

**TECHNOLOGY OF BRONZE AGE COOKING
WARE FROM AKROTIRI, THERA**

VOLUME 1

Noémi Suzanne Müller

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Department of Archaeology - The University of Sheffield

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Abstract

Cooking wares have been pivotal to the study of technological variation and function in archaeological ceramics. The present study investigated the rich cooking ware assemblage from Neolithic and Bronze Age levels at Akrotiri, Thera in Greece. Using a range of techniques, archaeological materials were analysed to retrieve information on provenance, technological choices and performance characteristics.

Thin section petrography was employed in combination with X-ray diffraction methods, Fourier transform infrared spectroscopy and scanning electron microscopy to identify variability in the archaeological material. Changes in local manufacturing procedures were observed, in addition to the presence of imported vessels from other Cycladic islands.

Based on the archaeological material, experimental briquettes were manufactured varying the shape, type and proportion of temper, the base clay and firing conditions. The influence of these manufacturing parameters on selected performance properties was assessed through material testing. Strength, toughness, thermal shock resistance and thermal conductivity were all investigated on the briquettes and evaluated for their applicability to archaeological ceramics. Computer modelling by finite element analysis provided further information, relating vessel shape to material properties. Data generated by the experimental work have implications beyond the specific case study, to the performance of other clay vessels

In the case of cooking ware from Akrotiri, a varied picture emerges. Variability observed within certain chronological phases may be connected with different cooking methods employed, and perhaps with specific consumption preferences based on performance criteria. On the other hand, two major shifts in local manufacturing technology are detailed that are unrelated to the performance of the cooking vessels.

While the results of this study illuminate the development of a specific technology over much of the Bronze Age, the methodology developed is suggested to have broad applicability in the study of cooking pot technology which has been so central to concepts of ceramic performance.

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Damaged zone (grey) with radius r_{eff} around spherical inclusion (radius r_i).

Figure V.2 322

Cross section: damaged zones around the edges of a disk shaped particle with maximal blunt edges, platyness factor $a = 5$.

Figure VI.1 328

Influence of thermal conductivity and wall thickness (different curves) on the time needed to bring water to boiling. The constraints applied and material parameters employed are described in the text.

Abbreviations

EDX	Energy dispersive X-ray spectroscopy
FEM	Finite element method
FT-IR	Fourier transform infrared spectroscopy
IR	Infrared
MOR	Modulus of rupture
PE	Thin section petrography
S/CFS ratio	Strain/critical fracture strain ratio
SEM	Scanning electron microscopy (<i>or</i> microscope)
TEM	Transmission electron microscopy (<i>or</i> microscope)
TRS	Transverse rupture strength
XRD	X-ray diffraction
XRF	X-ray fluorescence

Chronological terms

LN	Late Neolithic
FN	Final Neolithic
EC	Early Cycladic
MC	Middle Cycladic
LC	Late Cycladic
EM	Early Minoan
MM	Middle Minoan
LM	Late Minoan
EH	Early Helladic
MH	Middle Helladic
LH	Late Helladic

Chapter 1

Introduction

It is some while ago that archaeologists have first recognised the influence of manufacturing parameters on the performance of a ceramic vessel and therefore on its suitability to fulfil certain functions. Braun (1983, 126) noted that

'potters can control the mechanical performance of a vessel by manipulating vessel size and shape, and the composition [...] of the vessel walls. The potters thereby can control not only the suitability of a vessel for a particular range of tasks, but also [...] its ability to perform over a reasonable life without failure'.

Awareness that the way of manufacture steers the material properties of a ceramic vessel and these in turn govern its performance is growing. The knowledge of how and why a potter's choices influence the physical properties of the ceramic material, however, is still inadequate (Tite *et al.* 2001), and in too many cases is the interpretation of manufacturing patterns with respect to the relative suitability of the archaeological material based on speculation alone.

Cooking vessels have taken centre stage in the technological investigation of archaeological ceramics. This owes to the fact that this nearly ubiquitous type of vessel has to resist a variety of stresses it is exposed to in daily use. It has for example been suggested that changes in tempering practices over time were related to the technological development of cooking vessels found in west-central Alabama (Steponaitis 1984). Subsequently, although admitting the beneficial effect of certain temper materials on the performance of a cooking pot, the need of placing such technological studies in context and taking into account the multitude of other factors that influence technological choices has been emphasised (Tite and Kilikoglou 2002). While not *per se* explaining technological variation, an understanding of performance properties provides a valuable baseline for the consideration of the overall reasons for the technological choices, which are observed in archaeological ceramics (see also Kilikoglou *et al.* 1998).

When a macroscopic examination of the Bronze Age cooking ware assemblage of Akrotiri on the island of Santorini (Thera) in Greece revealed great variations in form and fabric, therefore, the question arose how these related to the performance of the vessels. Did changes in manufacturing procedures result in improved cooking vessels? Might it be that cooking vessels were imported due to their superior properties? And, if performance properties cannot account for the observed variation, what other motivations might there have been?

