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Crucibles from Palaikastro, East Crete: insights into metallurgical technology in the Aegean Late Bronze Age

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ABSTRACT

The recovery of two groups of crucibles from the Neopalatial and Postpalatial phases of the Bronze Age settlement at Palaikastro on Crete permits the investigation not only into how their fabric was made up, how they were used and what materials they were producing, but also to what extent these matters had changed in the two intervening centuries in the third quarter of the 2nd millennium BC. Though the same resources were tapped by both sets of artisans, different preferences and prevailing habits can be discerned. The Neopalatial set shows a bias towards one non-calcareous clay source, for phyllite inclusions and animal hair tempering; the Postpalatial for a range of clays subjected to a uniform preparation with the addition of sand and vegetal temper. Both preferred to include their fuel within the crucible charge, which was thus heated from the inside, but the Neopalatial craftsmen arguably also used an external heat source. The ability of the Neopalatial artisans to access tin may be reflected in its higher presence then, as opposed to the leaded bronzes visible later.

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1. Introduction

The settlement of Palaikastro, situated on the east coastline of Crete (Fig. 1), is a long-lived town. Its beginnings in the Early Bronze age (Early Minoan I–III) are witnessed by ossuaries and some structures in the area; the present site was developed in the subsequent Protopalatial era (Middle Minoan IB–IIIA). After a fire it was carefully laid out anew in its most prosperous and largest manifestation, lasting through the Neopalatial period (Middle Minoan IIIA to Late Minoan IB). Severely damaged by fire once more, it was resettled in LM II, and continued into LM IIIB, by which time the Palatial life-style had ceased. The town was abandoned at this point; a nearby flat-topped promontory saw a new defensive site established at the end of the Bronze Age in LM IIIC (MacGillivray and Sackett, 1992).

Recent excavations have opened up parts of at least seven houses (MacGillivray et al., 1987–1992, 1998): two have yielded significant groups of debris associated with the melting and casting of bronzes. The two collections provide an excellent opportunity to investigate a central part of the metalworking process, namely crucibles, at times distinct both in chronological terms and potentially in those of the societal workings under which they were produced. The research here reported was undertaken to see if any changes in technological strategies could be detected in the choices and composition of the ceramic fabrics themselves. Changes in design and shape of the crucibles themselves were felt to be too minimal to offer any insight into this matter.

In terms of material properties metallurgical crucibles had to withstand considerable temperatures during their use. For their production clays were preferred: malleable into any form desired, the material was relatively inert at high temperatures. Generally clays used for pottery in antiquity were fired at temperatures of 850°C-1100 °C, above which they distorted. Unfortunately, it is just these higher levels that are necessary for common metallurgical processes. This failing is due to the nature and chemical composition of the commonly utilised raw materials, comprising significant amounts of basic components such as CaO, MgO, K_2O or Na_2O, which start to react at comparatively low temperatures (Noll, 1991).

The refractoriness of ceramics, i.e. the property of withstanding high temperatures, is usually negatively correlated with the proportional fractions of these same basic components present. The situation can be improved by selecting certain clays of 'superior' quality or by tempering with non-plastic and silicate-rich materials, such as quartz. The use of actual fireclays, i.e. kaolinitic clays,

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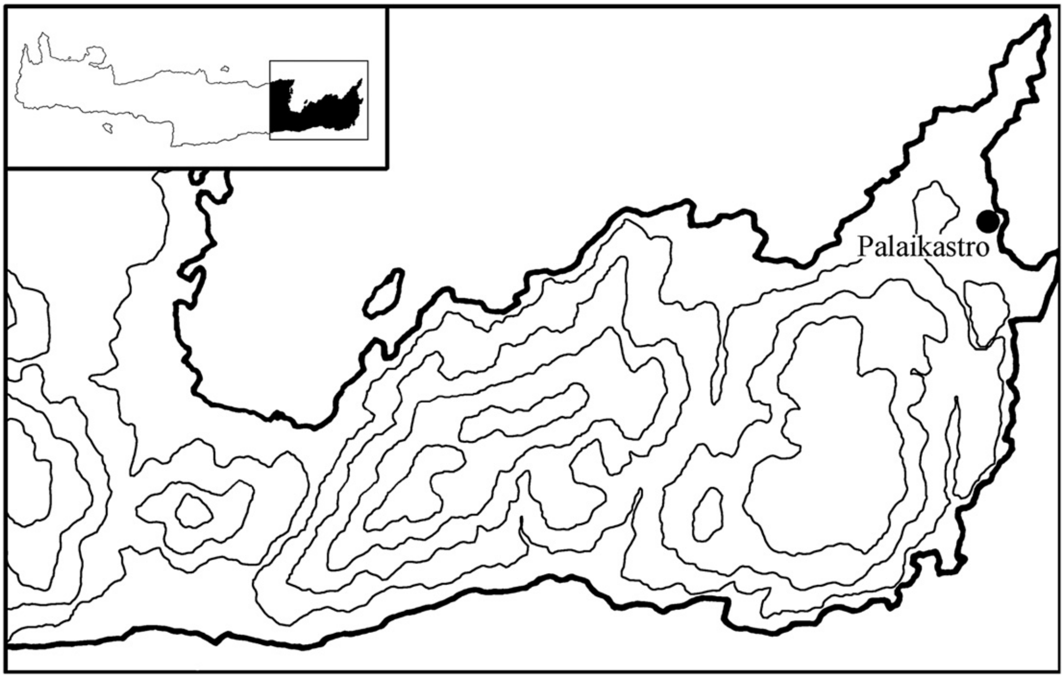

Fig. 1. Map of Crete, showing the position of Palaikastro.

for the fabrication of pyrotechnical ceramics became common only from the Roman period onwards (Freestone and Tite, 1986). Only thenceforward did it become possible to fabricate thin-walled crucibles which could be heated solely from the outside. In the Bronze Age, even though according to recent research also other solutions were followed occasionally (Thornton and Rehren, 2009), a metallurgical crucible was fabricated routinely with rather thick walls and is believed to have been heated preferentially from inside or from above (Freestone, 1989).

As seen too with metallurgical furnaces, the texture of the ceramics used in crucibles usually exhibited a high porosity, intentionally generated both by including organic temper and by specific construction methods. This recipe affected particularly the thermal conductivity of the ceramics in terms of heat insulation and heat efficiency (Hein and Kilikoglou, 2007, in press). Indeed, thin-walled crucibles from later periods, which were fired before use, exhibit fundamentally different thermal properties as they were heated from the outside (Martinón-Torres et al., 2006; Martinón-Torres and Rehren, 2009).

2. The crucibles, their findspots and their position in Cretan practices

The two groups of crucibles excavated at Palaikastro derive from Building 1 (Evely forthcoming) and a spot close to Buildings 5 and 6; these physical locations are indicated on Fig. 2. The earlier context comprises solely crucibles and is associated with LMIA ceramics (c. 1600–1500 BC; firmly Palatial and within the Minoan system) used as filling material in the course of preparing the ground/floors in the construction of Building 1. The later, and broader, set was recovered in a pit, and is associated with pottery from LM IIIB (c. 1330–1200 BC; postpalatial and potentially influenced by mainland habits). Tuyères, crucibles and two sorts of clay mould fragments were located (Hemingway, 1996). Both groups, then, were out of their primary use contexts; the first involves perhaps a dozen crucible specimens at least, whilst the later is smaller with a stated minimum restorable count of three. In fact this present research shows that more were represented in the later set, albeit in a fragmentary form.

In appearance, the earlier group (Fig. 3a) is hemispherical, more or less, with a pulled lip and a channel (aka ‘rocker-groove’) worked up on the exterior at the centre of the very base. Their diameters range between 10 and 20+ cm, with most lying in the 16–18 cm range; their internal heights are a little less than half the diameter as a rule. Their volume extends from around 250 cc up to just over 4000 cc. The later group (Fig. 3b) is based on the same form: they are perhaps a little more ovoid (thanks to the pulling out of the pouring lip) and quite lack the basal channel. Proportionately they are essentially identical to the earlier examples. A full catalogue of the sampled crucible fragments can be found in Appendix I.

The history of crucibles in Bronze Age Crete (and thus to some extent the whole Aegean) can be succinctly summarised as follows, in the light of present knowledge and with some extrapolation from material discovered outside the island.

Recent discoveries of Early Minoan date from Crete would imply that the Platonic ideal for a crucible – namely *a bowl, perhaps with a pouring lip* – might be expected to appear at any time from the Late Neolithic into start of the Bronze Age (Poros, Herakleion: Dimopoulou-Rethemiotaki et al., 2007). Thus, the most persistent crucible type found all over and equally early in Crete is surprising. These, dating mostly from the Early into Middle Bronze Age (3000–1700 BC), are more complex. The bowl is set on a low stem, through which runs a hole, often tapering in size and usually ovoid or square in section (Fig. 3c). They look as if they might be somewhat top-heavy when carrying molten metal. This *pierced-stem* variety very likely owes its presence in Crete to Cycladic connections and influences (Doonan et al., 2007), as the earliest known is from the Aghia Photia cemetery by Siteia (Davaras and Betancourt, 2004). Knossos, Myrtos Pyrgos and Kommos show its successful and widespread continuation (Evely, 2000; Blitzer, 1995). Examples from Gournia and Knossos show that the bowl could be divided across the centre by a thin wall to provide two cells. The form continues to be used into the Neopalatial period, as indicated by the Kommos examples.

