Journal of Archaeological Science 34 (2007) 141–154

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Chemical and mineralogical examination of metallurgical ceramics from a Late Bronze Age copper smelting site in Cyprus

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Received 10 October 2005; received in revised form 10 April 2006; accepted 13 April 2006

Abstract

For metallurgical processes in antiquity functional materials were required, which were sufficiently heat resistant. Commonly, ceramics were used for the production of furnaces, tuyères and crucibles. Because normal pottery usually could not withstand the extreme temperatures, which were needed for metallurgical operations, the ceramic production process had to be modified. An analytical case study will be presented on refractory ceramics from the Late Bronze Age copper smelting site Politiko-*Phorades* (Cyprus). Cyprus had a major role in copper production, starting from this period, and the selected site is the earliest primary smelting site discovered in Cyprus until now. Furnace and tuyère fragments were analysed chemically and mineralogically, in order to investigate ancient ceramic technology in view of heat resistance.

Keywords: Ancient refractory ceramics; Neutron activation analysis; X-ray diffraction; Scanning electron microscopy

1. Introduction

The Late Bronze Age copper smelting workshop at the site of Politiko-*Phorades* was discovered in 1996, during the Sydney Cyprus Survey Project (SCSP). It is located in the copper-rich north-central foothills of the Troodos Mountains (Fig. 1). The workshop was subsequently excavated by a joint team from the University of Glasgow and the University of Cyprus under the direction of A.B. Knapp and V. Kassianidou [12,13,16,18–20]. The excavation brought to light a large quantity of archaeometallurgical finds indicating a primary smelting workshop, which according to the ceramic typology and radiocarbon analysis dates to the 16th–15th centuries BC, in other words the earliest phase of the Late Bronze Age on the island. This is the Late Cypriot I, the period during which Cyprus begins to emerge as one of the most important copper producers and exporters in the Eastern Mediterranean. Therefore, Politiko-*Phorades*, the earliest known excavated primary copper smelting workshop in Cyprus, offered a unique opportunity to study and understand the smelting technology of this period.

The workshop is situated on the bank of an ancient creek bed where flat working surfaces were constructed with river pebbles. No architectural remains have been discovered, showing that the smelting was done in the open air, clearly at a time of the year during which the weather allowed for such activities to take place. The slag produced was piled against the creek's bank, eventually forming a small heap. A total of 3.5 tons of slag deriving from the smelting of copper sulphide ores was collected at the site. However, the most interesting finds from *Phorades* were the remains of the smelting installations. More than 6000 fragments of furnace rims, walls and bases have been collected, as well as 600 fragments and 50 almost complete tuyères. This is the largest collection of such finds collected from any known site on the island.

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doi:10.1016/j.jas.2006.04.005

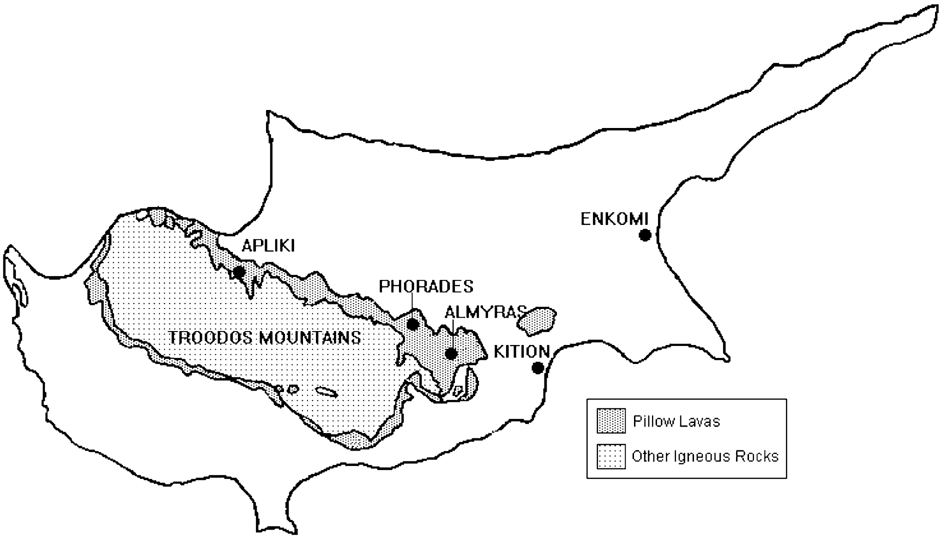

Fig. 1. Map of Cyprus: indicated apart from other sites is the location of Politiko-*Phorades* in the NE of the Troodos mountains.

It is apparent that ceramics used for high temperature processes should be able to withstand heat and rapid temperature changes. During the copper smelting process enduring temperatures of 1200–1300 °C could be expected at the inner surface of a furnace and at the tuyère tips. The raw materials used for the production of the refractory ceramics in antiquity, however, were basically similar to those used for contemporary pottery but with a modified production process, in order to withstand higher temperatures. Common methods were the construction of rather thick walls and the addition of non-plastic temper, such as quartz. Quartz itself is refractory and as an addition to low refractory clays it could improve their refractoriness [6]. The same applies to other heat resistant non-plastic materials. Coarse particles, however, probably remained inert and did not react with the clay matrix during the time of furnace operation, but reduced the shrinkage and strengthened the ceramic body. Furthermore, non-plastic temper generated porosity by cracks, which developed when the clay matrix was shrinking during drying. High porosity, finally, reduces heat transfer and improves the mechanical strength by suppressing crack propagation. Apart from non-plastic temper a common way for generating porosity was the addition of organic temper burning out during the firing and leaving voids. Another advantage of organic fibres like

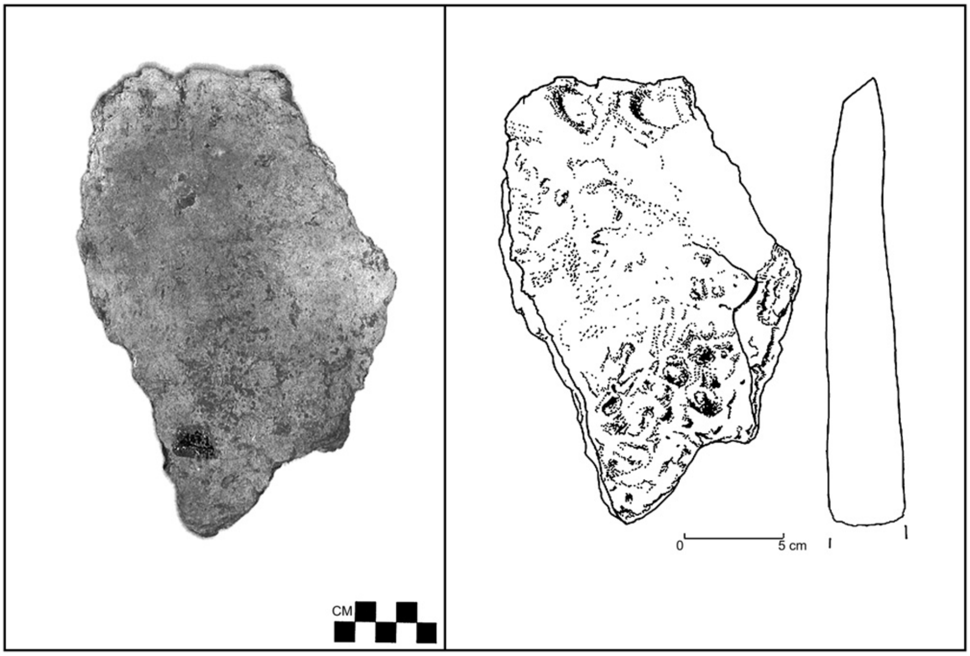

Fig. 2. Furnace rim fragment, one of the longest preserved examples.

Fig. 3. Furnace base fragment with finger impressions on outer circumference.

chopped grass or straw was the stabilisation of the unfired clay body.

In order to examine the refractory properties of the smelting installations excavated in Politiko-*Phorades*, 40 samples, comprising 15 tuyère fragments and 25 fragments of furnace walls and bases, were selected for physico-chemical analysis [11]. The main objective of this work is to reconstruct the technology of manufacture of the ceramics used in the metal production, by characterising the provenance and manipulation of the raw materials. Furthermore, the results, which are presented here, will illustrate the suitability of the examined ceramics to withstand high temperatures and possible modification of the clay conducted by the ancient craftsmen in order to increase the refractoriness of the ceramics.