In order to tackle these questions, an analytical programme was undertaken which assessed the influence of various manufacturing parameters on the performance of traditional ceramics on replica briquettes. Transferring the results of these investigations to the archaeological case study would then allow an assessment of the observed variations.

In a first step, the archaeological samples were analysed in order to detect variation in raw materials and manufacturing methods. Thin section petrography was chosen as the main analytical technique since, besides from illuminating the provenance of a ceramic vessel, the technique also reveals production traditions, such as the addition of temper material. These are known to have a crucial influence on the performance of the finished vessels (Tite *et al.* 2001). Once the variations and changes in the archaeological samples had been established, experimental briquettes were manufactured to assess the influence of the parameters identified. They were tested on their performance properties. When examining cooking vessels, the emphasis is mostly laid on their ability to survive exposure to thermal stresses (Tite and Kilikoglou 2002), but also mechanical stresses during handling play an important role. Furthermore, the ability to transfer heat is important for a vessel which is used to cook food. The performance characteristics investigated therefore included strength, toughness, thermal shock resistance and thermal conductivity. Using the results of the material tests on laboratory specimen as a baseline, technological change and variation in the cooking ware assemblage of Bronze Age Akrotiri were examined.

The Akrotiri cooking ware assemblage proved in many ways ideal for such a technological investigation. Firstly, the site produced a sequence of domestic pottery which is unique in the Cyclades in that it spans from the Late Neolithic through to the Late

Bronze Age. The assemblage includes a rich variety in vessel shapes, and a major shift in manufacturing practice, the change to more calcareous clays with the transition to the Middle Cycladic period, was known already from macroscopic examination (I. Nikolakopoulou pers. comm.). Furthermore, the period under investigation is one of continuity but also of great changes in the region, so that further variation in the cooking ware was expected. As the Bronze Age Aegean has been researched intensively, a large corpus of contextual information is available that could feed into an interpretation of results. Furthermore, the location of the site on an island which is part of an archipelago with fairly varied geology facilitates in many cases relatively straightforward provenance assessments, so that the identification of differences in local manufacturing techniques and differences in provenance did not pose many problems.

This study examines a specific type of functional vessel, the ceramic cooking pot, for a selected case study. Beyond their relevance to the particular case study, however, the results obtained on replica briquettes are applicable more generally. When examining the influence of technological choices on the performance of a vessel, it becomes soon clear that the matter is rather complex since any technological choice influences many material properties. It is the microstructure which is affected primarily by the potters' choices such as the addition of temper material or the selection of certain firing regimes (unfortunately not always in a straightforward way), and which in turn directs a ceramic's mechanical and thermal properties. The key factor to any performance assessment is therefore knowledge of a ceramic's *microstructure*. Importantly, the study of mechanical and thermal properties on replica briquettes, besides permitting the assessment of the influence of individual technological parameters on selected performance characteristics, allows us to relate variations in material properties to microstructural changes. The investigation of this relationship formed a central part of the present study, as it ultimately allows statements regarding the performance and suitability of archaeological pottery.

The present volume is divided into four main sections: after the introductory chapters, two experimental parts follow - the first concerned with analyses carried out on the archaeological sherds, the second with the material tests on replica briquettes -

before the results obtained in the various stages are brought together in the final chapter.

Chapter 2 outlines the importance of performance criteria in an assessment of technological change and variation for ancient ceramics, and gives an account of previous studies which employed performance characteristics to assess the suitability of clay ceramics for certain functions. The methodological approach adopted in the present study is introduced. The subsequent Chapter 3 provides the archaeological context of the case study and presents the cooking ware assemblage from the site of Akrotiri.

The first experimental part presents the outcome of the analytical studies that have been carried out on the archaeological samples, so as to identify patterns in manufacturing technology. Chapter 4 presents the results of the petrographic characterisation, focusing on the determination of provenance and the identification of variations in local manufacturing procedures. The petrographic data were supplemented by using additional analytical methods on selected samples, namely powder X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscopy (Chapter 5).

The performance-related material properties and the influence of various manufacturing techniques on those are presented in the second experimental part. Chapter 6 rationalises the replication design and specifies how the ceramic briquettes were manufactured. The next two chapters present the results of the material tests that were performed on these experimental briquettes. After a brief introduction to the basic principles of fracture mechanics, Chapter 7 presents the results of the mechanical tests and discusses the parameters which influence the strength and toughness of traditional ceramics. Chapter 8 assesses the influence of structural variations on the thermal properties of clay ceramics, namely thermal shock resistance and thermal conductivity. Based on the results of the material tests on the laboratory specimens, computer simulations using the finite element method were carried out to further examine the response of cooking vessels to mechanical and thermal stresses (Chapter 9).