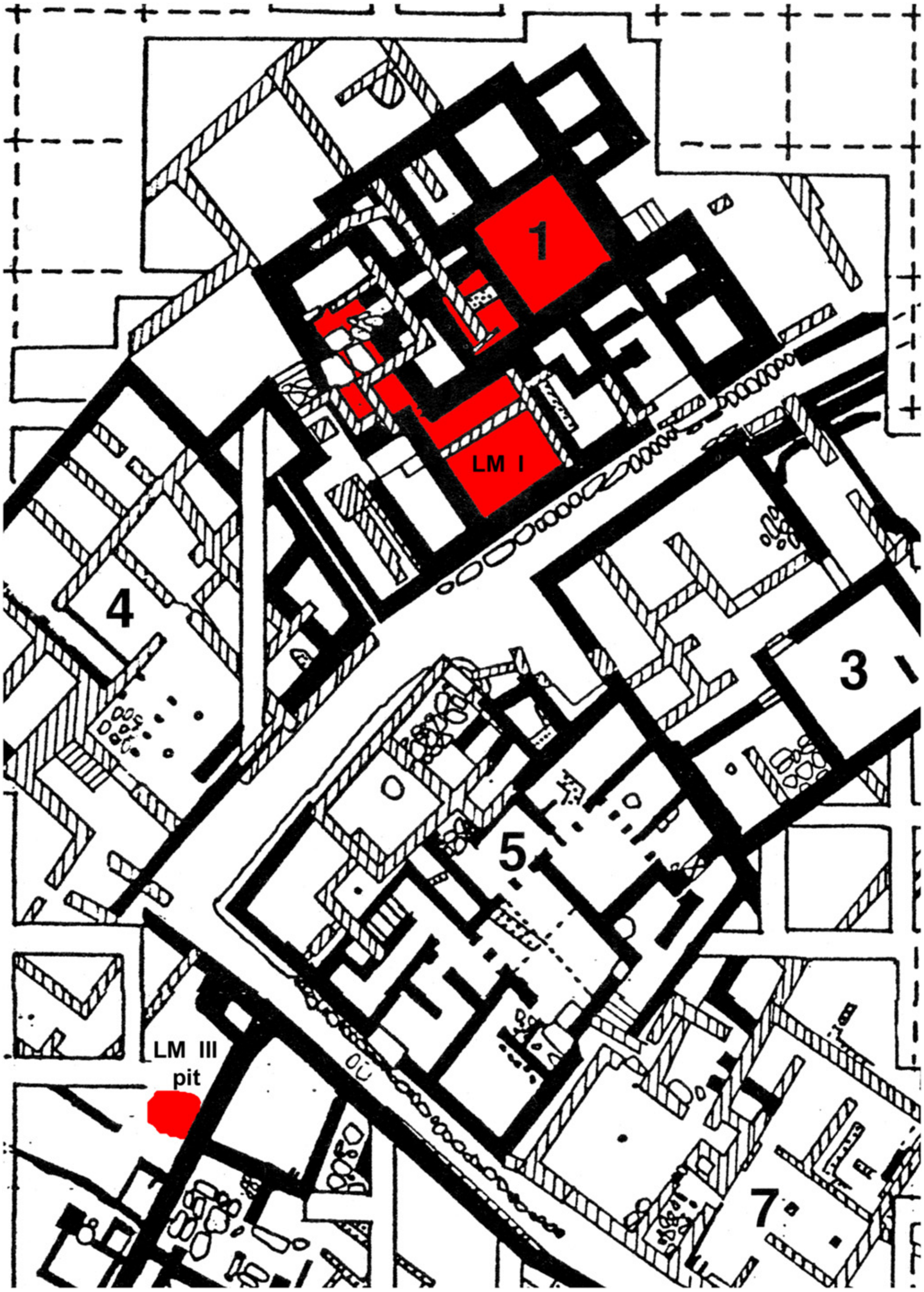

Fig. 2. The position of the two groups of material: the Neopalatial in Building 1 (top) and the Postpalatial in the pit to the south of Buildings 4 and 5 (bottom).

In this light, the LM IA 'rocker-groove' sort at Palaikastro may be seen as a sensible development: by reducing the pierced-stem to a simple groove, the potential danger of accidental spills is probably reduced. The basal groove still permits manipulation from below, in conjunction with the rim. Not yet parallelled elsewhere on Crete, there are comparable pieces from Late Cycladic Kea, which are said to have precedents in the Middle Bronze age of the region (Davis, 1986; Cummer and Schofield, 1984; Blitzer, 1995). A potential Cycladic connection continues.

Finally the groove disappears. Handling will have needed to change somewhat too: perhaps tongs now played a greater role (though one must note the Egyptian use of paired withies: one passing below the crucible, one above). The next Cretan group of note is from the Unexplored Mansion at Knossos (LM II, 1425–1390 BC). Generally these are a vague hemisphere in form – if smaller and shallower now (Catling, 1984). They introduce the bridged spout: the last was probably of assistance in holding back in the pour surface scum and 'dirt' floating on the molten metal's surface (Fig. 3d). Some of the smallest have ledge-handles at the back (i.e. opposite to the spout), ideal for handling by tongs (Fig. 3e). This last and tinier sort was also used to deal with precious metals. (That this account may be overtidy is shown by the existence at Knossos of slightly larger versions of the ledge-handled sort in what seems to be a context dating to around the time of the creation of the First

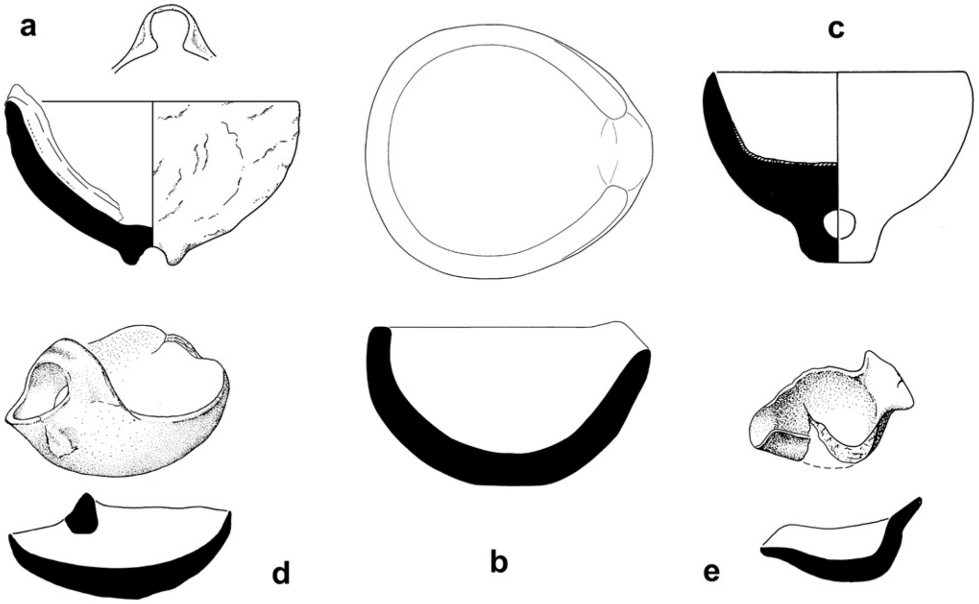

Fig. 3. Crucible types within bronze-age Crete. Not to scale.

Palaces – unpublished; and others towards the end of the same at Malia – Poursat, 1996.)

The second group from Palaikastro date some two centuries later. Their broad resemblance to the first (pace 'rocker-groove') could proclaim some sort of continuing metallurgical traditions here that are not overly effected by introductions and events at the centre of the island, as represented by the Unexplored Mansion crucibles. Certainty is not absolute, though. By LM IIIB one might expect an amalgam of customs to have been more broadly established throughout the island, though it should be remembered that the East was later the domain of the so-called Eteo-Cretans, those considered to be truly native and of older-stock. Perhaps Minoan ways lingered more vigorously there? In the centre, at Malia, by contrast another sort is seen around this time: more rectangular in plan, it has a socket at the narrow end opposite the pouring lip into which a removable handle was slotted to lift it clear of the hearth (Quartier Nu, unpublished). These are seen earlier still off-island.

3. Sample selection

Following provenance work on the metals from LM IA Palaikastro (through Lead Isotope) analysis conducted at Oxford; Evely and Stos, 2004), in which crucible fabrics were touched upon, the present programme of analyses sought to select from among the less well-preserved pieces, so as not to overduly compromise the collection. Preference was given to those with good amounts of the entire wall's thickness present, as well as those with slagged interior. The presence of any Cu prills gave opportunities to investigate the metal alloys being worked. For the LM IIIB group, the better pieces were again targeted: choices were made from within the slighter items, with rim and upper body fragments more heavily represented – probably as better preserved. All have vitrified products inside, and many show the presence of copper/bronze remnants and prills. Six items come from the earlier material (Neopalatial), five from the later (Postpalatial).

4. Analytical approach

The investigation of metallurgical ceramics in general and of crucibles in particular requires an interdisciplinary approach. Parameters related to ceramic technology as well as related to metallurgy have to be considered (Tylecote, 1982). As for their functionality, the chemical analysis of the ceramic matrix usually concerns both the identification of raw materials and also the assessment of the refractoriness (Freestone, 1989; Tite et al., 1990). The microstructure is commonly examined, in order to identify inclusions present in or added to the clay as temper (Hein et al., 2007). In the case of metallurgical ceramics special emphasis is given to identifying remains of organic temper (Oberweiler, 2005) and on examining inclusions and surface layers related to the metallurgical process (Thornton and Rehren, 2009). Finally, the temperature the ceramic was exposed to can be estimated: this commonly varies with the distance from the surface at the heart source. In this way temperature gradients achieved during the metallurgical process can be reconstructed, thus allowing for the estimation of operating conditions (Tite et al., 1990; Hein and Kilikoglou, 2007). Due to the restricted sample number and size, an approach combining thin section petrography and scanning electron microscopy was chosen for the crucibles from Palaikastro. For the technical details of the methods applied, see Appendix II.

5. Results and discussion

5.1. Petrographic fabric groups

The aim of the petrographic analysis was to refine the macroscopic observations on the mineralogical composition of the clay fabrics, investigate the clay recipes for the manufacture of these ceramics and look for possible changes between the LM I and the LM III period. The analysis established the existence of two main fabric groups corresponding to the chronology of the samples. All the specimens were manufactured from coarse, red-firing clays containing large rock fragments, mostly of metamorphic origin. The elongate voids in the clay paste are characteristic of tempering with organic matter. The principal characteristics of the groups are presented below. Full petrographic descriptions are provided in Appendix III.

5.1.1. Fabric group 1

Samples: PK6723, PK4352, PK4406, PK4363, PK4349, PK4337 (Figs. 4 and 5).

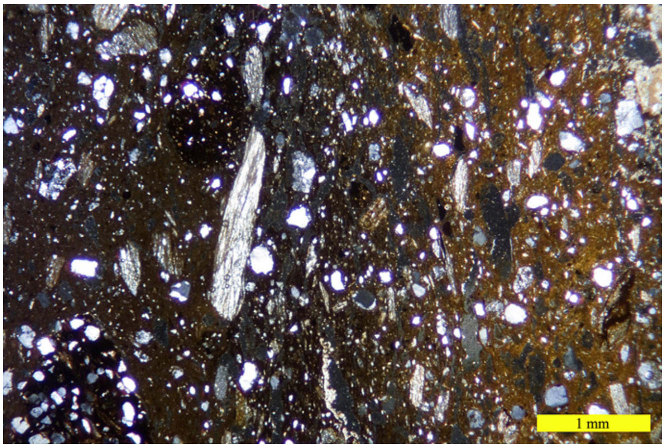

Fig. 4. Fabric group 1 (×25) with metamorphic rocks (phyllite) and small quartz fragments.

This fabric group is characterised by a dark brown, almost black and optically inactive groundmass (in XP). The non-plastic inclusions consist of large fragments of phyllite whose colour ranges from golden-brown to brown and silvery grey, the last being the most frequent. The other non-plastic components consist of few to rare fragments of monocrystalline quartz and some fragments of quartzite/quartzarenite. There are also very few dark brown, almost black textural concentration features. The amount and distribution of the voids present in the fabric are indicative of tempering with organic matter. The porosity in this group reaches ca. 8%. The voids have a planar shape: they are short and elongate, displaying in most cases a preferred orientation parallel to the vessel margins.