2. The furnaces and tuyères from Politiko-*Phorades*

All of the furnace fragments derive from free-standing, cylindrical structures with well-defined rims and flat bases, made entirely of coarse clay mixed with plant fibres. In the majority of the fragments, the thickness of the walls ranges between 2.5 cm and 4.5 cm while the thickness of the bases ranges between 4 cm and 7.5 cm (Fig. 2). Despite the high number of furnace fragments many of which are large and diagnostic it has not been possible to reconstruct a complete furnace or even a complete profile. However, based on some of the larger rim and body fragments it is estimated that the furnaces would have been at least 30 cm high with an estimated diameter of approximately 42–44 cm. Fingerprint impressions on the exterior circumference (Fig. 3), usually where the wall joins the base, show how the furnaces were constructed: first a thick, flat, circular disk was formed on which the cylindrical body was built with slabs. It is clear that the furnaces were constructed in the round, not in a pit or against a stone wall. Had this been the case, the outer surface would not have been so smooth and finger impressions would have been on the interior surface where the maker would have pushed the clay against the pit or the stone structure, as for example at Timna [23], and at Ayia Varvara-*Almyras* [4]. The closest parallel in Cyprus for the *Phorades* furnaces is the well-known 'crucible' from Enkomi (Inv. 1640) [1,2], which Tylecote [27] identified as a smelting furnace. This was found in Enkomi's Area III where a series of copper workshops were uncovered. The "crucible" came from the floor of a room of the Level IIB building, which dates between 1300 BC and 1230 BC [2]. It is, therefore, later than the examples from *Phorades*. Furthermore, there is a difference in the size: the one from Enkomi is smaller having a diameter of 30 cm and a preserved height of 20 cm [1]. This may indicate a different use, possibly melting, in order to cast ox-hide ingots, rather than smelting like in *Phorades*.

Equally impressive is the collection of tuyères from the workshop. The majority are cylindrical, apart from a single elbow tuyère and a rare intriguing group of double walled tuyères (Fig. 4) [18,19]. As none of the tuyères has been found complete, the possibility must be considered that more elbow tuyères did exist. In the examples where the nozzle is preserved, it is slagged and highly vitrified. The tuyères seem to have been made according to specific standards: all the examples which could be measured have an outer diameter ranging between 5–7 cm and an air-hole, which is rarely perfectly cylindrical, or symmetrically positioned, ranging between 2.5–3.5 cm. None of them is fully preserved but one of the best examples has a length of *c.* 30 cm (Fig. 5). Tylecote [27] identified three types of tuyère from Bronze

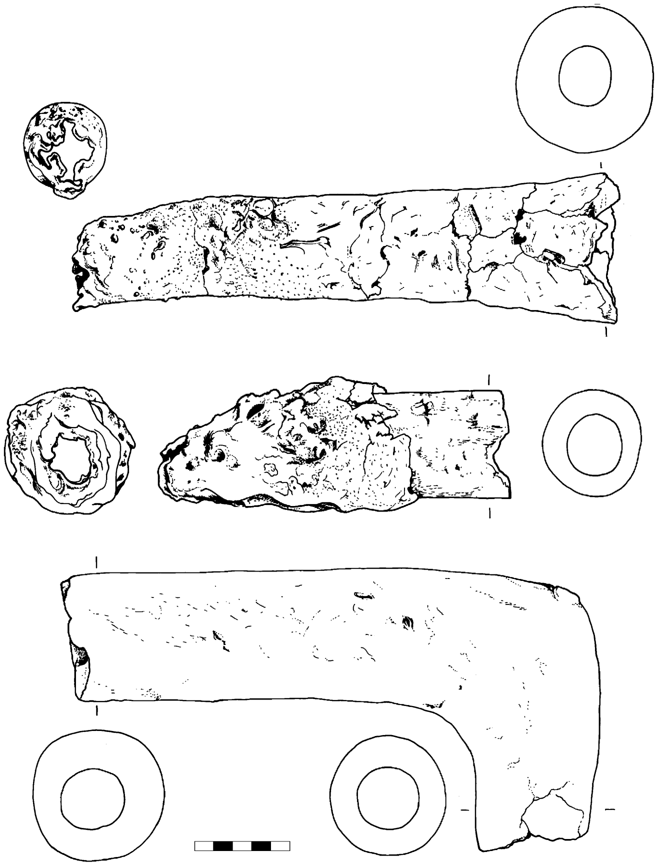

Fig. 4. Types of tuyères.

Fig. 5. One of the best preserved tuyères from the site.

Age sites in Cyprus: the straight cylindrical, the straight ‘D’ shaped, and the elbow tuyère. In general, the tuyères from *Phorades* conform to this classification and are similar in shape and material to those from Apliki [3] and Enkomi (e.g. Inv. Numb. 2336/9 [2]), although the ones from Apliki are rather more massive in their construction.

3. Analytical approach

First, all fragments were examined with naked eye and under the binocular microscope. The fragments were classified according to their fabric, dimensions and characteristics concerning colour or surface. Representative samples were selected for the fabrication of polished sections perpendicular to the surface. The polished sections were first studied under the optical microscope, then carbon coated und studied under the scanning electron microscope (SEM), using a JEOL 5310 SEM with an Oxford energy dispersive X-ray spectrometer (SEM EDS), which had been calibrated with geological standards. The degree of vitrification observed in the ceramic body provided information about the temperatures that the ceramics had been exposed to in particular areas. The analysis with the EDS provided information about nature of inclusions and about the major element composition of the ceramic body. Therefore each sample was analysed in different representative areas, i.e. in areas presenting the typical fabric without coarse inclusions or contaminations. Disregarding coarse inclusions, such as quartz or slag, assumedly will provide results underestimating SiO_2 or FeO contents, as they would be given by complete bulk analysis [5]. The area covered for one analysis was typically 2.6 mm × 2.0 mm. The actual ceramic matrix, without inclusions larger than 6 μm, was analysed as well, covering at different spots areas of typically 65 μm × 50 μm.

From the same samples also thin sections were fabricated in order to be studied under the optical microscope with transmitted light. The petrographic examination was focused on the provenance of the raw materials, particularly in relation to the local geology [29], and on technological questions.

In order to determine trace element compositions and to investigate the chemical variation of the assemblage bulk samples of all fragments were analysed by neutron activation analysis (NAA). The samples were powdered after removing their surface and cleaning them from obvious contaminations, such as slag remains. The analysis followed the routine measurement procedure for archaeological ceramics, which is described in detail elsewhere [9].

To study the mineral phases and their transformations during firing as well as development of microstructure, small fragments from selected samples were cut and refired under oxidizing and under reducing conditions. Reducing atmosphere was created by passing air/hydrogen mix through the tube furnace during firing containing 4% H_2. The temperatures applied were between 950 °C and 1200 °C with heating rates of 200 K/h and soaking times of 1 h at the peak temperature. Additionally, some pieces were refired in oxidizing atmosphere at 950 °C with soaking times of 5 h and 10 h, respectively, in order to examine the effect of long exposure to high temperatures in relation to the operation time of the furnace.

Samples of refired pieces and selected fragments were analysed by X-ray diffraction (XRD), using a Siemens D 500 spectrometer with a Cu-Kα source. Additionally, multiple samples were taken along sections from the inner to the outer surfaces from two large specimens coming from the base and the wall of a furnace. These samples were also analysed by XRD, in order to map the mineralogical changes of the ceramic material in relation to the distance from the heat source, i.e. the smelting load, inside the furnace. From the refired pieces and some selected furnace and tuyère fragments fresh fracture surfaces were prepared in order to examine the degree of vitrification in their microstructure under the SEM. In fresh fracture surfaces the extent of the developing glass phase, i.e. the degree of vitrification, is more clearly to observe, whereas the position inside the sample is more exactly to control in a polished section [26].

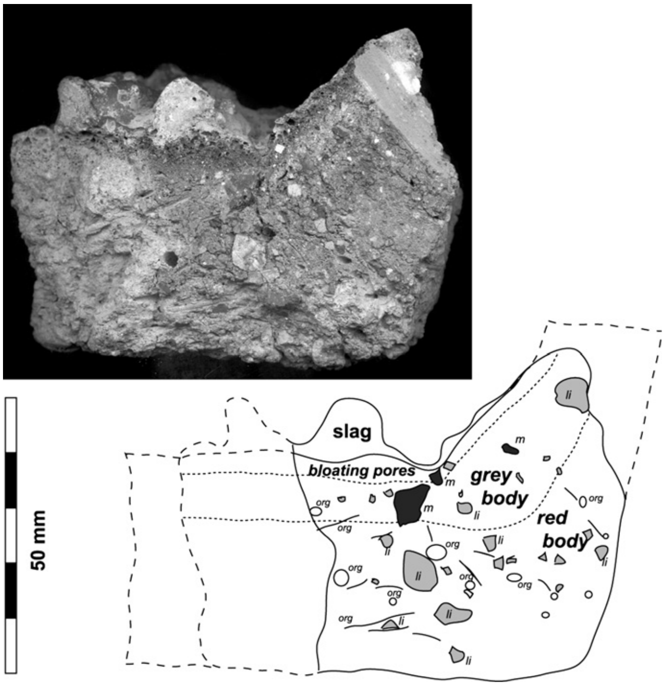

Fig. 6. Cross-section of a furnace base fragment with schematic distribution of inclusions and voids: the main kinds of inclusions are metallic/slag (m) or lithic (li). Voids, originating from burned out organic fibres (org) are visible either as cavities or as traces parallel to the cut.