The final chapter draws the results obtained on archaeological material and laboratory samples together. The data generated is employed to discuss the changes and variations in raw material and manufacturing techniques observed in the assemblage, in view of issues related to suitability and optimisation by taking into account contextual information. Besides discussing the archaeological case study, also the methodology employed for establishing the performance characteristics is assessed and points of interest for future research are identified. In addition, the various analytical techniques employed have been critically assessed for their applicability to the specific research problem in the course of the study. While the general outline of the approach is assessed in Chapter 10, the limitations, potential and suitability of the individual analytical techniques to the study of ancient ceramic material are discussed in the respective experimental chapters.

Chapter 2

Analysing the performance characteristics of archaeological ceramics

This chapter outlines the importance of the performance characteristics strength, toughness, thermal shock resistance and thermal conductivity in the assessment of technological change and variation in ancient ceramics. There follows a review of previous studies which employed such performance characteristics to assess the suitability of clay ceramics to perform certain functions, and some of the subsequent critique of a purely functional interpretation of technological change. The second part of this chapter presents the practicalities of assessing the influence of manufacturing parameters on performance characteristics and provides a short overview of the methodological approach adopted in the present study.

Various performance characteristics, such as toughness and thermal shock resistance, have been put forward in the archaeological literature to explain technological choices observed in utilitarian ceramics, mainly in transport jars and cooking vessels (for early examples see for example Braun 1983; Steponaitis 1984; Feathers and Scott 1989). The initial enthusiasm for connecting changes and variation in manufacturing practices to the optimisation of performance properties of the finished vessel was soon somehow dampened; so pointed Woods (1986) at the production of apparently 'unsuitable' vessels over long periods of time. Moreover, the need to consider the social context of production and consumption when examining technological choices has been emphasised (Sillar and Tite 2000). The necessity of taking into account the non-technical factors influencing pottery manufacturing techniques when examining the performance properties of functional ceramics has been referred to in various instances (e.g. Kilikoglou *et al.* 1998, epilogue; Tite and Kilikoglou 2002). The fulfilment of performance requirements remains, however, a popular avenue for examining technological choices, in particular when it comes to cooking ware (e.g. Pierce 2005).

Importantly, although a variety of studies have investigated the influence of different manufacturing practices on performance properties of ancient ceramic materials -

mainly strength and toughness - our knowledge is still far from complete (Tite *et al.* 2001). Even more restricted is our understanding of thermal shock resistance. Although this characteristic is drawn upon regularly to explain tempering choices (e.g. Hoard 1995; Killebrew 1999; Broekmans *et al.* 2004), only rarely are such explanations based on experimental studies, and the complexity of the concept of thermal shock resistance is frequently overlooked. Another property deemed to be important for vessels exposed to heat, namely thermal conductivity, has received very little attention in the archaeological literature as yet (Hein *et al.* 2008b). For an in-depth discussion of all these performance properties and their significance for ceramics used in cooking activities, as well as for an overview of previous studies referring to archaeological material, the reader is referred to Chapter 7 and 8.

Although it might be tempting to relate certain choices in manufacture with functional requirements of the ware type examined, as long as this is not based on reliable experimental data, the validity of any interpretation of technological change or variation which argues for functional optimisation - or, in fact, against it - is severely compromised. The present study seeks to assess and discuss changes and variations observed in the manufacture of cooking ware pottery from Akrotiri, Thera, in Greece, taking into account the resulting differences in performance properties. To provide a valid baseline for such a discussion, the influence of different parameters which are under the potter's control on a series of performance properties will be examined, thereby approaching a more general object of study, namely the advancement of our understanding of the mechanical and thermal characteristics of clay ceramics.

The first part of this chapter briefly defines strength, toughness and thermal shock resistance and thermal conductivity, and outlines how these performance characteristics are important in a ceramic material. This includes an overview of how technological choices and their influence on performance characteristics have been assessed in the archaeological literature.

2.1 Performance characteristics

Strength, toughness and thermal shock resistance are the performance properties used most often in the archaeological literature to assess the suitability of a ceramic to perform use-related functions (Tite *et al.* 2001). Additionally, 'heating effectiveness' has been introduced, in order to quantify heat transfer in cooking vessels (Skibo *et al.* 1989; Schiffer 1990). The present study will assess fracture strength, toughness, thermal shock resistance and thermal conductivity (the concept of 'heating effectiveness' being difficult to rationalise - see Chapter 8), as all of these are significant for cooking ware.

Fracture strength gives a measure of the amount of stress a material can be exposed to until cracks initiate (Davidge 1979; Tite *et al.* 2001). In the case of brittle materials the initiation of a crack is usually equivalent to the failure of the vessel, but in a tougher material, a propagating crack can be arrested through different mechanisms. Therefore, assessing only the strength of a ceramic vessel does not necessarily provide information on when it will lose its structural integrity. But since fracture strength does give a measure of the threshold for crack initiation, it is related to the ability of a vessel to retain fluid contents, at least when its surface is not sealed.