The dark colour of the matrix and the absence of optical activity indicate that the crucibles have been subjected to high temperatures. This is also reflected in the vitrification of the matrix which can be restricted to the internal surface of the crucible or can be more widespread in the matrix. Sample PK4352 (Fig. 6) is an example of total vitrification, with large bloating pores across the section, whereas in Sample PK6723 the degree of vitrification diminishes from the inner surface which has bloating pores to the outer surface which is devoid of pores. In most samples the inner surface bears remnants of the metallurgical operations in the form of bright red and/or green concentrations (possibly slag and copper prills respectively).

Sample PK4337 (Fig. 7) is slightly different from the rest of the group; the groundmass is dark red-firing (instead of dark brown/black) and optically inactive. There are areas in the matrix which have a greenish colour and a glassy texture due to the high firing temperature. Unlike a certain variability in the non-plastic inclusions seen in the other samples, this sample is characterised by a golden-brown fine-grained phyllite and lacks the small quartz fragments seen in the other samples. There are only a few quartz and rare polycrystalline quartz/quartzite fragments. The matrix and the inclusions of this sample are reminiscent of the coarse domestic pottery of Palaikastro.

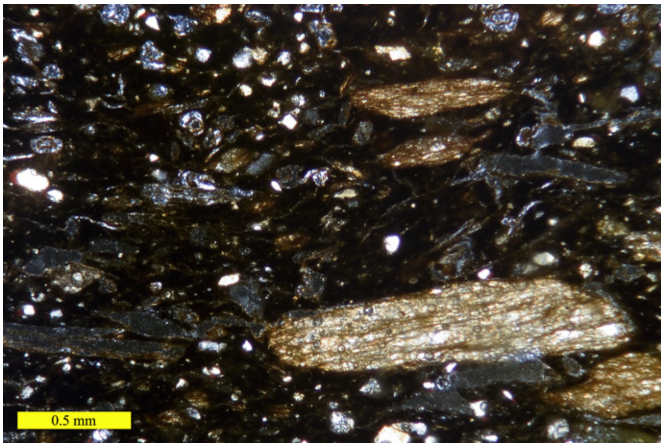

Fig. 5. Fabric group 1 (×50). Note the voids indicative of tempering with organic matter.

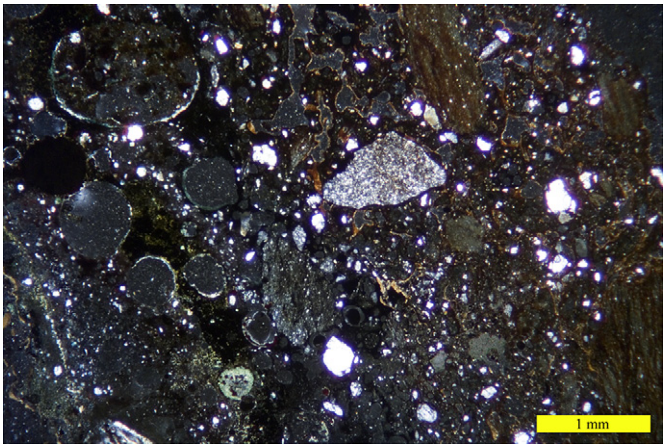

Fig. 6. Sample PK4352 (×25), total vitrification with bloating pores.

5.1.2. Fabric group 2

Samples: PK4627, PK3428, PK4612, PK4614, PK4616 (Figs. 8 and 9).

This fabric group has the same dark brown, almost black and optically inactive groundmass as Fabric group 1. The main difference is the predominance of quartzite/quartzarenite (instead of phyllite) as the main non-plastic component. The other inclusions consist of monocrystalline quartz and very few to rare pieces of chert and siltstone. The quartz occurs in larger fragments than in Fabric group 1, which are more densely packed and evenly distributed in the clay matrix. In this fabric the porosity is higher, ca. 10%, the voids are larger and more irregular: in some cases they are randomly oriented, in others they display preferred orientation parallel to vessel edges. In most cases they are surrounded by a brown and optically active fine-grained crystallitic b-material.

As was the case for Fabric group 1, some samples (PK3428) display different degrees of vitrification from the inner to the outer

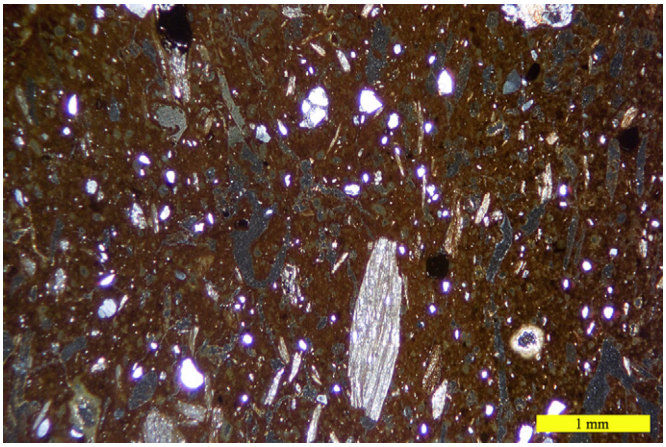

Fig. 7. Sample PK4337 (×25) with metamorphic rocks (phyllite) and very few quartz fragments.

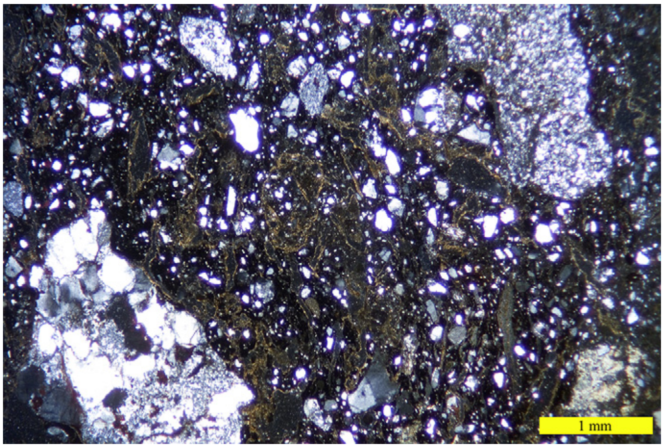

Fig. 8. Fabric group 2 (×25) with characteristic voids and large quartzite fragments.

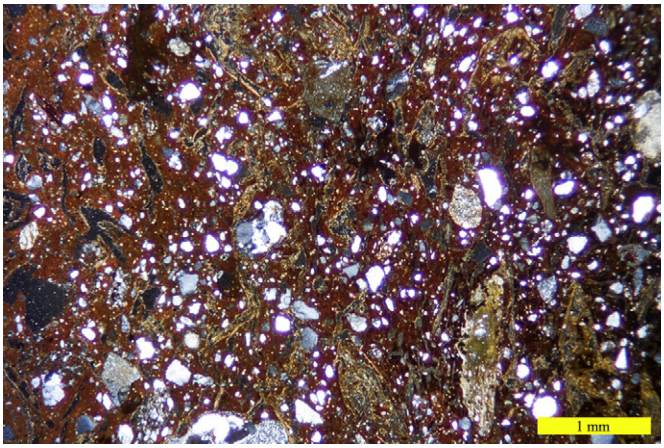

Fig. 10. Sample PK4627 (×25) with red matrix and characteristic voids. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

surface; on their interiors there are also remnants of the metallurgical process, such as copper prills and slag.

5.1.3. *Petrographic loners*

Samples PK4627 and PK4612 bear compositional similarities to Fabric group 2 but were not included in this group because they differ in some of their mineralogical and/or textural properties.

Sample PK4627 (Fig. 10) differs in the colour and porosity of the matrix. Contrary to the dark colour seen in Fabric group 2, the matrix here is red-brown with a dark brown margin, whereas the porosity is higher as indicated by the elongate voids created by the burnt out organics that were added as temper. The voids are surrounded by the brown and optically active crystallitic b-material seen also in Fabric group 2. The groundmass is optically inactive. The main non-plastic component is the large fragments of polycrystalline quartz/quartzite. The other inclusions consist of monocrystalline quartz evenly distributed in the clay matrix, as well as rare fragments of sandstone.

Sample PK4612 (Fig. 11) has the same dark brown and optically inactive matrix encountered in Fabric group 2 but differs in the main type and the granulometry of the inclusions. The non-plastic components have an average size smaller than the samples of Fabric group 2 and they consist mainly of small quartz fragments evenly distributed in the clay matrix. There are only a few fragments of polycrystalline quartz/quartzite (which is the main component in Fabric group 2) as well as a large fragment of mudstone. The large elongate voids are indicative of tempering with organic matter.

5.1.3.1. Comment. The petrographic analysis of the crucibles from Palaikastro led to the establishment of two fabric groups corresponding to the Neopalatial and Postpalatial period respectively. Both groups recognised are characterised by a coarse to semi-coarse, non-calcareous clay paste, in which the predominant non-plastic components are of metamorphic origin. In addition both groups show evidence for extensive tempering with organic material but the shape and distribution of the voids is again different for each group.

The differences between the two groups are mainly textural and lie in the amount and distribution of the non-plastic inclusions as well as the size and shape of the voids. In Fabric group 1 (Neopalatial) the non-plastic inclusions are more heterogeneous (various types of phyllites, quartzites, mono-and polycrystalline quartz), and they are sparsely distributed in the clay matrix. In Fabric group 2 (Postpalatial) the non-plastic inclusions are more homogeneous, they consist almost exclusively of quartzite and small quartz fragments, the latter being densely packed and evenly distributed in the clay matrix. It is likely that they were purposefully added in the clay mix in the form of tempering with sand.

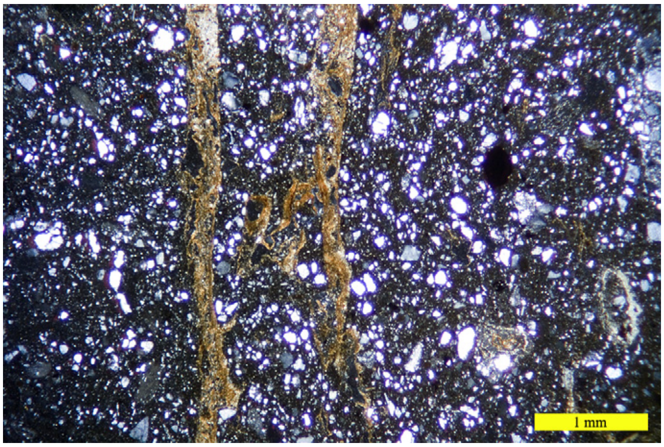

Fig. 9. Fabric group 2 (×25) with characteristic voids and small quartz fragments evenly distributed in the clay matrix.

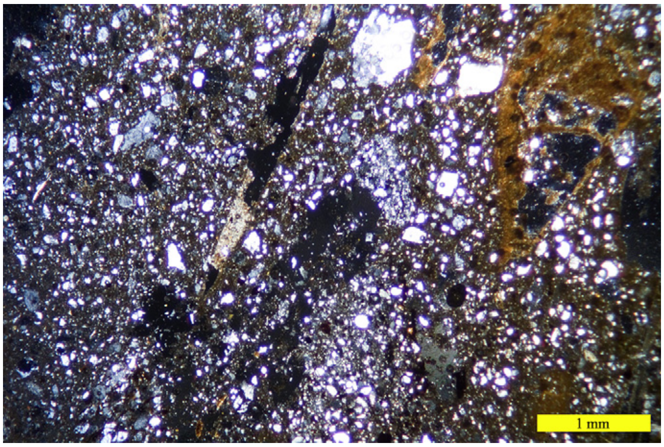

Fig. 11. Sample PK4612 (×25) with small quartz fragments and large void in the centre characteristic of tempering with organic matter.