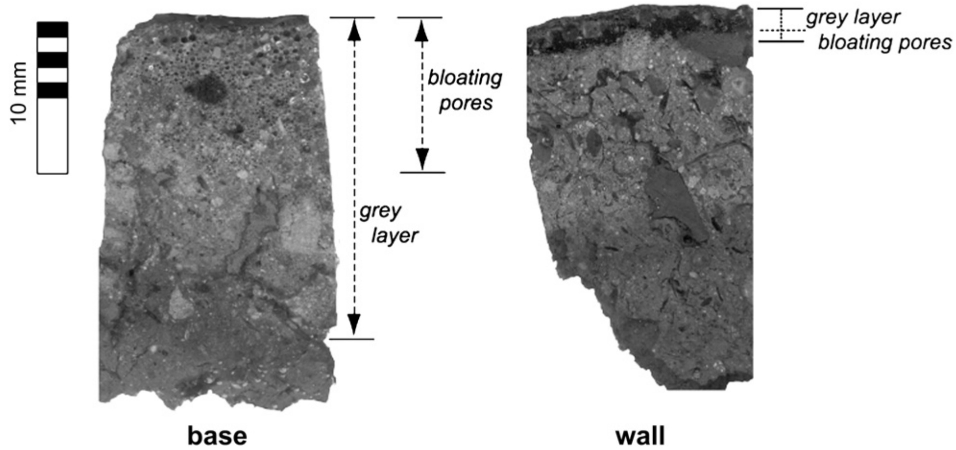

Fig. 7. Sections of a furnace base and a furnace wall fragment: both fragments were covered with a slag layer at the inner surface. Indicated are the thickness of the grey layer and the depth of the areas with bloating pores.

4. Results and discussion

4.1. Structure of the ceramic body

The ceramic samples when examined under the binocular microscope gave a coarse and porous impression with frequent and large inclusions, apparently rock fragments, reaching up to several millimetres (Fig. 6). The colour variation observed is attributed to temperature gradients and varying redox conditions during the operation of the furnaces. Almost all fragments presented remains of slag on their surfaces, most obvious being the continuous slag layers on the inner surfaces

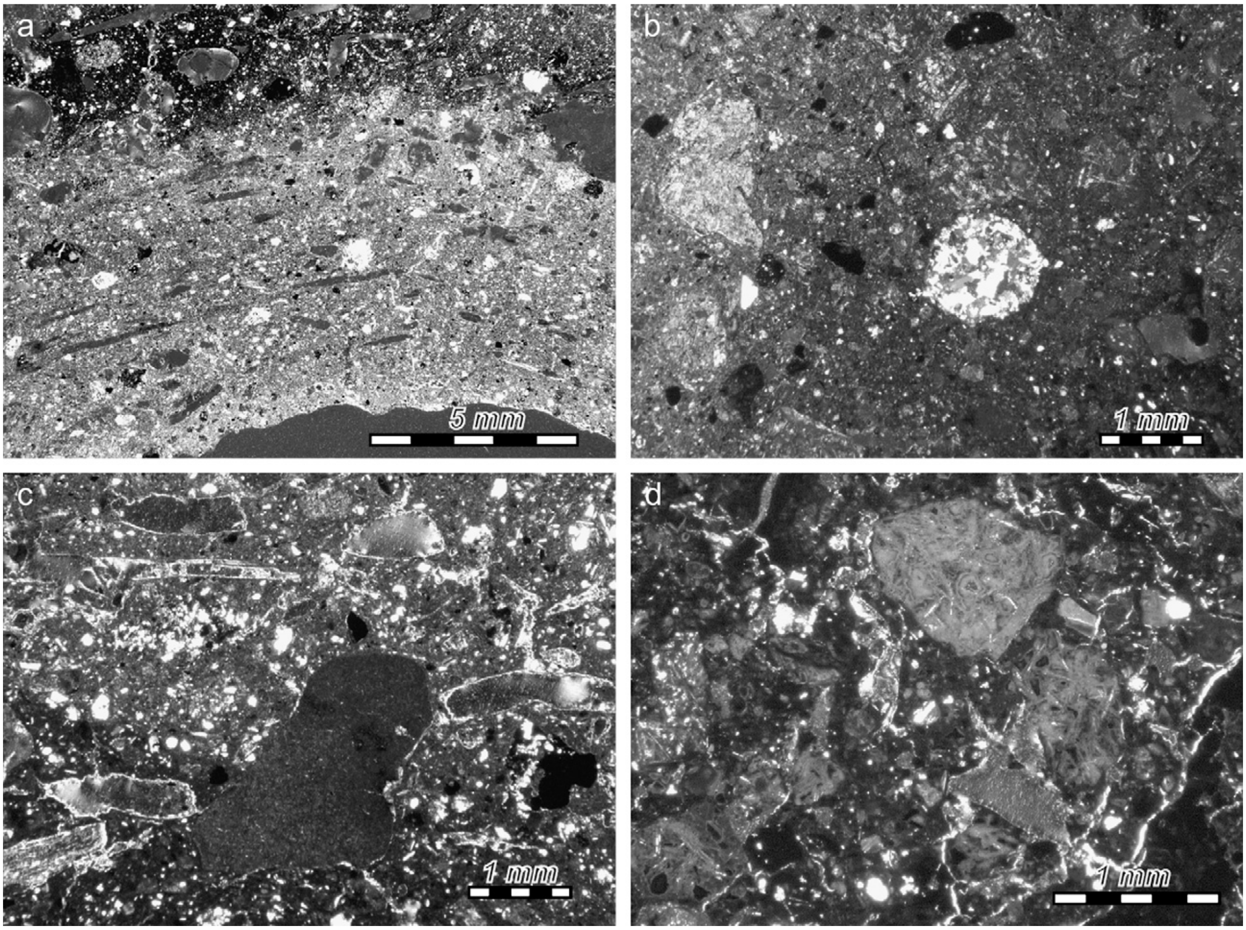

Fig. 8. Photo micrographs of thin-sections: (a) cross-section of tuyère PHT1 with elongated voids parallel to the surface; (b) furnace fragment PHF14 presenting ophiolithic rock fragments and a rounded polycrystalline quartz inclusion; (c) fine-grained inclusion in tuyère PHT4; and (d) rock fragments and developing cracks in furnace fragment PHF23.

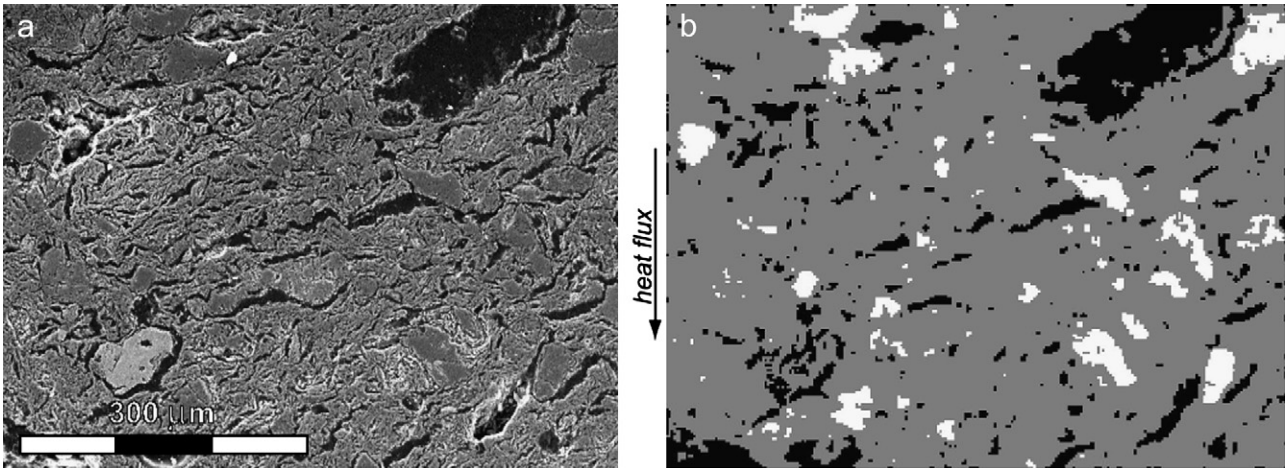

Fig. 9. (a) SEM picture of the fabric in a tuyere fragment PHT1; and (b) Three phase model based on the SEM picture with assumed direction of heat transfer: the first phase corresponds to the actual ceramic body, the second phase to the quartz inclusions and the third phase corresponds to the voids.

of some furnace fragments and the slag layers covering the tuyère tips. In the ceramic layers, which were in contact with the slag, bloating pores were visible with naked eye, indicating the extreme temperatures these areas were exposed to. A noticeable difference between furnace base fragments and furnace wall fragments was the variation in the extent of the inner layers affected most by the heat (Fig. 7). Dark grey layers and areas with bloating pores were thicker in base fragments.