Toughness is the property that indicates the ability of a material to survive impact without breaking, as it is a measure of the intrinsic fracture energy, required for crack initiation, and of the energy that is absorbed during crack propagation (Tite *et al.* 2001). If a material can absorb energy through mechanisms such as deflection and arrest, cracks can be stopped before they lead to failure.

Thermal shock resistance specifies whether a material is able to withstand rapid changes in temperature (Kingery *et al.* 1976, 822). *Thermal conductivity*, finally, is a measure of the heat transfer in a material under a particular temperature gradient (Kingery *et al.* 1976, 584).

Various factors have been recognised to influence the performance characteristics of clay ceramics. These include the amount, size, shape and kind of aplastic inclusions as well as firing temperatures. Importantly, also the *orientation* of anisotropic inclu-

sions is expected to affect the performance properties greatly.¹ The matter is rather complex, however, since any technological choice influences a variety of material properties.

To illustrate the meaning of these performance properties as well as the interplay between them, exemplifying that any 'optimisation' or 'design' inevitably includes compromises, we can outline briefly how performance characteristics could be employed to assess a material's suitability for use in the manufacture of cooking vessels.

Requirements placed on cooking ware include that a vessel retains its fluid contents (high fracture strength), survives impact during handling, cleaning or cooking activities such as stirring (high toughness), survives repeated sudden changes in temperature, when put over a fire (high thermal shock resistance) and effectively heats up its contents (high thermal conductivity). Unfortunately, most technological choices that result in higher toughness and - as frequently argued - also in enhanced thermal shock resistance of a clay ceramic material, such as the addition of temper or the use of lower firing temperatures, simultaneously decrease fracture strength. Luckily there are alternatives to having a high strength in order to retain fluid contents: vessels may be impregnated with a resin or treated otherwise to seal pores and cracks (Skibo 1992; Sillar 2000). In the case of cooking ware the actual process of cooking results in the deposition of organic material in cracks and pores and may be regarded in itself as a sealing process, so that no extra treatment is necessary. Based on these considerations, one could, for example, argue that toughness is a more significant performance property for a cooking vessel than strength. In this case, an optimisation of a cooking ware fabric would more likely involve technological choices which increase the toughness of the material, rather than those that increase strength.

It is also important to be aware that the properties of a material are not equal to the properties of a vessel. In the case of fracture strength, for example, geometrical factors such as curvature or wall thickness influence the actual strength of an object. In the case of thermal shock resistance, factors influencing the thermal gradient through

¹ This is important insofar as different forming techniques manifest themselves in the orientation of temper material, but also of voids, a fact that has been used to study shaping techniques (Whitbread 1996).

a vessel wall, such as saturation of pores or the temperature difference between contents and heat source, become important. Material testing on bars does not take these factors into account. The influence of geometrical factors on mechanical and thermal properties, however, can be assessed through computer modelling (Chapter 9) if the physical properties of a material are known. Computer modelling also allows the investigation of temperature constraints on the magnitude of thermal stresses.

Furthermore, it should not be forgotten that choices in manufacturing technology may influence different stages in the life-cycle of a vessel. Rather than improving a property relevant for a finished vessel, certain technological choices might be motivated by properties relevant during manufacture. Specific temper types might for example be chosen to improve the workability of a clay paste or to aid the drying process rather than for improving the toughness of a vessel produced from it.

When looking at those physical properties which are relevant for a finished vessel, a distinction can be made between requirements that it has to fulfil during everyday use and those that would be required so that the vessel survives accidental abuse. Such abuse situations - for example being dropped on the floor - can be avoided by careful handling. As the above distinction divides between potentially acceptable (failure caused by abuse) and not acceptable (failure during normal use activity) failure, it may help to designate performance characteristics that are susceptible to optimisation.² It can be hypothesised that those mechanical properties which influence unacceptable modes of failure are more susceptible to optimisation processes than those influencing acceptable failure.

In addition, the context of production and consumption could be argued to play a role in determining the importance of certain performance properties. While in a context of mainly domestic production, performance properties which are apparent during manufacture, and those perceptible during use, might be considered of similar importance, the picture is not as clear in a context where pottery is not a domestic product (Braun 1983). Here, it is the technological choices which are relevant during manu-

² Furthermore, one could argue that failure in abuse situations is potentially anticipated (e.g. vessel breakage caused by dropping it), while failure during use would normally tend to be less so (e.g. the cooking pot disintegrates during filling).

facture (e.g. those that result in increased workability of the clay paste) which are more immediately perceived by the potter and, perhaps, could be of more immediate relevance to him/her (at least until the outraged customers bring their defective pottery back!). In a context where craftspeople are dependent on the revenue generated by their products and potentially operate in an environment of competition from other producers or other materials, things become further complicated (Davis and Lewis 1985; O'Hear 1986). One could for example go on to argue that while high quality vessels would potentially attract customers, a manufacturer more concerned with increasing the output and keeping production costs low might have been more competitive.