Another important component of both fabrics is the voids which indicate tempering with organic matter. The percentage of the pores was calculated by optical criteria under the microscope according to the principles set by Kemp (1985) and modified by Whitbread (1995). The size-range of pores considered range from 0.05 to >2 mm. In Fabric group 1 the percentage of the pores is ca. 8%, the voids are smaller, linear and oriented parallel to the vessel margins; in Fabric group 2 the percentage is higher (ca. 10%), the pores are larger, more irregular and randomly oriented, this difference reflecting two different types of added material, probably animal hair and vegetal temper respectively. This observation is in agreement with SEM analysis where a similar patterning of the porosity has been noted, although the porosity estimated by SEM is proportionally higher for both groups because considerably smaller pores are included in the estimation. Similar were the findings of the experimental work carried out by Oberweiler (2005).

The rock and mineral suite present in both fabric groups is in accordance with the geological environment of the broader area of Palaikastro. The metamorphic rocks derive from the Phyllite-Quartzite series outcropping in the area, whereas the non-calcareous based clay is compatible with the alluvial deposits (IGME, 1959) of the Palaikastro plain. Moreover, the composition of the crucible fabrics also matches the pottery encountered in many east Cretan sites and identified as imported from Palaikastro (Nodarou, 2007, 2010).

As to the technology of manufacture, the clay pastes used for the crucibles of the LM III period are different from their earlier counterparts in the use of quartzite instead of phyllite, the addition of sand and the change in the type of organic temper. These changes, although not drastic, seem to result in a more standardised final product.

5.2. Microtexture

All examined fragments presented a rather coarse texture with large non-plastic inclusions and moderately high porosity. The pores and voids, which have been apparently generated by adding organic temper burnt out by a moderate baking (‘curing’ or bisque-firing) before use or during the initial phase of the metallurgical operation, presented a preferred orientation parallel to the surface, especially so in the earlier set (Fig. 12). This kind of texture has been observed before in smelting furnaces and it can be related to the low thermal conductivity of such material which was probably intentionally selected to promote heat insulation (Hein et al., 2007; Hein and Kilikoglou, 2007).

Using image processing of SEM micrographs in backscattering mode, the typical porosity of the crucibles was estimated at 16–20%, with exceptions of the Neopalatial crucibles PK4363 and PK6723, which presented significantly lower porosities of approximately 10–13%, and the Postpalatial crucible PK4614, which presented an average porosity of about 23%. The apparent discrepancy with the above presented porosity estimations based on petrographic examination is due to the consideration of pores and voids down to a minimum size of 78 μm^2, which corresponds to a diameter of 10 μm in the case of round pores. Concerning the nature of organic temper used, apparent differences between the Neopalatial crucibles and the Postpalatial crucibles were confirmed. While the later crucibles were tempered obviously with vegetal material, the majority of the LM I crucibles presented cavities which indicated rather the use of animal hair. These frequent cavities showed a more regular round or oval shape with diameters of c.100 μm (Fig. 13). Apparent differences in total porosity between Neopalatial and Postpalatial crucibles as well as the trend to smaller pore sizes in the fabric of the Neopalatial crucibles must have had an effect on the thermal conductivity of the ceramics, in terms that the heat transfer from the interior of the Postpalatial crucibles into the environment was suppressed more efficiently than in the case of the Neopalatial crucibles (Hein and Kilikoglou, 2007).

In another study of Minoan crucibles from Kommos, Malia and Palaikastro (Oberweiler, 2005), two different types of pore structure were detected, which were individually related to the Neopalatial period and to the Postpalatial period – in similar a manner as to the present study. The descriptions there of the pore structures corresponded well with the observations in the present study, even though the voids in the later crucibles were described as rather non-orientated. Based on experiments and simulating different kinds of organic temper, Oberweiler (2005) came to the postulation that sheep hair was used in the earlier crucibles as organic temper and animal dung in the later.

Another difference noticed between the Neopalatial and the Postpalatial crucibles were the non-plastic inclusions, which were either intentionally added as temper or which were already a natural component of the raw materials. The typical inclusions in the ceramics of the Neopalatial crucibles presented an elongated shape with a size of some 100 μm up to several mm (Fig. 14). The characteristic chemical composition of these inclusions a showed

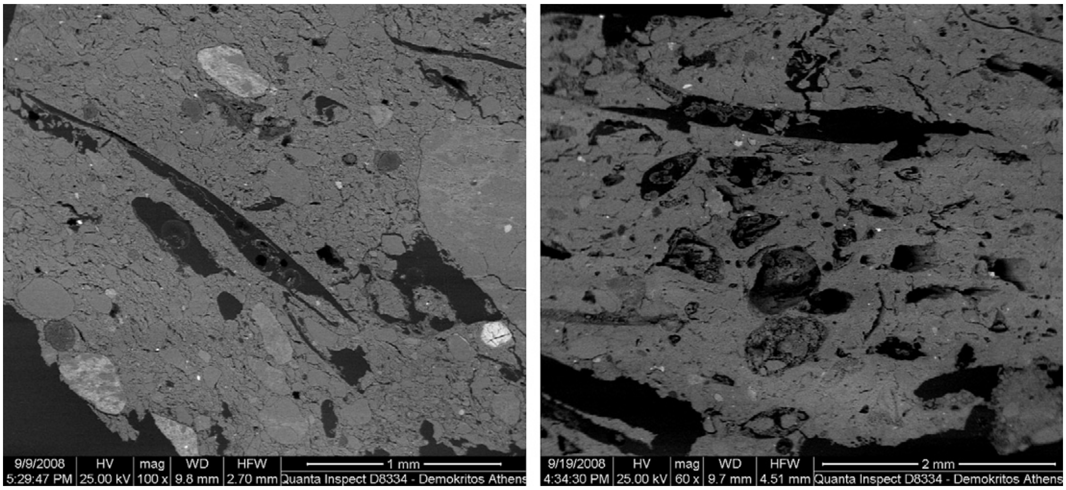

Fig. 12. SEM micrographs in backscattering mode of Sample PK4616 (left) and Sample PK4627 (right). The body exhibits large cavities which are related to burned out organic temper, in this case apparently vegetal fibres.

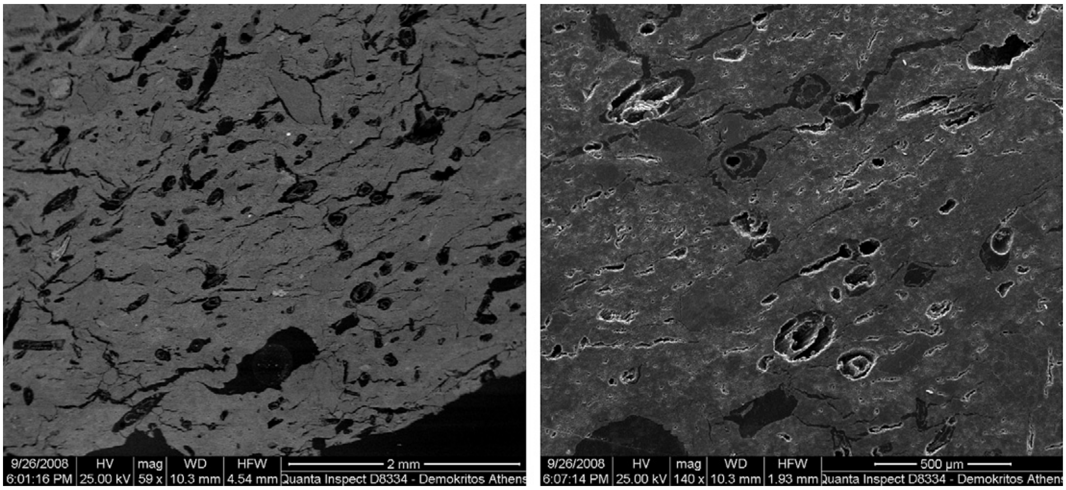

Fig. 13. SEM micrographs of the ceramic body of fragment PK4349 in backscattering mode (left) and in secondary electron mode (right). The texture presents characteristic cavities probably related to burned out animal hair.

a ratio of SiO_2 to Al_2O_3 of c. 3:1 and enhanced concentrations of K_2O: this combination resembles schist or phyllite (Table 1). On the other hand the Postpalatial crucibles presented rather Si-rich inclusions, in most cases quartz but also occasional other rock fragments (Table 1). This observation was in concordance with the petrographic examination and reflects on the definition of the two different fabric groups.

The ceramic texture reflects the metallurgical use of the crucibles. Large bloating pores were visible even to the naked eye at the internal surfaces: evidence for the high temperature processes taking place. In the case of Sample PK4352 the vitrified area ranged over the entire section. Furthermore, the majority of the samples exhibited slag layers at their internal surfaces. Indeed, in some cases slag layers were observed below the actual surface zone, which could indicate the occasional repair or renewal of crucibles with an internal clay lining (Fig. 15). Finally, some of the crucibles presented metal prills incorporated in the ceramic body, which also constitute direct evidence of the specific metallurgical processes they were used for.

5.3. *Chemical bulk composition of the clays*

The bulk analyses of the ceramics indicated various compositions representing, it is assumed, different clays or clay pastes used for the fabrication of the crucibles (Table 2).

The samples showed typically a non-to low calcareous composition with a CaO content of below 3 wt%. The only exception was Sample PK4337, where the main ceramic body presented a higher CaO content of 7.2 ± 0.8 wt%. The calcium was apparently part of the actual clay matrix, while the phyllite inclusions had a clearly lower Ca concentration. The crucible, however, had been covered at its internal surface with a layer of low calcareous clay (CaO: 2.2 ± 0.7 wt%). This layer was apparently applied as a kind of lining either for technological reasons or for repair of the crucible (Fig. 16). As for the specific chemical compositions, Fig. 17 shows a ternary diagram presenting the SiO_2 content, the Al_2O_3 content and the sum of the basic components, which are reacting at relatively low temperatures. Ceramics produced from kaolinitic fireclays would be found for example in the lower left corner of the ternary diagram. The analysed fragments, however, rather correspond to the composition of micaceous clays or illitic clays with high smectite content (Köster and Schwertmann, 1993). The samples can be roughly subdivided in different groups according to their chemical composition.

5.3.1. *Chemical group A*

Samples PK4349, PK4363, PK4406, PK4614, PK6723.