Examination of thin-sections revealed that the most abundant non-plastic inclusions were ophiolithic rock fragments (Fig. 8), constituting in some cases more than 50% of the sample [29]. These volcanic inclusions, clearly related to the geological environment of the site, were heat resistant and thus improved the refractoriness of the ceramic body. As for mineral inclusions, frequent small angular to sub-angular quartz grains with a size of approximately 50–100 µm, constituted approximately 5–10% of the samples (Figs. 8 and 9). Additionally, occasional larger rounded polycrystalline quartz grains were present with a typical size of approximately 1 millimeter (Fig. 8b). Apart from rock fragments and quartz, frequent fine-grained inclusions with rounded to subangular shape and a size of some 100 µm up to several millimetres could be identified (Fig. 8c). Even though in some cases they gave the impression of clay clots these were most probably heavily altered basalts. Finally, small slag fragments and metallic inclusions with sizes of typically 100 µm were present in the ceramics. Their infrequent occurrence, however, indicated that they were either unintentionally introduced to the clay paste or entered the ceramics as contamination during the smelting process, particularly in regions close to the slagged surfaces. The overall impression was that the non-plastic inclusions were not added as temper to a finer clay. Most probably they have been already a component of the selected raw material. Nevertheless, even in this case the raw material was intentionally selected because of its large fraction of coarse non-plastic inclusions, beneficial for the thermal and mechanical properties. Due to their high melting point they remained inert during the furnace operation and prevented the furnace structure from collapse. On the other hand, compared to other imaginable temper, such as quartz, the thermal conductivity of basic rock is smaller and rather similar to this of the actual ceramic matrix.

The open porosity of the ceramics was estimated by water saturation, with approximately 25% in the tuyères and up to almost 40% in some of the furnace fragments. A major part of the observed porosity was generated with fibrous organic material, probably straw or chaff, which was added to the clay paste and burned out during firing (Figs. 6, 8a and 9). The remaining cavities were oriented parallel to the surface and in the case of the tuyères parallel to the main axis. Another type of elongated voids apparently originated from the non-plastic inclusions causing cracks in the clay matrix during drying and firing (Figs. 8d and 9). The development of this kind of voids appeared to be related to the processing of the raw material, obviously performed without intense

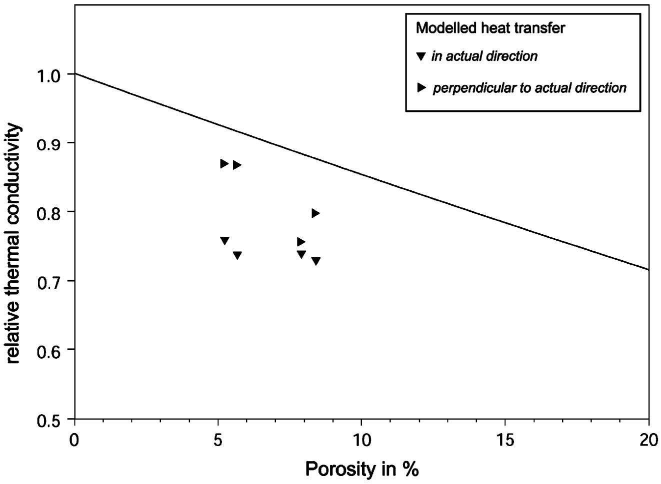

Fig. 10. Reduction of the thermal conductivity due to porosity: the curve corresponds to theoretical values for arbitrarily distributed pores and the symbols correspond to values calculated for particular areas in the model presented in Fig. 9 for heat transfer in the actual direction and perpendicular to it.

Table 1
Average chemical compositions of two groups of fragments

	Phorades A (15 samples)			*Phorades* B (13 samples)			ave. exp. error%
	mean	stdev	stdev %	mean	stdev	stdev %	
As	5.1	2.2	42	13.7	2.9	21	4.1
Ba	91	22	25	78	18	24	11
Ca%	2.2	0.4	16	1.7	0.5	28	8.0
Ce	24.2	3.8	16	13.6	1.6	12	2.5
Co	43.1	6.7	16	47.2	8.5	18	1.5
Cr	79	24	30	118	26	22	2.5
Cs	0.91	0.13	14	0.55	0.12	21	2.4
Eu	0.99	0.05	5.4	0.63	0.04	6.9	2.9
Fe%	8.42	0.33	3.9	10.56	0.98	9.3	1.1
Hf	2.73	0.25	9.2	2.15	0.12	5.6	2.4
K%	0.92	0.10	11	0.98	0.08	7.9	10
La	9.7	1.3	13	5.1	0.5	10	3.5
Lu	0.38	0.03	7.3	0.31	0.02	5.2	5.7
Na%	1.38	0.13	9.7	0.51	0.10	20	5.8
Ni	48	15	31	35	10	30	7.1
Rb	21	3	13	18	2	11	4.0
Sb	0.32	0.03	8.6	0.82	0.15	18	4.9
Sc	34.0	2.5	7.4	33.6	3.5	10	1.8
Sm	3.24	0.29	9.0	2.11	0.07	3.5	5.8
Ta	0.43	0.07	17	0.26	0.05	19	4.9
Tb	0.75	0.07	8.8	0.62	0.07	11	9.8
Th	2.6	0.5	18	1.5	0.3	19	1.4
U	0.73	0.18	24	0.57	0.07	13	7.9
Yb	3.09	0.14	4.5	2.37	0.12	5.0	5.7
Zn	510	77	15	373	35	9.4	14
Zr	124	36	29	105	32	30	19

Group A contains the majority of the tuyère fragments and a part of the furnace wall fragments. Group B contains the rest of the furnace wall fragments and one tuyère fragment. All concentrations are given in ppm, except for those of Ca, Fe, K and Na, which are given in wt%. The last column presents the average experimental error of the NAA setup [9].

mixing and compressing. Also these voids presented preferred orientation parallel to the surface and resulted in a rather layered ceramic structure. Possibly the layered structure was intentionally created by the craftsmen during the construction of the clay body like in a comparable case of crucibles from a Classic bronze workshop in Olympia in Greece [24]. Computer modelling of heat transfer in porous ceramics indicated that the reducing effect, which porosity caused on the thermal conductivity of the ceramic matrix, was enhanced because of the voids' preferred orientation perpendicular to the direction of the heat transfer [10]. Fig. 9b shows a two-dimensional three-phase model of the ceramic fabric with indicated direction of the heat transfer. The porosity was estimated with 11.8% and the quartz content with 6.3%. However, the size of the voids, which can be considered in this model, is limited by the pixel size, in this case 2.6 μm. The relative thermal conductivity in relation to the porosity was estimated with Finite Element Analysis (FEA) examining areas of 100 × 100 pixels, arbitrarily selected in the modeled ceramic fabric. Fig. 10 shows a clear reduction of the thermal conductivity compared to the case of arbitrarily distributed porosity or the case of heat transfer in another direction.

A further benefit of the observed inclusions and porosity was the enhancement of toughness of the ceramics. Cracks due to thermal stress were supposedly not necessarily leading to catastrophic failure of the entire furnace but to stable crack propagation because the total fracture energy was higher than in the case of low porous and rather brittle ceramics [14].

4.2. Geochemical and mineralogical characterization

According to the NAA of the bulk samples the ceramics were low calcareous with a CaO content of not more than 3%, but with rather high iron concentrations (FeO >10%). All metallurgical ceramics from Politiko-*Phorades* appeared to have been produced from the same or very similar raw materials. Nevertheless, the chemical compositions could be divided in two groups, Group A, comprising almost all the tuyères and one fraction of the furnace fragments, and Group B, comprising a large fraction of the furnace fragments and one tuyère fragment (Table 1). Group A presented clearly higher concentrations of most of the trace elements, particularly the rare earth elements (REE), Th and U, whereas Group B presented higher concentrations of Fe, Co, Cr, K and Sc and also As and Sb. The higher concentrations of the REE in Group A is most probably attributed to the fact that the raw materials were finer compared to Group B and therefore richer in clay minerals, which accommodate usually the bulk of the REE [22]. On the other hand a higher proportion of ophiolithic rock fragments, bearing high Fe, Co, Cr and Sc concentrations due to their mafic origin, probably was the reason for

Table 2
Chemical compositions of three clay deposits in the Eastern part of the Troodos mountains [7]

	Sanida (10 samples)		Kornos (2 samples)		Vasilikos 1 sample
	average	stdev	average	stdev	
Al%	9.55	0.93	9.60	0.61	7.18
Ca%	4.1	0.7	1.3	0.1	10.6
Ce	12.2	3.2	23.2	5.1	17.3
Co	36.6	3.9	40.0	2.3	52.3
Cr	288	148	152	35	240
Cs	0.44	0.25	0.85	0.11	1.10
Eu	0.66	0.09	0.96	0.01	0.73
Fe%	6.09	0.68	8.51	0.33	6.41
Hf	1.99	0.45	3.09	0.44	1.37
K%	0.53	0.13	0.96	0.20	0.42
La	5.8	2.2	12.2	2.4	10.7
Lu	0.38	0.08	0.44	0.03	0.38
Mn	763	258	1847	46	2103
Na%	1.42	0.13	1.93	0.39	0.78
Rb	12	3	27	3	23
Sc	34.9	2.8	41.0	2.7	32.1
Sm	2.26	0.50	3.31	0.22	1.49
Ta	0.22	0.11	0.42	0.09	0.33
Tb	0.57	0.13	0.72	0.16	0.62
Th	1.17	0.64	2.91	0.40	1.80
Ti%	0.31	0.11	0.46	0.20	0.24
Yb	2.23	0.36	2.66	0.14	2.08
Zn	282	250	175	21	125

The samples were measured by NAA at the Missouri University Research Reactor. Geochemical similarity indicated the use of particularly the clay from Sanida in Bronze Age pottery production [8]. All concentrations are given in ppm, except for those of Ca, Fe, K, Na, Al and Ti, which are given in wt%.