On a slightly different note, one might also ask oneself to which extent a consumer would recognise flaws in material and manufacture to be responsible for the failure of a vessel and not put the blame on actual or imagined abuse or indeed look for cause-effect relationships in the realms of superstition and belief systems.

Finally, we have to be aware that what is measurably different is not necessarily perceived as being different, and - by consequence - not necessarily behaviourally relevant. When comparing two materials for their toughness for example, it might well be that although different values are found in laboratory tests, both materials are too weak to be of any practical use. Alternatively, if toughness is very high, both materials would result in exceedingly durable vessels. Even if values lie in a window where differences in the material property do result in differences in performance which could potentially be perceived (say cooking vessels from producer A last for three months while those from producer B last for six months), this does not imply that these differences are inevitably noticed. Finally, if the requirements that are placed on a material exceed its capacity greatly, differences in capacity do not translate to differences in behaviour. This is the case, for example, for the impact exerted on a pot when being dropped on a hard floor. In this case, strains are usually high enough to cause failure in any case, so that differences in toughness do not result in any different behaviour.

All this should not discourage us from employing performance criteria when studying technological choice, rather it should simply remind us that when using perform-

ance properties to assess the suitability of ceramic vessels, we usually assume that differences in those properties were recognisable and recognised by the people producing and using those vessels. This entails an assumption that the people whose objects we are studying shared our perceptions and preferences. Although this cannot be verified in an archaeological context, such a consideration still provides us with a starting point for an assessment of the relevance of the experimental data obtained from the measurements of mechanical and thermal properties, especially when supported by ethnographically gained insights on the way people conceive suitability and acceptability. Yet, especially when arguing for technological development, it is crucial to keep in mind what the performance properties actually stand for, and be aware of the limitations of our datasets. Furthermore, it is important not to restrict consideration to a single performance characteristic, as technological choices influence a range of potentially relevant properties. The choice of the performance characteristics that are to be examined in a study depends on the type of material and the information sought, and must be made carefully.

2.2 Approaches to the assessment of technological choices

In the mid twentieth century, mainly in the American literature, variation in pottery technology as expressed by the use of different temper, shapes or decoration has been considered as only culturally determined; different manufacturing technologies were ascribed to different people and changes and patterns in those technologies could thus be explained by the movement of different cultural groups (Trigger 1989, 148-206). In this school of thought, referred to as culture history, the variation in material culture was seen as a passive reflection of cultural groups, so that the examination of the archaeological record led to the reconstruction of the areas those groups lived in and to the tracing of migration movements.

In the 1980s a group of mainly North American researchers started to examine how different manufacturing technologies, especially the use of different kind of temper material, influenced the performance characteristics of the produced vessels (e.g. Braun 1983; Steponaitis 1984; Bronitsky and Hamer 1986; Feathers 1989). The recognition that different technologies actually resulted in objects with different per-

formance characteristics such as toughness or thermal shock resistance led to the explanation of diachronic changes occurring in an assemblage from an evolutionary point of view, in the sense that a directed evolution, i.e. optimisation, took place³. Synchronic differences were explained by the fact that, depending on the intended use of a certain type of vessel, it had to withstand different kinds of stresses. These studies have been put in an explicitly Darwinian context (O'Brien *et al.* 1994). Since such assumptions presume that there is a 'natural' i.e. predetermined tendency to optimisation that will invariably occur, the individuals as such do not have an influence on this process. Rather, the degree of correspondence to a theoretical ideal has been identified as a mean of judging the 'fitness' or 'expertise' of potters or cultural groups (Bronitsky and Hamer 1986).

Although the introduction of new *types* of cooking ware to a geographical region, as well as their possible subsequent spread, is frequently linked to cultural identity if not of the people producing, then at least of those consuming them (e.g. Killebrew 1999; Joyner 2007; Birney 2008; but see Ben-Shlomo *et al.* 2008 who explain further spread by processes of diffusion), variations in their paste recipes are often explained by functional requirements. To look for a reason for specific manufacturing techniques solely in the realm of functional fitness or optimisation, whether it is on the level of the finished product or in a different step of manufacture, is arguably not only a rather restricted point of view, but may also be misleading when interpreting patterns of such manufacturing techniques. Critique of the mainly technical interpretation of paste variability did occur; Woods (1986) argued that performance characteristics might play a less crucial part in the production of vessels, based on the observation that theoretically unsuitable cooking pottery kept being produced over a large time span in Great Britain. Examples of assemblages that cannot be explained by a purely functional approach or where functional efficiency of fabrics indeed is lessened in favour of cultural factors have been published (Blinkhorn 1997). Much in contrast to the culture history approach, however, these see variation in manufacture technology not as passive reflection of culture but rather as an active expression of identity (see Day 2004 for an ethnographic example).

³ See also Feathers (2006) who, however, expands the evolutionary approach to other factors that - although they ultimately influence performance of the ceramics - are not material properties themselves.