These four fragments of LM I crucibles and one of LM III (PK4614) showed a distinct chemical composition with high

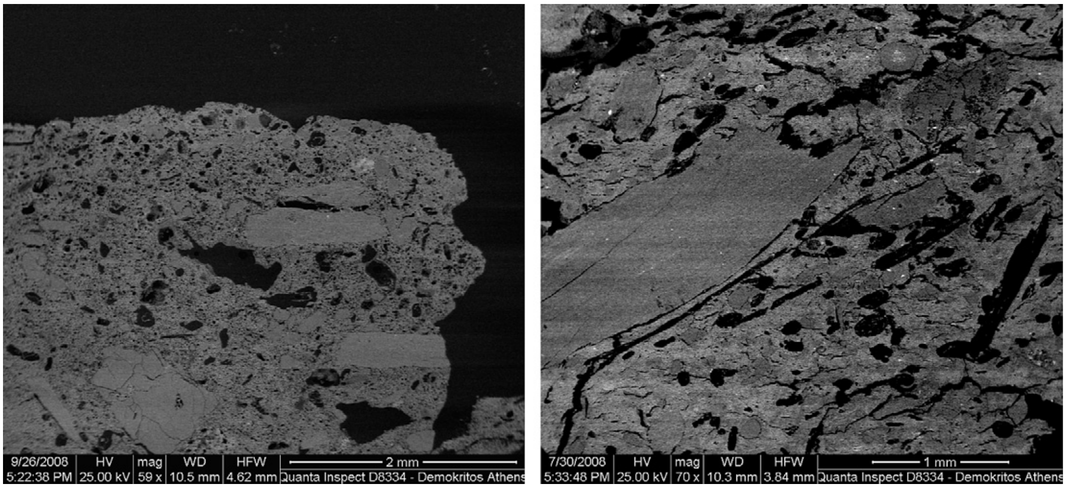

Fig. 14. SEM micrographs of the ceramic body of fragment PK4349 in backscattering mode presenting large elongated inclusions.

Table 1
EDS measurements of typical inclusions in the clay matrix. The numbers in parentheses correspond to the number of individual measurements.

				Na_2O	MgO	Al_2O_3	SiO_2	SO_3	Cl_2O	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CuO
LM I	PK4349	inclusions (6)	*average*		0.7	23.5	67.4	0.3	0.3	2.0	0.4	1.5		3.5	0.4
			stddev		0.4	3.2	2.1	0.2	0.1	0.8	0.1	0.3		1.6	0.1
	PK4363	inclusions (6)	*average*	0.7	0.9	22.1	65.2	0.5	0.3	3.1	0.5	1.4	0.3	4.6	0.4
			stddev	0.2	0.2	3.0	4.5	0.2	0.1	0.7	0.2	0.5	0.1	1.5	0.2
	PK4406	inclusions (3)	*average*		0.4	22.3	69.1	0.5	0.4	1.8	0.38	1.6	0.3	3.0	0.3
			stddev		0.1	5.0	5.6	0.2	0.1	0.6	0.05	0.1	0.1	0.5	0.2
	PK6723	inclusions (4)	*average*	0.9	0.8	19.7	68.7	0.5	0.4	3.2	0.5	1.5	0.3	2.9	0.6
			stddev	0.2	0.1	3.6	5.5	0.3	0.1	0.8	0.1	0.3	0.1	0.3	0.1
LM III	PK4616	inclusions (3)	*average*	0.4	0.5	8.2	81.7	0.2	0.3	1.3	0.4	0.8	0.7	5.3	0.5
			stddev	0.1	0.1	2.7	4.0	0.2	0.1	0.5	0.2	0.4	0.2	3.5	0.1

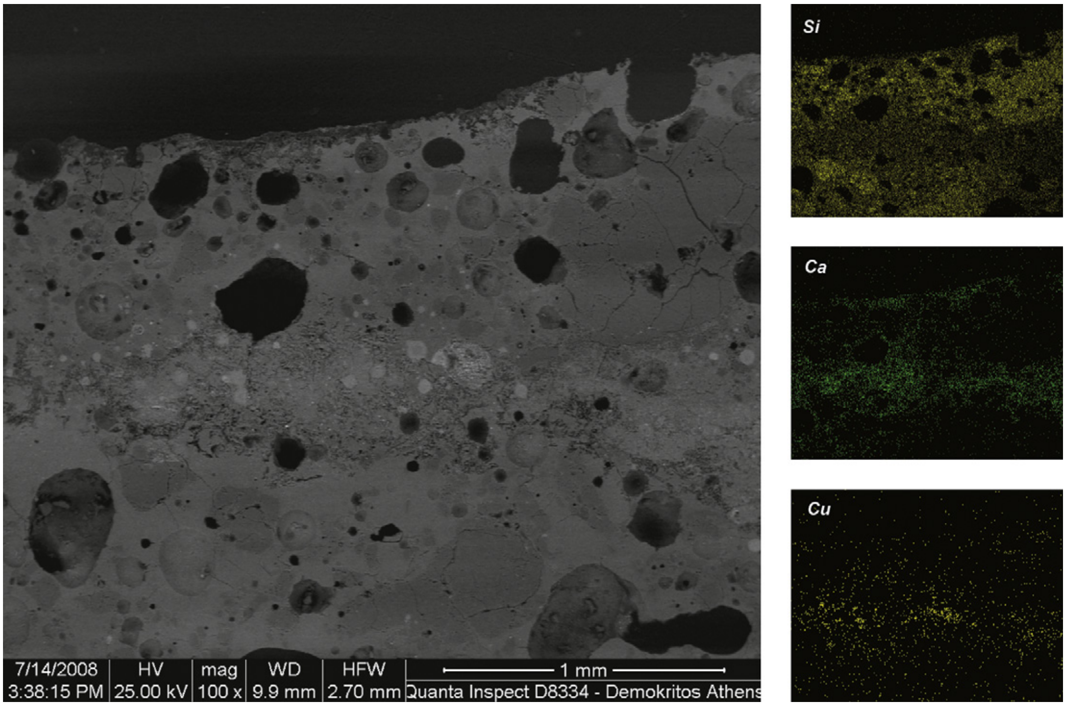

Fig. 15. SEM micrograph in backscattering mode of the internal surface of Sample PK3428 with corresponding element maps for Si, Ca and Cu, with enrichment of the latter two elements indicating slag layers. A copper slag layer can be identified c. 0.5 mm below the actual surface.

Table 2
EDS measurements of the clay body of the examined crucible fragments. The numbers in parentheses correspond to the number of individual measurements.

				Na_2O	MgO	Al_2O_3	SiO_2	SO_3	Cl_2O	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CuO
LM I	PK4337	*clay body (19)*	*average*	1.0	1.5	20.4	57.2		0.3	2.9	7.2	1.2	0.3	7.9	0.3
			stddev	0.4	0.2	1.0	1.5		0.2	0.2	0.8	0.2	0.1	0.6	0.2
		lining (6)	*average*	1.2	1.5	12.5	70.1		0.4	4.2	2.2	1.1	0.3	6.0	0.9
			stddev	0.2	0.4	2.3	3.2		0.2	0.7	0.7	0.3	0.2	1.3	0.3
	PK4349	*clay body (11)*	*average*	0.6	1.4	19.8	62.9	0.5	0.6	2.9	1.2	1.1	0.3	8.6	0.5
			stddev	0.2	0.2	2.2	2.2	0.2	0.2	0.3	0.2	0.2	0.2	0.9	0.2
	PK4352	*clay body (9)*	*average*	1.4	1.9	17.7	61.8	0.3	0.3	3.7	2.4	0.9	0.2	7.9	1.5
			stddev	0.4	0.8	2.7	4.1	0.1	0.1	0.5	1.8	0.1	0.1	2.5	0.7
	PK4363	*clay body (9)*	*average*	0.6	0.9	20.4	64.3	0.4	0.3	2.5	0.9	1.2	0.3	7.6	0.5
			stddev	0.1	0.1	1.4	2.0	0.2	0.1	0.2	0.2	0.1	0.1	0.7	0.2
	PK4406	*clay body (11)*	*average*	0.9	1.1	18.4	67.6	0.4	0.4	2.6	0.9	1.0	0.2	6.5	0.4
			stddev	0.2	0.2	2.0	3.2	0.3	0.2	0.8	0.2	0.2	0.1	0.8	0.2
	PK6723	*clay body (9)*	*average*	1.2	1.4	20.5	61.4	0.4	0.4	3.2	1.2	1.0	0.2	8.2	0.7
			stddev	0.3	0.3	1.3	2.7	0.1	0.1	0.6	0.7	0.2	0.1	1.8	0.4
LM III	PK3428	*clay body (16)*	*average*	2.3	1.2	12.4	70.0	0.5	0.6	3.9	3.0	1.0	0.2	5.7	1.4
			stddev	1.5	0.4	2.8	4.0	0.2	0.2	1.1	1.9	0.2	0.1	1.9	1.4
	PK4612	*clay body (7)*	*average*	0.9	1.4	13.0	68.0	0.3	0.3	2.9	1.5	1.4	0.5	8.6	1.4
			stddev	0.4	0.2	1.5	1.9	0.2	0.1	0.5	0.4	0.2	0.2	0.8	0.7
	PK4614	*clay body (24)*	*average*	0.5	1.3	17.0	67.5	0.4	0.3	2.5	1.2	1.1	0.3	7.6	0.5
			stddev	0.2	0.2	3.1	4.9	0.3	0.1	0.5	0.4	0.2	0.2	1.3	0.2
	PK4616	*clay body (12)*	*average*	0.9	1.7	13.6	70.4	0.4	0.4	2.3	1.7	1.0	0.3	6.5	0.9
			stddev	0.3	0.4	1.7	3.9	0.1	0.2	0.5	0.9	0.2	0.1	1.2	0.9
	PK4627	*clay body (10)*	*average*	0.7	1.1	15.9	64.3	0.2	0.4	3.0	2.2	1.2	0.3	10.0	0.8
			stddev	0.3	0.2	1.5	3.4	0.2	0.1	0.6	0.9	0.2	0.2	1.0	0.5

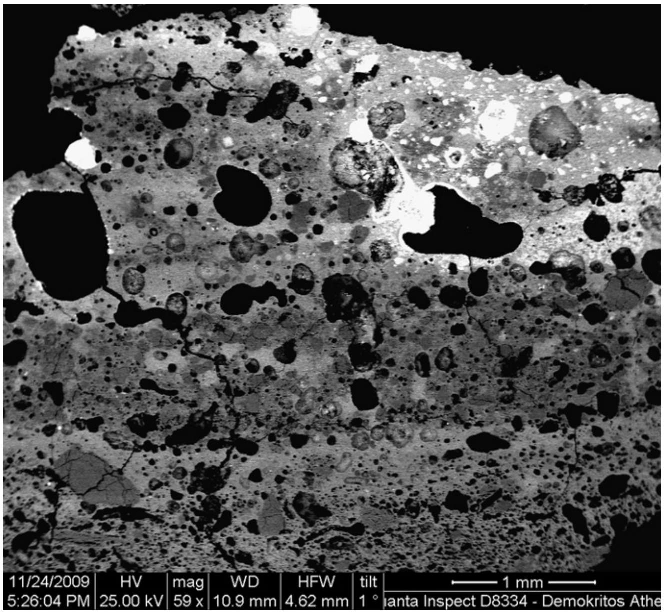

Fig. 16. SEM micrograph in backscattering mode of the internal surface of Sample PK4337. Two layers are distinguishable on top of the calcareous base clay: a) low calcareous lining (c. 1–2 mm, dark) – b). slag layer (c. 1–2 mm, bright).

