorbed water and of total mass loss, and the absence of micas, the firing process resulted up to 1000 °C.

• Finally, there was one sample, with similar analytical and mineralogical findings with the above mentioned two samples, but different thermal profile suggested a firing process <700 °C, due to the presence of small amounts of calcite and soluble hydrated salts.

Acknowledgements The authors are grateful to Archaeologists Mrs. E. Zachariou and her collaborator S. Eleftheriou, Department of Antiquities, Republic of Cyprus for providing us with the ceramic samples, G. Zachariadis for ICP-AES measurements and Mr. J. Nazlis, Archaeological Museum of Thessaloniki and Chr. Palaiochorinou.

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