In order to evaluate these various approaches to explain differences in manufacturing techniques, (i.e. being an expression of one group distancing itself from another or indicating an adaptation to different conditions), we have to give the potter a more active role, as it is his/her choices, consciously or unconsciously, that shape pottery manufacture. Once the potter has knowledge of the respective techniques and access to raw material sources, he/she can either adopt the technology producing 'more suitable' vessels, or to keep to the traditional way of doing so, to mark cultural membership. Equally important are the consumers' choices: they cannot only influence a potter's actions, but they also result in consumption patterns which will be reflected in the distribution of pottery in the archaeological record. Choice depends on perception, which itself may be regarded as formed and shaped by the world in which we live and by experiences, either personal or historical (i.e. of the group we are affiliated with). If we regard technologies and technological choices as dynamic strategies that are often related to social identity and difference but are additionally structured and determined by function and material constraints (Lemonnier 1993), the position of material suitability and performance optimisation is shifted. Rather than being the ultimate driving force behind technological development, it can be seen as providing a baseline against which social factors can be assessed. To be able to make valid suggestions on the underlying reasons and mechanisms, therefore, the variation in manufacturing techniques must be contextualised and viewed against socio-economic, cultural and political backgrounds.

Acknowledging the fact that there may be more and other than purely functional properties that are important for the manufacture, use and discard of a vessel opens up different ways to interpret variation in manufacturing techniques that manifest themselves in performance characteristics. It should also make us wary of making judgments on the level of development by assigning the 'fitness' or 'expertise' of a cultural group by its ability to produce 'state of the art technology'.

2.3 Methodology of the present study

So far, this chapter has been concerned mainly with the reasons why performance characteristics of ancient ceramics are worthwhile assessing when it comes to tackling issues related to technological change and how their study can contribute to our understanding, not only of the ceramics we study but also of the people producing and consuming them. The following section goes on to present the practicalities of assessing the influence of manufacturing parameters on performance characteristics, more specifically, it presents how this study has proceeded to assess them, rationalising the methodology that was followed.

As stated in the beginning of this chapter, the aims of this study are several. It seeks to assess technological change for a specific case study, namely for Bronze Age cooking ware from the site of Akrotiri, Thera. In order to accomplish this task, the influence of different manufacturing parameters on a series of performance characteristics needs to be examined, thereby advancing our understanding of mechanical and thermal characteristics of clay ceramics on a more general level. This entails the design and assessment of a methodology for the determination of those performance characteristics, applicable to traditional ceramics in general, and it is an additional purpose of the present study to produce a recommendation of a protocol for the determination of performance characteristics of archaeological pottery.

The research objectives of the thesis are closely intertwined: the assessment of performance properties for the particular ceramic cooking ware assemblage, which comprises an investigation of the influence of several parameters on the physical properties of clay ceramics, and the evaluation of a methodology to assess such properties. During the course of the study, data has been generated that helps to discuss the changes and variations in raw material and manufacturing techniques observed in the assemblage, in view of issues related to suitability and optimisation. Simultaneously, the various analytical techniques employed are critically assessed for their applicability to the specific research problem, in order to achieve the second objective of the study. Since these techniques are discussed in-depth in the relevant chapters, the following section is restricted to the presentation of the general outline of the approach.

The particular case study investigates the technology of prehistoric cooking ware from the site of Akrotiri, on the island of Santorini in Greece. The archaeological material - *c.* 170 samples of cooking vessels dated from the Final Neolithic to the Late Bronze Age - was analysed in order to detect syn- and diachronic variation in the raw materials and manufacturing methods. In order to assess the impact of these changes and variations on the performance characteristics of the ceramic cooking ware (both locally produced and imported), the mechanical and thermal properties of the different ceramic recipes were assessed through material testing. The studied properties included strength, toughness, thermal shock resistance and thermal conductivity.

2.3.1 Rationale for replication experiments

In previous experimental studies, performance characteristics of archaeological ceramics have been assessed in two fundamentally different ways. Mostly, they were determined on replicates (e.g. Bronitsky and Hamer 1986; Feathers and Scott 1989; Hoard *et al.* 1995) but occasionally also on archaeological sherds (Steponaitis 1984; Neupert 1995). The decision on whether to measure performance properties directly on the archaeological material or to follow a more indirect route by testing replicates and subsequently transfer the outcome to the archaeological material, has a profound impact on the overall methodological approach. It is for this reason that the rationale for adopting the indirect approach in the present work is discussed before presenting the detailed experimental procedure. There are several reasons that measurements on replicates were preferred over tests on archaeological material.

Firstly, material tests on archaeological sherds do not necessarily indicate the properties of the original object. In the various stages which follow its manufacture - such as use, discard and burial - a vessel is subject to alteration. Impact during use or discard, for example, can result in microcracking. During burial, weathering processes may lead to structural damage. As any microstructural changes profoundly influence the mechanical as well as thermal properties of a material, the residual properties of an archaeological sherd are in many cases not equal to the original properties of a

vessel after manufacture. Moreover, there is no unambiguous way to link a residual performance property measured on a sherd to the original property of the corresponding vessel, since alteration processes such as those discussed above are in most cases not reconstructable.