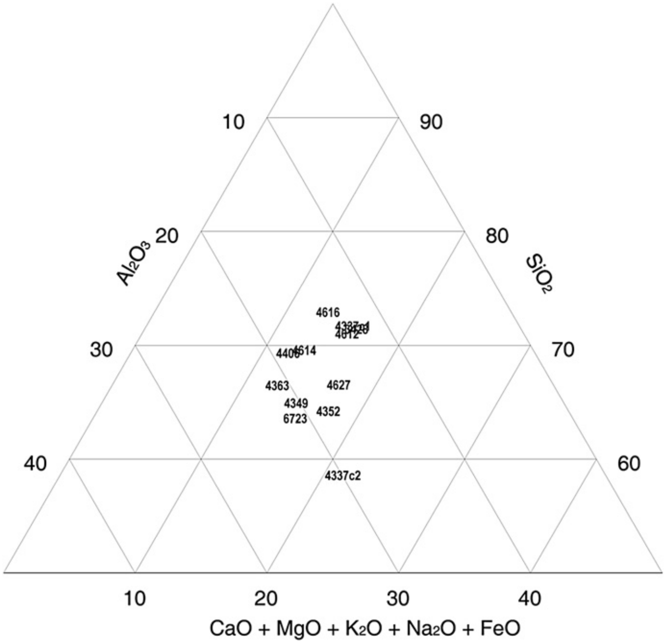

Fig. 17. Ternary diagram presenting the chemical composition of the samples, in terms of SiO_2, Al_2O_3 and the sum of the basic components. The numbers correspond to the sample codes.

aluminium concentrations and relatively low concentrations of silicon, potassium and calcium. According to their chemical composition these ceramics should have better refractory properties than the other samples, due to their relatively low fraction of basic oxides, may be apart from iron. It is noticeable that Samples PK4349, PK4363, PK4406 and PK6723 also presented rather similar non-plastic inclusions.

5.3.2. Chemical group B

Samples PK4612, PK4627.

These two samples from the LM III crucibles were relatively close to Group A, but they showed clearly lower aluminium concentrations and the highest iron concentrations of the analysed samples.

5.3.3. Chemical group C

Samples PK3428, PK4337 C1-lining.

These two samples, PK3428 and the low calcareous clay lining used in PK4337, come from the LM III and LM I sets respectively. They both showed a high silicon composition and also high potassium and calcium contents. On the other hand the aluminium and iron content was rather low.

Samples PK4337 C2, PK4352, PK4616.

The remaining two samples and the Ca-rich clay of the wall proper of PK4337 showed distinctly different compositions. The main variations between them were the aluminium and silicon concentrations. Except for the Ca-rich PK4337 bulk clay, Sample PK4352 showed the highest fraction of basic components with somewhat elevated concentrations of magnesium, potassium, calcium and iron.

5.4. Chemical compositions of slag layers and metal remains

As the study concerned the use as well as the manufacture of the crucibles, slag layers and metal remains wherever identified were analyzed with SEM-EDS. Table 3 presents some typical slag compositions. Almost all the examined slag layers presented copper concentrations in the range of some percent and in some cases also small concentrations of tin. In the case of the two

Table 3
EDS measurements of typical slag compositions found at the internal surfaces of the crucible fragments. In the case of Sample PK4352 also slag layers incorporated in the matrix were analysed. The numbers in parentheses correspond to the number of individual measurements. (1)Values are based on only one measurement.

				Na_2O	MgO	Al_2O_3	SiO_2	Cl_2O	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CuO	As_2O_3	SnO_2	PbO
LM I	PK4337	*slag (4)*	*average*	1.4	2.2	12.7	48.0	0.5	1.8	11.3	.0.8	0.3	12.9	7.2	1.3(1)	1.8(1)	n.d.
			stddev	0.5	0.2	1.7	3.7	0.1	0.8	3.7	0.2	0.1	1.2	6.9			
	PK4352	*slag in body (3)*	*average*	0.8	3.0	12.9	46.5	0.3	1.1	13.3	0.9	0.2	19.3	1.6			
			stddev	0.4	0.5	0.5	0.5	0.0	0.4	3.4	0.3		2.0	0.3			
		slag at surface (3)	*average*	1.8	3.7	7.5	36.2	1.1	0.4	17.6	0.5	0.2	13.0	14.2	0.9(1)	2.5(1)	n.d.
			stddev	0.6	0.5	1.0	4.0	0.6	0.3	2.2	0.1	0.1	2.4	1.8			
	PK4363	*slag (2)*	*average*	0.8	4.0	12.3	46.8	0.3	2.7	27.0	0.8	0.3	4.1	0.5			
			stddev	0.8	2.1	4.4	6.5	0.1	1.5	12.2	0.1		1.0				
	PK6723	*slag (2)*	*average*	2.2	2.7	13.2	46.6	0.3	1.1	14.1	0.7	0.1	6.7	12.0			
			stddev	1.5	0.9	0.4	0.2	0.1	0.7	3.9	0.1	0.1	0.7	4.8			
LM III	PK3428	*slag (4)*	*average*	2.8	3.5	11.7	52.2	0.5	1.9	18.7	0.9	0.2	6.9	5.5			
			stddev	1.2	0.4	0.4	2.5	0.2	1.2	2.0	0.2	0.3	1.7	1.2			
	PK4612	*slag (9)*	*average*	1.7	2.4	5.8	34.5	2.6	1.8	10.6	0.7	0.3	8.1	18.2	n.d.	3.9	9.4
			stddev	0.6	0.6	2.3	6.3	3.5	0.9	2.8	0.2	0.2	5.6	8.2		0.6	2.3
	PK4627	*slag (1)*		0.8	2.1	18.8	53.1	0.6	3.4	5.5	1.6	0.4	9.1	4.5			

Table 4
EDS measurements of copper prills and other metallic inclusions. The numbers in parentheses correspond to the number of individual measurements. In this table elemental concentrations are given instead of oxides because the metallic inclusions are only marginally corroded.

				Si	Cl	Fe	Cu	As	Sn	Pb
LM I	PK4352	*Cu prill (4)*	*ave*	0.6	2.3	n.d.	95.2	0.9	<0.5	<0.5
			stddev	0.3	0.3		0.8	0.2		
		metallic inclusion (3)	*ave*	1.8	0.2	1.3	91.2	0.7	4.5	<0.5
			stddev	0.7		0.3	2.0	0.3	0.7	
LM III	PK4612	*Cu prill 1 (3)*	*ave*	0.6	0.4	0.3	97.0	n.d.	0.7	0.9
			stddev	0.1	0.1	0.1	0.7		0.2	0.4
		Cu prill 2 (3)	*ave*	0.3	0.4	0.9	95.7	n.d.	0.8	1.9
			stddev	0.1	0.1	0.2	0.9		0.3	0.2
	PK4616	*Cu prill (3)*	*ave*	0.4	0.2	0.4	97.5	n.d.	0.3	1.2
			stddev	0.2		0.1	0.1		0.1	0.2
		CuCl (3)	*ave*	0.3	8.9	0.8	86.8	n.d.	1.1	2.2
			stddev	0.1	0.1	0.2	0.9		0.1	0.3

Neopalatial crucibles PK4337 and PK4352 furthermore the iron oxide concentrations were significantly increased in comparison to the ceramic matrix. Notable are finally the increased calcium oxide concentrations and to a lesser extent higher concentrations of sodium and potassium while the silica to alumina ratio remains approximately the same as in the ceramics. Except for the slag layers with the increased iron concentrations the slag compositions indicate a secondary melting process with the calcium enrichment resulting from the absorption of fuel ash (Tylecote, 1982; Georgakopoulou, 2007). However also the enrichment of iron could have been the result of melting using however unrefined copper. In the case of Sample PK4352 as well as the copper rich slag at the internal surface of the crucible fragment areas of iron-rich slag were also analyzed. These appear to be incorporated in the actual clay/ceramic body. Whether they were added intentionally or otherwise during the construction of the crucible or whether they are the remains of earlier use covered with an additional clay lining still has to be clarified. The slag composition of Sample PK4612 was notable in terms of presenting the highest compositions of tin and lead, an indication for the melting or alloying processes this crucible was used for.

Apart from the slags some metallic inclusions were examined. In three fragments (Samples PK4352; PK4612, PK4616) copper prills were determined and analysed (Table 4). Small amounts of tin were detected indicating the processing of bronze. Arsenic seems to be present at least in Sample PK4352. In the case of the Postpalatial crucibles PK4612 and PK4616 also the presence of lead could be certainly confirmed. The chlorine determined in some of the prills is probably related to post-depositional alteration most notable in a copper chloride layer on the internal surface of Sample PK4616. Finally in the internal slag of Sample PK4352 metallic areas were examined which contained as well rather high amounts of tin (Fig. 18). These areas could be the result of an uncompleted process: they demonstrate that a tin-bronze alloy was being sought.

5.5. Study of the temperature gradients

For the study of the degree of vitrification the samples were examined using high magnification (1000× or 2000×) on the prepared sections (Fig. 19). Polished sections usually present a less clear picture of the degree of vitrification compared to fresh fractured samples. Their advantage, however, is that the position of the studied area in the sample can be determined more accurately. This is particularly useful when examining samples like the crucibles, in which a gradient of temperatures is expected in relation to the distance from the internal surface, i.e. the primary expected heat source. The degree of vitrification depends not only on the temperature experienced but also both on the mineralogical composition of the sample and on the environmental conditions in the hearth in terms of oxidizing or reducing atmosphere. Preferably pieces of the sample should be fired or refired under controlled

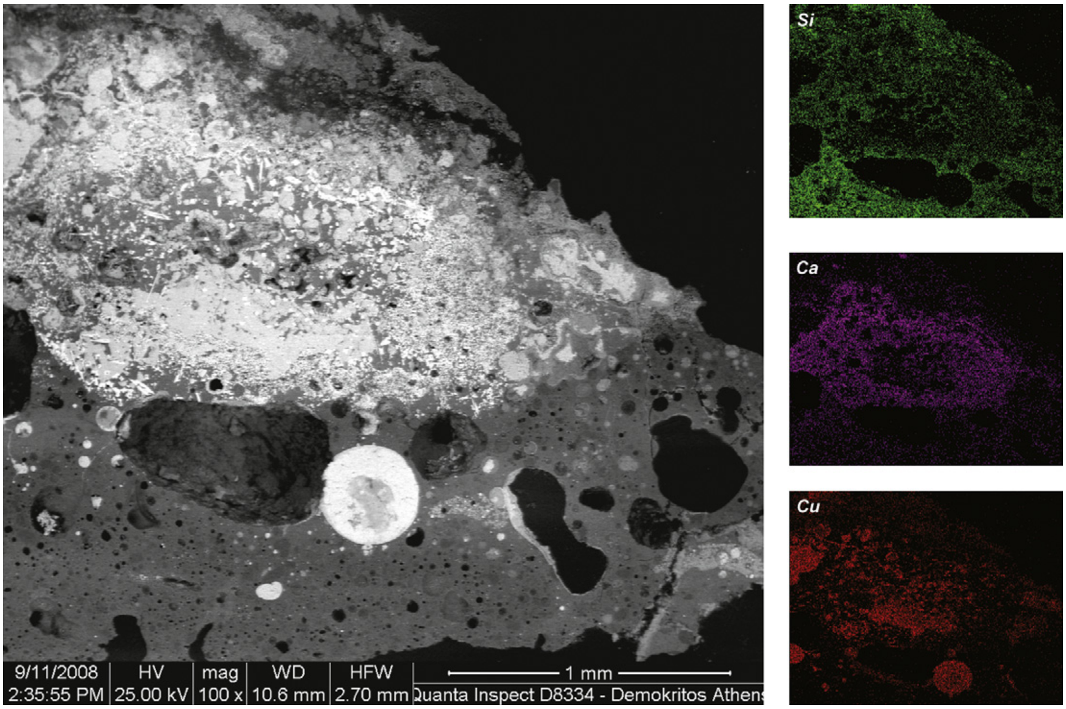

Fig. 18. SEM micrograph in backscattering mode with corresponding element maps of the internal surface of Sample PK4352 presenting a copper prill with a diameter of c. 300 μm and a large metallic inclusions apparently incorporated in a slag layer. While the calcium enrichment again indicates slag layers the copper is enriched even more in the metallic areas.