Table 3
Major element compositions of the ceramic matrix and ceramic body measured with SEM EDS in different areas in polished sections of tuyère and furnace fragments

			SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	K_2O	Na_2O	CuO	SO_3
Tuyeres													
PHT 1	Matrix	average	55.7	1.06	20.3	11.8	0.25	4.08	2.89	1.31	2.23		0.33
NAA A	4 points	stdev	1.8	0.12	1.2	1.2	0.04	0.80	0.57	0.21	0.69		0.06
	Body	average	61.9	0.92	16.9	10.0	0.49	3.80	2.67	1.27	1.68		0.33
	3 points	stdev	1.8	0.10	0.1	0.9	0.32	0.19	0.72	0.10	0.02		0.09
PHT 3	Matrix	average	59.1	0.91	17.0	10.9	0.37	4.74	2.02	1.51	1.88		0.20
NAA A-	3 points	stdev	2.8	0.19	1.8	0.9	0.21	0.78	0.05	0.75	0.15		0.06
	Body	average	61.2	0.94	15.9	9.4	0.28	4.36	3.08	0.78	1.63	2.20	0.25
	3 points	stdev	0.4	0.10	0.8	0.7	0.07	0.61	0.92	0.19	0.14	1.61	0.06
PHT 4	Matrix	average	56.8	1.15	20.1	11.8	0.43	4.06	2.28	1.34	1.68	0.65	0.26
NAA A	5 points	stdev	1.4	0.12	0.3	1.2	0.35	0.50	0.21	0.20	0.19		0.04
PHT 6	Matrix	average	57.7	0.99	18.9	12.1	0.27	3.95	3.26	0.90	1.58		0.42
NAA A	4 points	stdev	2.8	0.35	0.5	2.6	0.06	1.13	0.66	0.06	0.44		0.07
	Body	average	61.5	0.98	17.3	10.3	0.27	3.60	3.17	1.19	1.43		0.46
	2 points	stdev	0.0	0.06	0.9	0.2		0.49	0.07	0.04	0.04		0.13
PHT10	Matrix	average	58.4	0.94	20.5	9.5	0.2	4.35	2.36	1.55	2.23		0
NAA A	3 points	stdev	2.8	0.15	1.0	1.8	0.01	0.50	0.29	0.43	0.86		0
PHT 11	Matrix	average	56.1	1.13	17.9	13.0	0.69	5.05	3.14	1.56	0.89	0.45	0.68
NAA B	4 points	stdev	2.2	0.44	1.9	2.0		0.98	0.84	1.71	0.17		0.30
	Body	average	57.9	0.85	17.1	12.2	0.27	5.43	3.34	1.09	0.82	0.47	0.76
	5 points	stdev	2.6	0.01	0.6	1.5	0.03	0.90	0.32	0.10	0.05	0.10	0.20
PHT 14	Matrix	average	54.2	1.10	16.5	13.8	0.26	6.08	4.66	1.36	1.22	0.39	0.53
NAA B-	4 points	stdev	2.3	0.25	1.0	2.9	0.03	0.24	0.73	1.14	0.32		0.30
	Body	average	54.4	0.90	16.1	12.6	0.39	6.10	5.15	1.10	1.52	0.51	0.56
	4 points	stdev	1.6	0.04	0.4	0.7	0.04	0.33	0.27	0.23	0.19		0.18
Furnaces													
PHF 3	Matrix	average	59.1	0.83	17.7	10.3	0.44	5.74	2.74	1.54	1.53	0.36	0.34
No group	8 points	stdev	2.9	0.19	1.4	1.8	0.33	1.71	1.11	0.40	0.49		0.17
	Body	average	62.6	0.96	15.3	10.1	0.20	4.17	2.82	1.17	2.01	0.42	0.30
	1 point	stdev											
PHF 7	Matrix	average	59.3	0.87	19.5	9.5	0.79	3.76	2.32	1.25	2.73		0.29
NAA A	5 points	stdev	2.9	0.23	0.7	1.4	0.90	0.92	0.43	0.40	1.15		0.01
	Body	average	61.8	1.14	16.0	11.4	0.31	3.51	2.32	1.04	1.98		0.31
	1 point	stdev											
PHF 14	Body	average	60.7	0.94	17.1	12.6		4.19	1.84	1.22	0.68		0.36
NAA B	3 points	stdev	1.9	0.04	2.3	0.5		1.19	0.80	0.04	0.09		0.09
	Matrix	average	59.4	0.86	18.6	13.3		3.55	1.75	1.22	0.89		0.25
	3 points	stdev	2.2	0.17	2.9	1.2		0.54	0.59	0.56	0.27		0.07
PHF 16	Matrix	average	53.2	1.34	19.1	14.2	0.31	3.90	2.44	1.43	2.11	1.47	0.26
NAA A	3 points	stdev	1.6	0.37	0.6	1.8	0.07	0.42	0.76	0.94	0.64	0.93	0.06
	Body	average	60.7	1.25	16.2	11.7	0.78	3.38	2.89	0.87	1.81		0.20
	2 points	stdev	1.5	0.03	0.1	0.5	0.62	0.24	0.37	0.30	0.15		0.02
PHF17	Matrix	average	58.8	1.46	18.4	9.1	1.19	3.04	2.07	1.16	4.32		0.62
No group	3 points	stdev	1.2	0.17	1.1	1.0	1.25	1.45	1.00	1.64	0.73		0.24
	Body	average	61.4	1.05	17.4	11.5	0.68	3.08	1.46	1.16	1.69		0.85
	3 points	stdev	3.4	0.09	0.4	2.1		0.95	0.15	0.01	0.13		0.13
PHF 23	Matrix	average	55.6	0.73	17.7	12.2		6.88	4.23	1.04	1.27		0.28
NAA B	4 points	stdev	2.8	0.07	0.7	3.4		1.90	2.76	0.32	0.13		0.08
	Body	average	59.1	0.75	19.9	11.8		3.88	2.78	0.88			0.27
	1 point	stdev											
PHF 25	Matrix	average	58.1	0.87	21.6	11.0	1.08	4.00	1.91	1.53	0.94	0.35	0.15
NAA B	21 points	stdev	3.2	0.44	4.0	3.4	1.59	1.27	0.92	0.80	0.41	0.10	0.11
	Body	average	60.6	0.85	17.8	12.0	0.59	4.84	2.02	1.19	0.91		0.25
	5 points	stdev	2.3	0.06	1.0	0.8	0.36	0.35	0.40	0.28			0.01

The concentrations are given in wt%. The average values and standard deviations correspond to multiple measurements of different areas in the particular samples. Indicated are the particular attribution to the chemical NAA groups and the number of measurements.

enrichment of these elements in Group B. The higher concentrations of As and Sb, usually geochemically rather mobile elements, were noticeable in this context, because these elements are known to be related to pyrite [28].

Apart from the above-mentioned differences, the tuyère fragments presented also a lower chemical variation than the furnace fragments, probably related to their generally finer fabrics in comparison with the furnace fragments. The

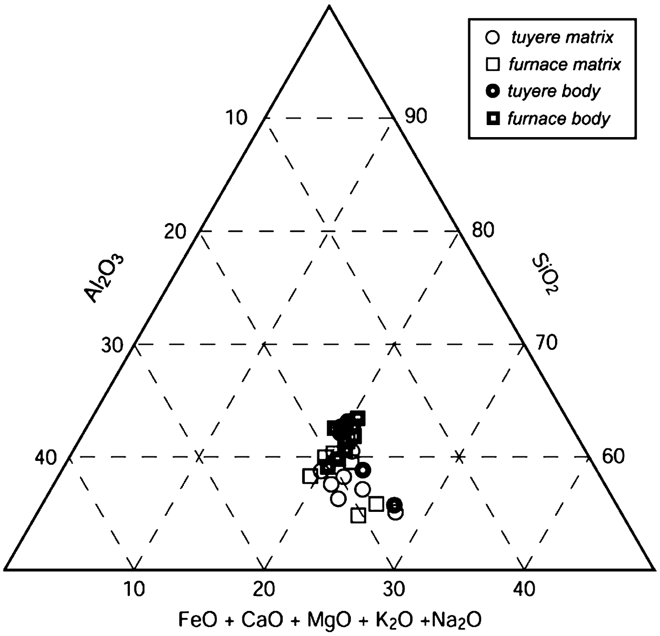

Fig. 11. Ternary diagram showing the major element compositions of the ceramic matrix and ceramic body in the tuyère and furnace fragments.

relatively fine fabric offered the tuyères a level of strength which enabled them to remain intact during the operation. Although both tuyère and furnace material were exposed to high temperatures, the material performance requirements were different. The furnace walls needed just not to collapse during the operation and therefore coarse material with high porosity and extensive crack networks was used for their manufacture. On the other hand tuyère bodies needed to be thinner than furnaces and exhibit enough strength to be handled with ease during the process. Their material, therefore, should be finer in the expense of toughness [14].