Secondly, the preparation of test specimens for the determination of mechanical and thermal properties requires a great deal of material. Most of the material tests are destructive and many require multiple measurements on different test bars. In many cases there is simply not sufficient material available for such tests, even if the whole sherd would be sacrificed, especially when a series of properties is to be investigated as in the present study. In addition, for most test set-ups, the test specimens must meet certain geometrical requirements. For example, it is a frequent prerequisite that two opposite sides of a test bar or disc are even and exactly parallel, a condition that is particularly difficult to achieve with the curved sherds that make up the majority of the archaeological record.

Finally and most importantly, replication experiments under controlled conditions permit us to trace and assess the influence of individual technological parameters (e.g. firing temperature) on selected performance characteristics. Importantly, the measurements on replicates allow us to link variations in material properties to microstructural changes, providing insights into the underlying principles which govern the dependencies of the studied properties. This knowledge in turn allows a more systematic assessment of the performance characteristics of archaeological material and is applicable well beyond a particular case study.

It is for all these reasons - alteration of the archaeological material, material requirements for the performance tests and in order to be able to generalise from the results of the study - that it was decided to assess the mechanical and thermal properties on replicates and not on the archaeological sherds.

2.3.2 Methodological framework

The methodological framework chosen at the outset to determine those performance parameters is explained below, while the individual analytical techniques employed are discussed in the relevant chapters. The experimental roadmap can be divided into three consecutive tasks, each with its own objectives and each building upon the results of the previous. These are: the characterisation of the archaeological material, the manufacture of experimental briquettes and the determination of the performance properties on these briquettes, and the interpretation of the data. The first step, the characterisation of the archaeological material, was performed on a carefully selected subset. The sample selection is of major significance, as it determines whether the analytical results obtained on these samples can be generalised to the assemblage they are derived from. It is therefore discussed before presenting the approach adopted to determine the performance properties of ancient ceramics, which is largely independent of the particular case study.

A - Sample selection and representability

Care was taken to sample only material which derived from undisturbed deposits, and which could be dated unambiguously. Sherds and vessels were selected that would belong to shapes typical of cooking ware of the particular period or show clear traces related to cooking activities, such as sooting, incrustations or burnt residues (*cf.* Figure 3.2). In addition, several samples were taken from hearths and baking pans, the rationale being that these utensils, similar to cooking vessels, are exposed to elevated temperatures during use. It must be kept in mind though, that although hearths, baking pans and cooking vessels are all inherently linked to heat and heat transfer, the requirements posed on the different ceramics vary according to their function.

Emphasis was placed on sampling the whole spectrum of shapes as well as all macroscopically distinguishable fabrics. This allowed - in the first instance - the detection and confirmation of off-island provenance for imported ware, but also revealed variations and changes in the local cooking ware technology. Although samples can

also be linked to general statements about fabrics and shapes of the different phases, it was not a primary objective to representatively sample the assemblage, so that quantitative observations made on the sample cannot be directly transferred to the cooking vessel population. Also, it should be pointed out that the samples derive from different types of deposits: so pottery from the early phases comes mainly from rock-cut chambers which had been back-filled in antiquity while the latest occupational horizon is a destruction level, which provides, thanks to the exceptional circumstances of its formation, a snapshot of a specific moment in time⁴. It is for these reasons that conclusions derived from the analytical examination of the sampled material are in a first instance qualitative rather than quantitative, although - should it be required - the large sample size does allow some quantitative argumentation, especially when the outcome of the analytical study on the sampled sherds is used for a re-evaluation of the cooking ware assemblage at Akrotiri.

B - Characterisation of the archaeological pottery

At first, the samples selected from the archaeological assemblage were characterised, using a suite of analytical techniques. Methods were chosen which would facilitate the classification of the pottery into compositional groups relating to different production traditions and provenance. Importantly, these methods should reveal variations in manufacturing parameters which are under the potters' control and which potentially influence the performance characteristics of the finished vessels. The detailed discussion of these analytical techniques is provided in the respective chapters, while the following section is restricted to presenting the general approach.

As a first step, all samples were studied by thin section petrography (Chapter 4), a method which is ideally suited for the analysis of coarse ceramics, such as the cooking ware pottery of the present case study. Thin section petrography permits the identification of the coarse inclusions, as well as the determination of the amount and

⁴ Also for this special case, however, it cannot be excluded that bias has been introduced in the deposit. The fact that (with very little exception) no precious objects were discovered during excavations, suggests that the inhabitants selectively depleted the assemblage when evacuating the site, by taking the more valuable and easily portable objects with them (Doumas 1983, 134). It cannot be excluded with absolute certainty that these did not include some highly valued cooking utensils.

grain size distribution of temper material. Importantly, it also identifies the orientation of temper particles or pores. The examination of the groundmass also provides rough estimates for ancient firing temperatures. As well as shedding light on provenance, the technique thus enables the classification of an assemblage according to raw material selection and manufacturing techniques.