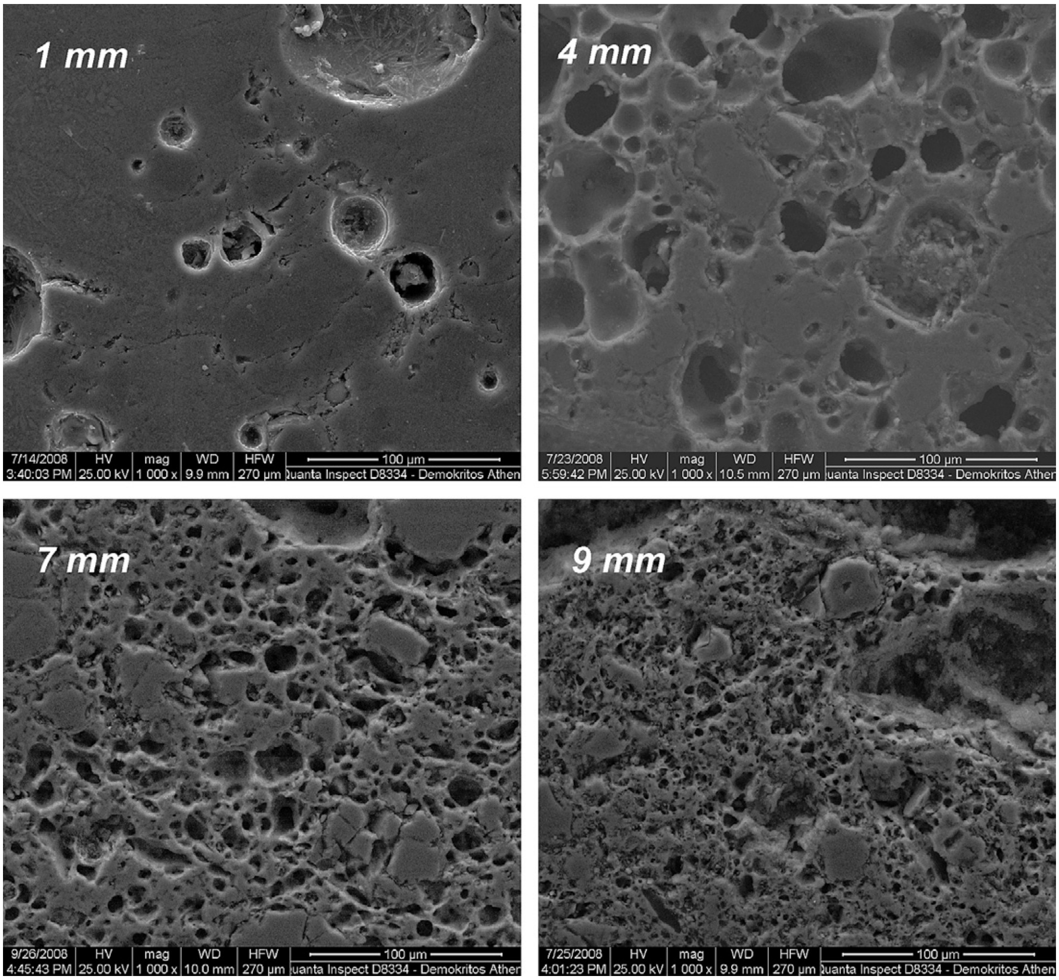

Fig. 19. PK3428: Different degrees of vitrification in increasing distances from the internal surface.

conditions to provide accurate measurements. This procedure, however, was not here possible due to the rather small amounts of material being worked with. Instead, SEM micrographs of non-to low calcareous metallurgical ceramics recorded in a former study in Cyprus were taken as reference for the temperature estimation (Hein et al., 2007).

As a result, it could be confirmed that the samples were all heated from the inside, as they present, apart from Sample PK4352, an increasing drop in temperature the further one gets from the internal surface. Another indication for this was given by the porous ceramic textures, which result in low thermal conductivity of the material and exhibit therefore insulating properties (Hein and Kilikoglou, 2007). As for sample PK4352, the ceramic body presented total vitrification with almost no variation over its entire section, indicating a temperature in the range of 1100–1200 °C. Thus, the sample was either fired before use at an exceptionally high temperature or it was actually and additionally heated from outside. In this context it is also noticeable that the Sample PK4352 had the thinnest wall.

The other samples were examined to identify the regions of total, intermediate, intensive and initial vitrification, correlating the corresponding reference temperatures to their respective distances from the internal surface. Thereby, and assuming a linear temperature gradient, the temperatures at the internal and the external surface during use of the crucibles could be estimated (Table 5).

The remarkable result of this study is that for some samples, particularly those from the Late Minoan I period, the estimated external temperatures were rather high (>800 °C). It can be demonstrated that high temperatures like these at the external surface can be achieved with solely internal firing only if the external surface is attached to a solid material like a clay lining on brick or on stone or is in continuous contact with the floor (Hein and Kilikoglou, 2007). If this is not the case, and certainly enough of the samples are from the higher portion of the crucible (rim and upper body pieces), then such external temperatures can be reached by exposing the crucible to an external heating source. An alternative explanation could be the baking of the crucibles in a fire before use. In this case, however, a more homogeneous degree of

Table 5
Estimated temperatures at the internal and the external surfaces of the crucibles during use. The uncertainty of these estimations is assumedly at least ±50 °C.

		Thickness [mm]	Tin [°C]	Tex [°C]
LM I	PK4337	22	1110	900
	PK4349	21	1110	850
	PK4352	10	1200	1200
	PK4363	16	1120	910
	PK4406	17	1120	800
	PK6723	15	1200	920
LM III	PK3428	21	1230	590
	PK4612	11	1180	930
	PK4614	18	1230	490
	PK4616	24	1180	710
	PK4627	17	1100	600

vitrification across the section might be expected, with the increased levels being found only fairly close to the internal surface as a result of the internal heating there. To answer this question recreation experiments will be needed. Either way the estimated temperature gradients indicate a difference in practice between the LM I period and the LM III period.

6. Conclusions

Excavation at Palaikastro produced two sets of metallurgical ceramics deriving from house debris and dating to the Neopalatial and the Postpalatial period respectively. Although these small assemblages were both out of their original use contexts, 11 crucible fragments were selected for scientific analysis. Using thin section petrography and SEM the technology of manufacture and technological properties of the specific artefacts were examined and potential differences between the two periods were investigated.

In terms of their manufacture both sets are made in low to non-calcareous, coarse/semi-coarse, buff to red-firing clays which compositionally are connected to the Phyllite-Quartzite series of the area of Palaikastro. The clay types themselves – micaceous or illitic (with a high smectite content) – are also quite typical of the alluvial deposits across the Palaikastro plain. All the samples had high porosity due to tempering with organic matter and the large bloating pores. Despite this general homogeneity in the clay recipes there are significant differences between the two groups. The Neopalatial set, represented by petrographic group 1, is characterised by phyllitic rock fragments and a texture with short and regular voids (possibly from animal hair), whereas the chemical composition is rather consistent, indicating a high degree of standardisation in choice and handling of clay. The Postpalatial crucibles, represented by petrographic group 2, are characterised by more densely packed quartzite and quartz fragments and large irregular voids indicating a different kind of organic temper (possibly vegetal matter). The presence of petrographic loners reflects less standardisation in the recipes of manufacture and greater variability in the clay sources used.

Worked up by hand from their clay matrix, the crucibles could be used more than once: successive and distinct layers of vitrification products are discernable. Both sets have examples with five or more such superimposed layers. It has been proposed (Evely, forthcoming) that this re-use was accompanied by fresh relinings of clay, each in turn being converted to 'slag' by the next melting operation. Sample PK4337 indeed has just such a lining identified; PK4352 has apparent slag particles within the fabric (perhaps inclusions accidentally acquired when the crucible was being made in the metalworking area), and others not published here show an unaltered piece of clay trapped between vitrified zones.

The manner of use of the crucibles still leaves room for uncertainty. First – were they fired before use? Second – was the heat source applied solely from *within* by mixing the fuel with the metals inside the crucible, or was this combined with an external source achieved by setting the crucible within a pile of charcoal? The two queries are linked.

Probably the crucibles were fired moderately before use in a kind of 'bisque-firing' or were heated quite slowly in the initial stage of their first use. This preliminary heating had to be done both to remove at least the residual water if not also the molecular water and to burn out the organic temper. The high temperatures estimated for the external surface in the case of the Neopalatial crucibles, however, are probably not related directly to a firing of the crucibles in a potter's kiln before use (the only way to achieve firing temperatures at this level), but rather to the practice of heating the crucibles to achieve the melt simultaneously from outside as well as from within. One practical reason for so doing could be the reduction of the temperature difference between internal and external surface and thus the reduction of thermal stresses in the crucible wall. The case of PK4352 remains anomalous: the vitrification throughout the crucible wall here will need a different explanation. Exposure, be it deliberate or accidental, to a heat source on the outside would be an obvious solution. To further investigate those questions concerning the specific use of the crucibles recreation experiments will be needed.

Lastly, there is the question of what alloys were being produced: though this may reflect just what job in hand was being conducted, rather than any general rule of practice. For the Neopalatial period, high tin-bronzes seem indicated, by the testimony of Sample PK4352: even though the 23%-range is probably distorted by a local enrichment of its presence where sampled. This is to be expected for the time in Crete, though in the case of Palaikastro a lower tin content, and significantly a residual low arsenic presence, has been detected from Lead Isotope-based analyses (Evely and Stos, 2004). Two centuries later the ability to regularly acquire the needful tin and so produce good tin-bronze was not so readily achieved: at Palaikastro the tin levels have dropped to but 1% or so, the arsenic is still present at up to 2%, and significantly perhaps lead at 2–3% ranges is now introduced.