A comparison of the measured trace element compositions with reference data indicated the use of local raw materials from the eastern part of the Troodos Mountains, which were supposedly also used for the production of the contemporary White Slip pottery [7,8]. These are typically presenting low concentrations of the alkali metals, Th, U and of the light rare earth elements and relatively high concentrations of Co, Fe and Sc (Table 2). Even though the reference data represent deposits most probably distinct from those used in Politiko-*Phorades*, they showed a general geochemical similarity to the metallurgical ceramics from Politiko-*Phorades* and thus indicated a correlation regarding clay origin.

A similar picture was given by the major element compositions of the samples, which were examined with SEM: low-calcareous ceramics with a relatively high FeO content (Table 3). But the above-described two subgroups were not clearly reflected by SEM-EDS. Apart from seemingly higher FeO concentrations in samples attributed to NAA Group B there were no significant differences. It has to be considered, however, that coarse inclusions, which anyway would not have reacted with the ceramic body, were disregarded. Comparison of matrix compositions and body compositions showed in most cases enhancement of FeO and SiO_2 in the body due to inclusions. The increase of SiO_2, which was expected to reflect mainly the number of quartz inclusions in the body, was on the average approximately 5%, from approximately 55%–58% in the ceramic matrix to approximately over 60% in the ceramic body. As it is demonstrated in Fig. 11, the ratio of SiO_2 and Al_2O_3 to the other oxides was raised and therefore the refractoriness was improved, according to interpretations in former studies of ancient refractories [5,6]. This applied particularly to the furnaces. Nevertheless, mainly due to their high FeO content the ceramics from Politiko-*Phorades* could be classified as relatively low refractory [25]. Fig. 12 presents chemical compositions of Late Bronze Age and Iron Age metallurgical ceramics from the copper smelting site Timna in the Levant [5] and in comparison some Cypriot low calcareous to calcareous Bronze Age ceramics from Kition (Table 3.4 in ref. [17]). A comparison with typical clay compositions [21] indicated that the base clay was an iron rich illite/smectite mixture. Some of these clays are presented in Fig. 12 as well, among others clearly different compositions of kaolinites, or so-called fireclays. These were prevalently used as refractories only in later times [5,6] with the only exception known so far in the ceramics from Timna where they were found as a component [26].

The XRD detected quartz, albite and magnetite as being the most abundant minerals. In samples in which clay minerals were still present, these could be identified as illites or micas and probably montmorillonite, which confirmed the assumptions based on the SEM-EDS results. In general, the content of clay minerals was rather low and they were actually absent in most of the analysed samples due to the high temperatures

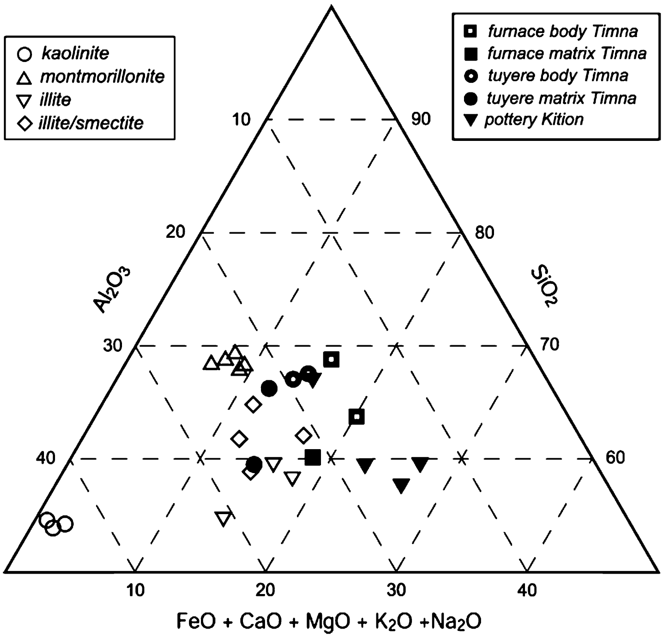

Fig. 12. Ternary diagram showing the major element compositions of comparable ceramics and clays: Presented are metallurgical ceramics from Timna [5], handmade Bronze Age ceramics from Kition (Cyprus) (Table 3.4 in ref. [17]) and typical clay compositions [21].

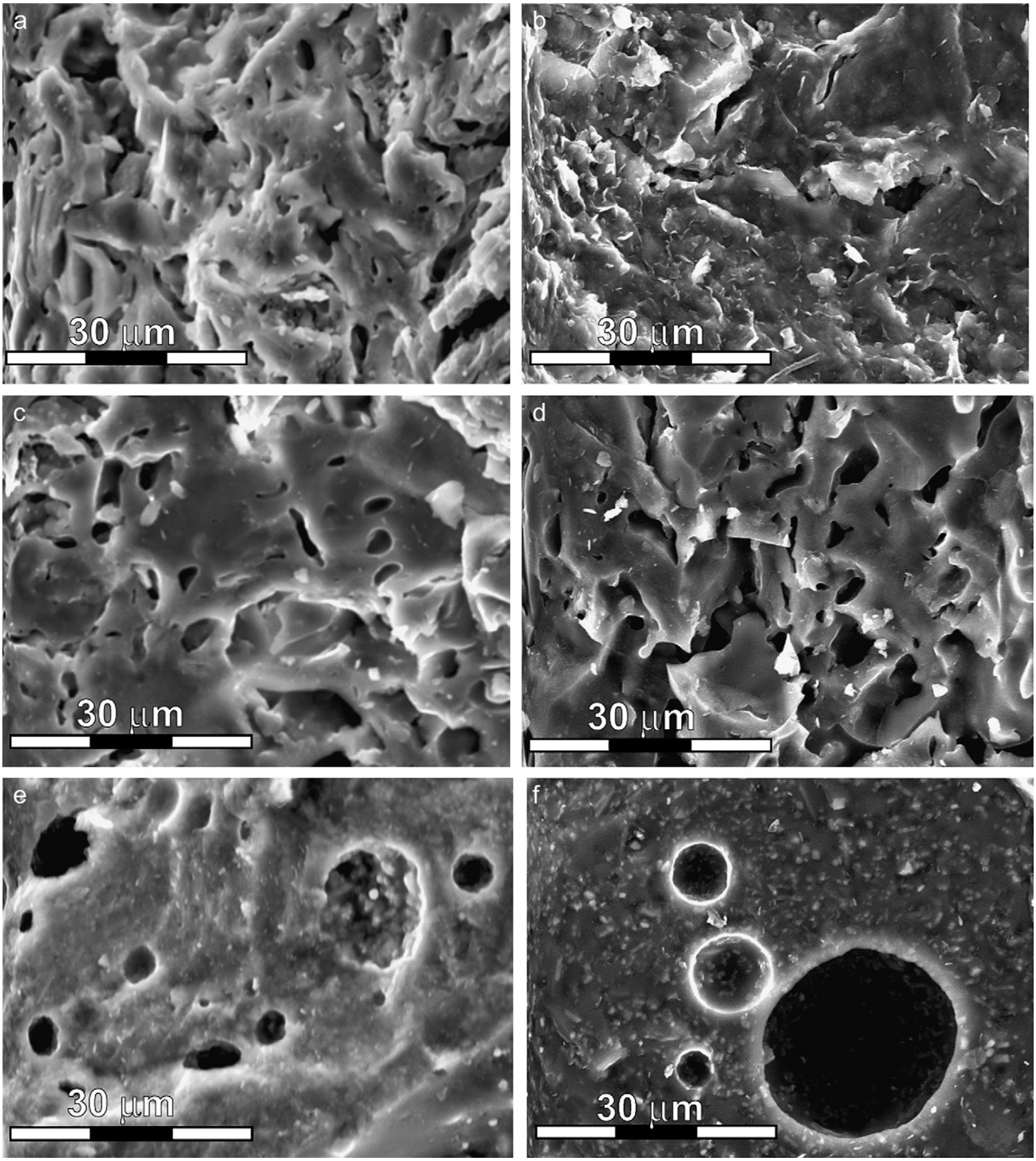

Fig. 13. SEM pictures of fresh fracture surfaces of samples refired in the laboratory with oxidizing (ox.) or reducing (red.) conditions: (a) PHT 6: 950 °C (red.); (b) PHT 11: 950 °C (ox.); (c) PHF 17: 1025 °C (red.); (d) PHF 21: 1100 °C (ox.); (e) PHT 11: 1100 °C (red.); and (f) PHT 11: 1200 °C (ox.).

the ceramics had been exposed to during furnace operation. Instead, these samples presented spinels, such as hercynite, which developed as high temperature phases. XRD of multiple layers confirmed the observation that the temperature gradients in the furnace walls were steeper than in the furnace bases.