In recent studies comparing metallurgical ceramics of these periods from Crete (Hakulin, 2004, 2008; Oberweiler, 2005) it has been suggested that the shape, the context, and most important, the technology of metal production changed considerably after the collapse of the palatial society. The earlier crucibles are often directly related to the palaces, though they are often encountered in settlements; metal production at the palatial centres may be more standardised, the result of the higher demand there for tools, weapons, and luxury items, and a greater access to copper and tin. After the destruction of the final palaces in LM IIIA2/B surviving metal artefacts are encountered more frequently in tombs; production becomes less and less standardised, while the practice of metal recycling becomes more widespread. At Palaikastro the changes from one period to the other are more subtle but still visible. The shapes of the crucibles and their chemical compositions do not vary greatly from one period to the other but there is difference in the raw materials. The techniques used for their manufactured are reflected in the two main petrographic groups and in the selection of similar but not exactly the same local raw materials. Moreover, the degree of standardisation is higher in the earlier examples and the temperatures reached in the melting process seem also to be higher.

Not much can be said about the type of the metal objects produced, even less about the identity of the people who worked metal at Palaikastro, on the basis of a few metallurgical ceramics found outside their original context. However, it seems that there is no abrupt change in the craft and that in the area of Palaikastro there was an established knowledge of metalworking lasting for at least two centuries.

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Appendix I

Catalogue of sampled material

(a) from LMIA contexts in Building 1.

PK6723 basal groove: orange-beige clay, semi-fine. Fragment of base with groove. Hpres. 4.5; 9 × 5.2; Th 1.4–1.9, with groove 2.7. Little true vitrification, but much affected by reducing atmosphere. 7534.

PK4352 hemispherical: fabric as above. Fragment, from wall and base. Up to 5.1 × 4.7; Th 1.1–1.9. Exterior has a finer added layer (Th 1 mm), over grey reduced surface. Interior covered with residue, one layer (Th c. 1 mm); grey-black, gassy. Occasional oxydized Cu presence and prill. 7550.

PK4406 residue with minimal wall of crucible preserved; grey-greeny slag, with bloating pores. Fragment. 2 × 1.7; Th 0.2. 2553.

PK4363 hemispherical: fabric as above, voids from considerable organic matter. Rim to lower wall fragment. Hpres 7.9; Wpres. 6.2; Diam.rim 15–16; Th 2.5. Exterior uneven and reduced; Interior blackened but no residue. 7550.

PK4349 hemispherical: fabric as above, much stone and voids from considerable organic matter. Rim and wall fragment. Hpres. 7; Wpres. 8.4; Diam.rim c.25; Th 2.9. Exterior smooth and uneven, reduced grey; Interior similar. 7554.

PK4337 hemispherical: fabric as above. Lower wall/base fragment 6.1 × 5.8; Th 1.2–2.4. Exterior smoothed; Interior has much residue, two or three layers (up to 8 mm thick); black, with bloating pores. Several oxydized Cu areas and prills. 7150.

(b) LM IIIB pit context, south of Building 5.

PK4627 hemispherical: red-orange fabric, coarse. Body fragment. 6.3; Th 2.5. Thick internal layer of green-yellow slag. Cu prills adhere. 3407.

PK3428 hemispherical: fabric as above, with white and black inclusions. Wall fragment. 11.4 × 9.8; Th 2.6. Interior has grey-green slag. Analysis by XRF (BradfordUniversity): little Sn, little Pb, a trace As – a low lead-bronze. 3407.

PK4612 hemispherical: fabric as above. Rim fragment. 9.2 × 4.1; Th 3.2–1.8. Interior with residue and Cu prills. Analysis by XRF (BradfordUniversity): some Sn, much Pb, a little As – a lead-bronze. 3408.

PK4614 hemispherical: fabric as above. Rim fragment. 5 × 4.3; Th 1.6. Interior has red-yellow slag, with Cu (?)prills visible. 3406.

PK4616 hemispherical: fabric as above. Rim and ?spout fragment. 6 × 4.3; Th 2.8–0.8. Interior has uneven layer of grey-yellow-green slag, traces of exposure to heat and very small Cu (?) prills. 3408.

Appendix II

Methodology of the analytical approach

The methods applied in the investigation of the metallurgical ceramics from Palaikastro are thin section petrography and scanning electron microscopy.

1. Petrographic examination

The selected crucible fragments were analyzed by thin section petrography on a Leica DMLP polarizing microscope using magnifications ranging from ×25 to ×100.

2. Scanning electron microscopy (SEM)

The eleven crucible fragments were examined under an FEI, Quanta Inspect D8334 scanning electron microscope, coupled with an attached energy-dispersive X-ray spectrometer (SEM-EDS). While the microstructural examination was focused on the characterization of the ceramics' texture and the degree of vitrification in different regions of the crucibles, the microanalysis concerned the elemental composition of the ceramics and the identification of inclusions and remains related to the metallurgical process. Cross-sections of the samples were prepared by cutting them perpendicularly to their surfaces. The sections were embedded in epoxy resin, and then ground and polished. After examination under the optical microscope the polished sections were carbon-coated for SEM analysis. Under the SEM the fragments were examined over the whole cross section both in secondary electron mode and in backscattering mode. The pore structure and the distribution of coarse inclusions were of particular concern because these textural parameters are known to affect the material properties of the ceramics, such as strength or thermal conductivity (Hein et al., 2007). Then, using higher magnification, the microstructure was analysed in terms of the degree of vitrification, i.e. the development of the glassy phase. In this way the temperatures to which the ceramics were exposed to during their use could be estimated, at different distances from their inner surfaces. Along the sections temperature profiles were compiled, which were expected to provide information about the operating conditions. Using SEM-EDS the bulk composition of the ceramic body was also explored. Arbitrary areas in the range of $100 \times 100°\mu m^2$ to $1 \times 1\ mm^2$ were selected in the polished sections and analysed for approximately 100 s. On the basis of the bulk compositions the raw materials used for the crucible production could be characterised, revealing also possible correlations between specific fragments. Microchemical analysis was applied, furthermore, in order to identify specific inclusions and to examine remains of the metallurgical process, such as slag layers or metal prills incorporated in the ceramic body.

3. Technological assessment

Based on the temperatures, as estimated by SEM, to which the ceramics were apparently exposed to during their use, the operating conditions of the crucibles were assessed. In this approach computer models were used which have been developed for the technological assessment of smelting furnaces (Hein and Kilikoglou, 2007). A basic assumption is the effectual homogeneity of the material in terms of thermal properties so that temperature gradients can be presumed as linear.

Appendix III

Petrographic descriptions

The descriptions follow the system introduced by I. K. Whitbread (1995). The following abbreviations are used: a: angular, r: rounded, sa: subangular, sr: subrounded, wr: well rounded, tcf's: textural concentration features, PPL: plane polarised light, XP: cross polarised light.

Fabric group 1

Samples: PK6723, PK4352, PK4406, PK4363, PK4349, PK4337.

Microstructure

Few meso- and macro-planar voids, very few meso-vughs, single-spaced. The planar voids display preferred orientation parallel to vessel margins. The non-plastic inclusions are in general randomly oriented but the phyllites have in some cases a crudely developed long axis parallel to vessels margins. There is limited evidence for tempering with organic matter. Presence of secondary calcite.

Groundmass

Homogeneous throughout the section. The colour is dark grey in PPL ($\times 50$) and dark brown to black in XP. The micromass is optically inactive. In some cases the margins are darker and with many bloating pores probably due to the contact with the hot metal.

Inclusions

c:f:v $_{10\ \mu m} = 30:62:8$.
Coarse fraction: 3.6–0.1 mm long diameter.
Fine fraction: <0.1 mm long diameter.

The matrix is rather fine with poorly sorted inclusions and bimodal grain-size distribution. The size of the coarse fraction ranges from granules to very fine sand. The fine fraction is of very fine sand and below. The packing of the coarse fraction is single- to double-spaced, that of the fine fraction is double- to open-spaced. It is matrix supported (wackestone texture).

Coarse fraction
Dominant: Metamorphic rock fragments, mainly phyllite, elongate, fine-grained, composed of biotite mica and quartz. The colour ranges from golden-brown to brown and silvery grey (in XP). Size: 3.6–0.24 mm long diameter. Monocrystalline quartz, equant, sa, evenly distributed in the clay matrix. Mode: 0.16 mm long diameter. Size: 0.64–0.1 mm long diameter.
Few: Quartzite/quartzarenite fragments in some cases ranging into quartzite-schist, equant, sa. Size: 1.3–0.2 mm long diameter.
Rare: Polycrystalline quartz, equant, sa. Size: 0.4–0.16 mm long diameter.

Fine fraction

Dominant: Monocrystalline quartz.
Few: Phyllite fragments.
Rare: Biotite mica laths.
Very rare to absent: Epidote.

Textural concentration features

In this fabric group there are very few to rare tcf's. They are equant, sr, dark brown to black and discordant with the micromass. The smaller fragments do not contain any inclusions, the larger ones contain small quartz inclusions. Size: 1.6–<0.1 mm long diameter.

Fabric group 2

Samples: PK4627, PK3428, PK4612, PK4614, PK4616.

Microstructure

Few to common meso, macro and rare mega planar voids, and channels. The voids are in some cases randomly oriented, in others they display preferred orientation parallel to vessel margins. They seem to follow flow lines and they are filled with secondary calcite. The non-plastic inclusions are randomly oriented. Evidence for organic tempering.

Groundmass

Homogeneous throughout the section. The colour is grey brown in PPL (x50) and black in XP. The micromass is optically inactive.

Inclusions

c:f:v $_{10\ \mu m} = 25:65:10$.
Coarse fraction: 2.8–0.1 mm long diameter.
Fine fraction: <0.1 mm long diameter.

The matrix is fine with poorly sorted inclusions and bimodal grain-size distribution. The size of the coarse fraction ranges from granules to very fine sand. The fine fraction is of very fine sand and below. The packing of the coarse fraction is close to single-spaced, that of the fine fraction is single- to double- -spaced. It is matrix supported (wackestone texture).

Coarse fraction

Predominant: Monocrystalline quartz, equant, a-sa. Mode: 0.16 mm long diameter. Size: 1.6–0.1 mm long diameter.

Frequent: Quartzite/quartarenite, equant to elongate. Size: 2.4–0.4 mm long diameter.
Very few: Polycrystalline quartz/chert, equant, sa. Size: 2.4–0.2 mm long diameter.
Rare to absent: Siltstone, elongate, dark brown, very fine-grained. Size: 2.8 mm long diameter. Micritic limestone. Mode: 0.8 mm long diameter.

Fine fraction

Frequent: Monocrystalline quartz.
Rare: Biotite mica laths Micritic limestone.
Very rare: Epidote.

Textural concentration features

In this fabric there are rare tcf's. They are dark red-brown to black in XP, equant, sr and discordant with the micromass. They do not contain any inclusions. Mode: 0.2 mm long diameter.

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