In the re-fired samples the observed mineral changes could be set in correlation with selected temperatures, even though for a comparison it had to be considered that the analysed ceramic fragments represented temperature ranges. In view of refractoriness it could be demonstrated that a temperature of 1200 °C must have been already critical for the metallurgical ceramics

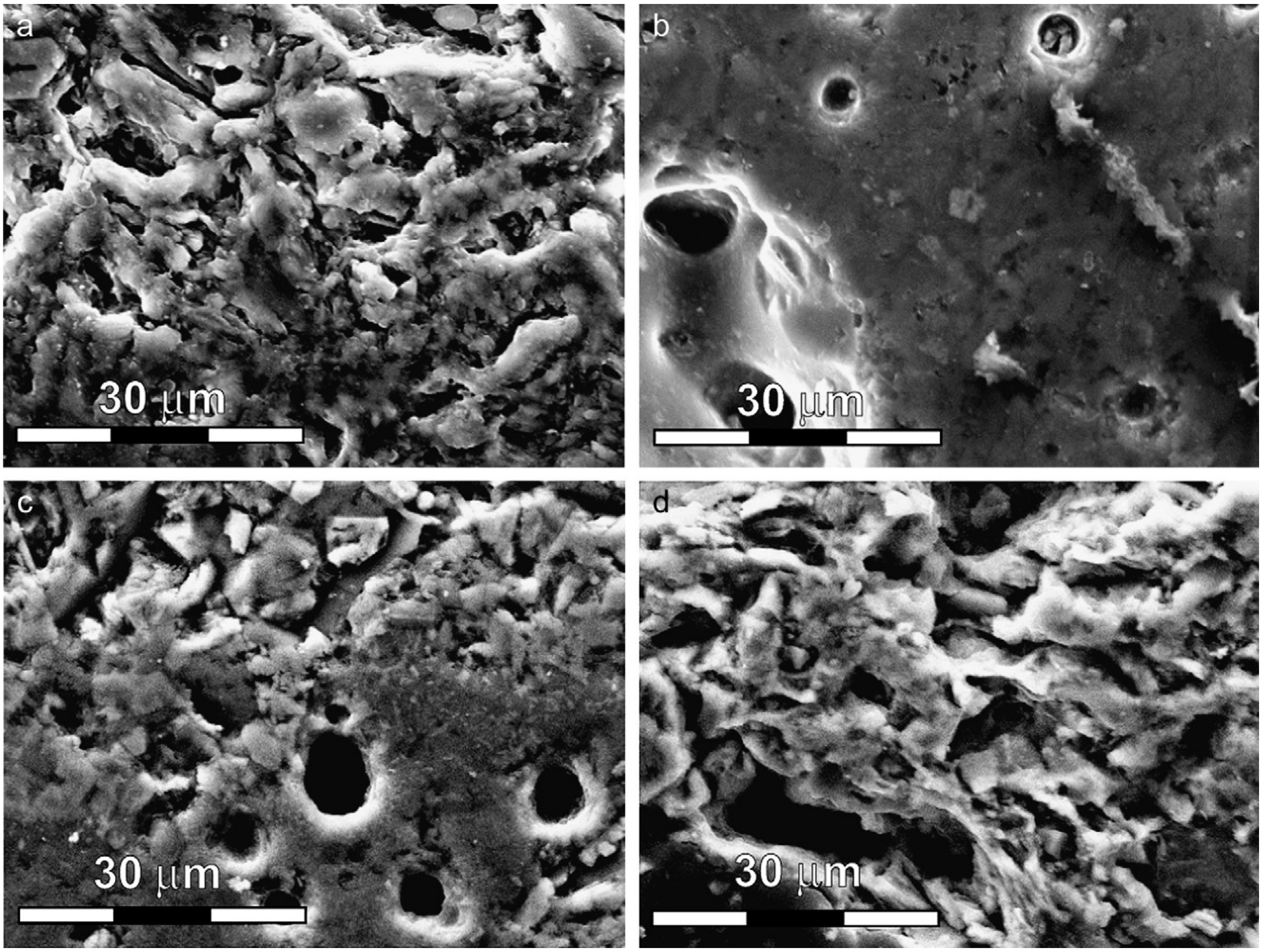

Fig. 14. SEM pictures of polished sections of tuyère fragments: (a) Initial vitrification in the centre of a tuyère fragment; (b) total vitrification in a tuyère tip, covered with slag; (c) Extensive to total vitrification of a tuyère fragment approximately 3 mm below the outer surface, covered with slag; and (d) initial vitrification at the inner surface.

from Politiko-*Phorades*. After being fired for one hour at this temperature, even in oxidizing atmosphere two out of four samples started to melt and to distort. This could be expected to some extent in view of the nature of clay minerals. Finally, a comparison with colour changes, observed in oxidizing and in reducing re-firings, indicated that the furnace walls, which showed only small grey layers at the inner surface, were fired rather in oxidizing conditions, compatible with the assumption that they were freestanding and exposed to air at the outside.

4.3. Vitrification and estimation of firing temperature

In order to estimate the temperatures to which the metallurgical ceramics were exposed to during the smelting process, the microstructures of the ceramic bodies were studied under the SEM. The fresh fracture samples of the refired pieces served as reference samples for transformations in the microstructure (Fig. 13), demonstrating the development of the glassy phase with increasing temperatures until complete vitrification and large bloating pores. Expectedly, the vitrification was slightly more progressed in samples which were fired in reducing atmosphere. Firing under reducing conditions had an effect which corresponded to a temperature difference of not more than 50–100 °C compared to samples fired in oxidizing atmosphere. A remarkable observation was that there was apparently no effect of operation time, because pieces refired with soaking times of 5 h or 10 h showed no significant differences to firings with a soaking time of 1 h.

Apart from areas which obviously were exposed to higher temperatures, the tuyères presented a rather uniform initial vitrification, probably because they were fired before use (Fig. 14a). A tuyère tip covered with slag presented the most progressed state of vitrification. The ceramic body was totally vitrified and bloating pores up to several 10 µm had developed, indicating a temperature of above 1100 °C (Fig. 14b). Another tuyère fragment, which was covered with slag only at its outside, presented different degrees of vitrification along the section. This illustrated the temperature gradient during its use (Fig. 14c,d). A possible reason for a firing of the tuyères before use were higher thermal stresses in comparison to the furnace walls, due to their thinner walls and to the air draft in and out the furnace, respectively.

As for the furnace fragments, the most progressed vitrification was expectedly observed in surface layers covered with

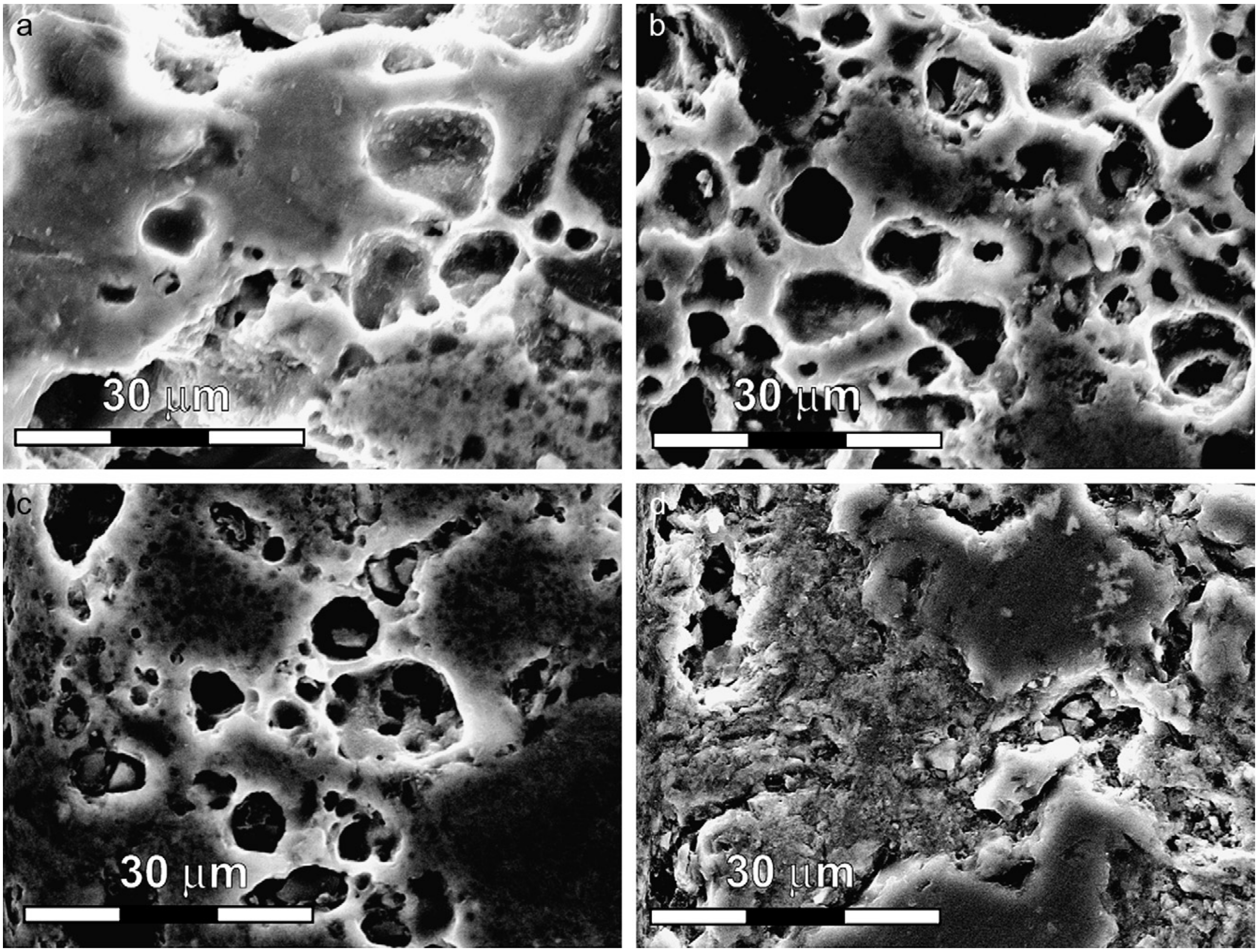

Fig. 15. SEM pictures of the polished section of furnace base fragment PHF 25 in different distances from the surface: (a) 3 mm: total vitrification; (b) 6 mm: extensive vitrification with spherical bloating pores; (c) 14 mm: continuous vitrification; and (d) 24 mm: initial vitrification.

slag. Here, the ceramics were totally vitrified and rounded bloating pores had developed, indicating temperatures above 1100 °C (Fig. 15a). In general, the extension of vitrified layers was larger in furnace base fragments compared to furnace wall fragments (Fig. 15). Assuming stable operation conditions and homogeneous properties of the ceramic body the temperature gradient can be regarded as linear. Hence, the estimated temperatures in different depths should show a constant slope. This would correspond to temperatures of approximately 1200 °C or 1150 °C, respectively, at the surfaces of the furnace bases presented in Fig. 16.

By evaluating these temperature gradients, in principle, apart from the inside temperature also the operation time of the furnace could be estimated. However, because the furnaces from Politiko-*Phorades* were probably freestanding and thus cooled by air from outside, the rather basic approach for estimation of temperature development which was applied on furnace linings in former studies [15,26], was inappropriate in this case. Therefore, a more complex furnace model considering thermal convection was developed and examined with finite element analysis. In the case that the furnace walls were cooled by air, the temperature gradient should have reached equilibrium after approximately 30 min with a stable outside temperature of probably below 800 °C, depending on the wind speed. This is in agreement with the observation of rather small layers of continuous vitrification in the furnace wall fragments. Whereas the temperatures in the furnace bases, which were in contact with the solid ground, should have increased perpetually over the entire furnace operation. The first results of this approach indicated a temperature of approximately 1150–1200 °C at the inside of the furnace base for at least 2 to 3 h, assumedly the minimum operation time [10]. Full account of this study will be presented separately.

On the basis of the degree of vitrification no conclusions could be drawn whether furnaces or tuyères were used more than once. The main reason was, that no significant effect of duration of heat exposure on the degree of vitrification could be detected.

5. Conclusions

The raw materials used for metallurgical ceramics discovered in Politiko-*Phorades* were not exceptionally heat resistant, and apparently they were at least in terms of chemical composition very similar to those used for contemporary pottery production. According to chemical and petrographic

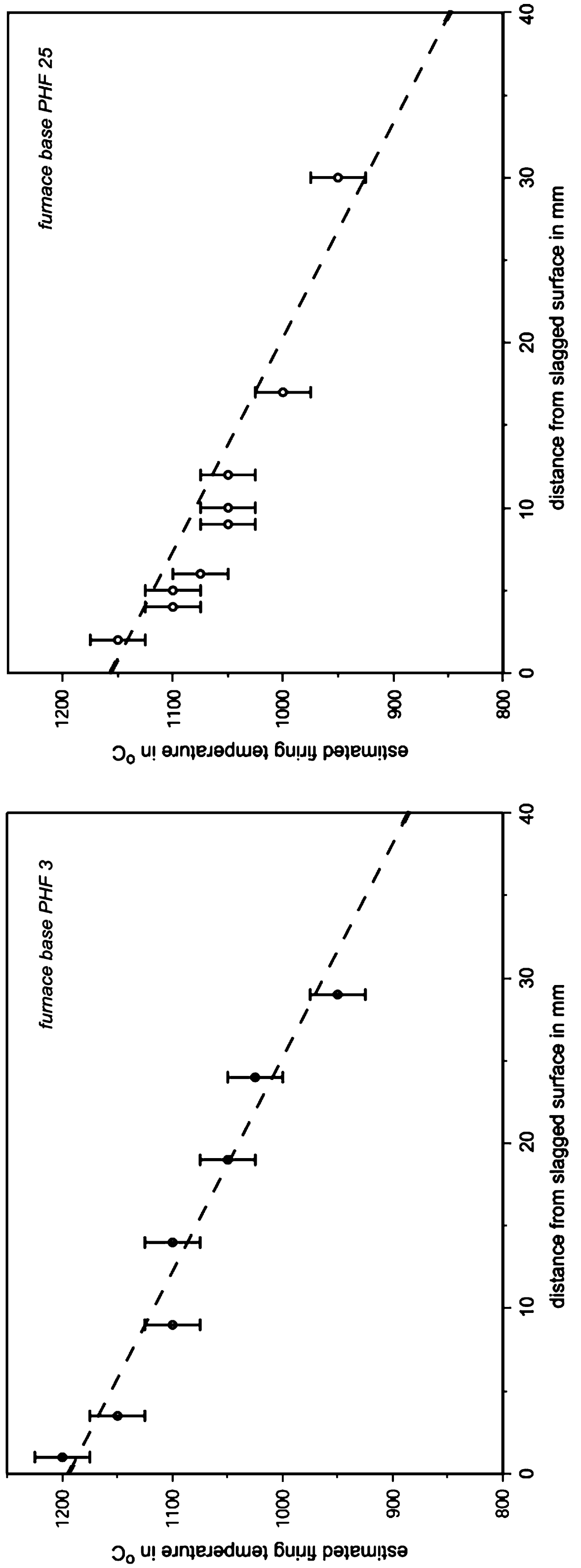

Fig. 16. Temperature gradients in two furnace base fragments based on firing temperatures estimated with SEM examination of the microstructure.

analysis, local clay deposits were exploited. Considerable improvement of the refractoriness was achieved with substantial amounts of coarse non-plastic rock fragments in the clay paste either added as temper or, even more probable, already present in the raw material. Due to their volcanic origin the rock fragments stayed inert during furnace operation and stabilized mechanically the ceramic body. At the same time they were less conductive than for example quartz temper. More important for the thermal properties of the ceramics, however, was their high porosity. The porosity was intentionally generated by incomplete mixing and compression of the clay paste and by adding fibrous organic material which was burning out during operation. Due to the large number of voids and particularly their orientation heat transfer perpendicular to the ceramic surface was clearly reduced and thermal stress suppressed.

As it could be demonstrated in re-firing experiments the actual ceramic matrix should have started to distort at temperatures close to 1200 °C. Therefore the inside of the furnace which was in contact with the smelting load was heavily affected by the heat and started to melt. But due to non-plastic inclusions, wall thickness and suppressed heat transfer the furnace structure remained stable. Also the tuyère tips, which were supposedly reaching right into the combustion zone, were probably starting to melt. But air draft and steep inclination angle prevented them from blocking.

Finally, a considerable standardisation of refractory ceramic production in terms of raw material selection, clay paste processing and moulding was noticed. Obviously, the ceramics were heavily affected by the heat in particular zones of the furnace. Nevertheless, the entire structure of furnace and tuyères was apparently sufficient for matte smelting, utilizing the local copper sulphide ores. The ancient metallurgists were producing copper or matte on a large scale and must have been satisfied with the performance of their ‘refractories’, because there was no evidence of attempts to improve the ceramic production process or to utilize alternative raw materials.

Acknowledgements

Excavation and project were funded by the University of Glasgow, University of Cyprus, Carnegie Trust for Universities of Scotland, American Schools of Oriental Research, the British Academy, Council for British Research in Levant, the Leverhulme Trust, the Arts and Humanities Research Board (Bristol, UK) and INSTAP. The authors would like to thank Y. Bassiakos who helped with discussions over the operation of the furnaces and P.M. Day for a short but fruitful discussion concerning the petrography. G. Vekinis kindly undertook the re-firings in reducing atmosphere.

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