In a second phase, the data obtained by thin section petrography was further refined by applying complementary analytical methods - namely X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR) - to selected samples of the previously identified compositional groups (Chapter 5). The particular analytical techniques were chosen in anticipation of their providing further information on raw materials and their assisting in the determination of firing temperature ranges. In addition, the results of the various methods were expected to show some overlap. All three techniques, for example, potentially provide information on ancient firing temperatures. This enables a refinement of their estimates, but also the mutual validation of the various techniques. X-ray diffraction and SEM are methods which are well established for the analysis of archaeological ceramics, FT-IR, however, is not. The evaluation of the potential and the limitations of FT-IR for the study of ancient ceramic material, especially in view of estimations for low firing temperatures, was therefore a declared subtask of the present project.

The full characterisation of the assemblage by thin section petrography, supplemented by XRD, SEM and FT-IR, identified changes and variations in the production technology of the cooking ware manufactured and consumed at Akrotiri during the time period studied. The identification of these changes allowed the determination of several key parameters, whose influence on the ceramics' performance properties was to be assessed on the replicates manufactured in the next step.

C - Fabrication of experimental briquettes for material tests

A systematic series of test briquettes was manufactured (Chapter 6) in order subsequently to assess the influence of the key parameters identified in the previous task on the performance properties.

The choice of the parameters which are varied in the manufacture of such experimental briquettes must be based on the observations made on the archaeological samples, so that the outcome of the material tests performed on the replicates can be transferred to the archaeological case study. It is crucial to recognise those changes in raw material use and manufacturing technology which potentially influence the performance properties of the cooking vessels, and to enable an evaluation of the influence of the relevant technological parameters through manufacturing appropriate experimental briquettes. Furthermore, a range of parameter values, which goes beyond but includes those observed in the archaeological material, must be tested in order to account for the influence of parameter variation as this may ultimately help explain preferences for specific parameter values observed in the archaeological material.

For the present case study, the key parameters varied in manufacture included the type of clay, type and amount of aplastic inclusions and firing temperature.

D - Material tests

Those physical properties which were considered relevant for cooking ware were determined on the experimental briquettes. These include strength and toughness as well as thermal conductivity and thermal shock resistance. It should be mentioned that the analysis was restricted to performance properties which are relevant to the *finished* vessels. As emphasised earlier, however, when discussing technological choices in view of optimisation and suitability, one must not forget that also the performance a ceramic material exhibits *during* manufacture (e.g. shrinkage or workability) can be a decisive factor for or against its selection.

It must be kept in mind that the physical properties relate to the material a vessel is made of, and not to the vessel itself. In order to assess the performance of an object, its shape must be taken into consideration as well. This can be achieved by computer modelling using finite element analysis. For the present study, where the physical properties of the material have been established, finite element analysis can readily build upon the previous results and has a great potential to add further valuable in-

sights. Computational analyses were therefore performed in order to examine the response of cooking vessels to mechanical and thermal stress and to study various aspects that are essential for cooking ware performance, such as the influence of shape and material constraints on the development of thermal stresses (Chapter 9).

E - Data interpretation

The results of the material tests provided the baseline against which the variability and the changes observed in the archaeological assemblage are discussed (Chapter 10), as they allow an assessment of the suitability of various ceramic recipes used in the production of cooking ware, and ultimately aid an explanation of the preferences which are observed in the archaeological record.

Ideally, tasks A to D should be performed consecutively. In reality, however, this cannot always be achieved, especially when a study needs to be completed within a sensible timeframe. In the present case for example, a second complementary sampling took place after the experimental programme and the replication (based on the results of the first sampling) had already started. When not all tasks are executed in a consecutive way, this theoretically bears the danger of not including relevant, but not immediately obvious, variables into the test schedule. This is, however, not a serious problem, since additional briquettes taking new or unexpected results into account, can always be fabricated at a later stage: thanks to the nature of the methodological set-up, such complementary testing and its results can be easily integrated into the overall analysis in retrospect, without having to repeat the entire study programme.

Chapter 3

Continuity and change in the Bronze Age Cyclades

The period covered by the present study is an eventful one. Geography provided the inhabitants of the Cyclades with a privileged position in sea trade and during the earlier part of the Bronze Age at least, Cycladic people seem to have been in charge of much of the maritime trade in the region. Long trading routes were travelled with a long-boat powered by a crew of oarsmen, with the ECII period being considered the peak of Cycladic-based trade activities (Broodbank 2000). During the Middle Cycladic period, Cretan influence appears to increase with minoanising⁵ traits appearing at various Cycladic sites (Broodbank 2004). At Akrotiri, Cretan influence perhaps reaches its height in the final occupation levels, an early phase of the Late Cycladic period (Knappett and Nikolakopoulou 2008). Metal objects, which are found in increased amounts in Bronze Age levels, have been frequently connected with maritime trade, but they are also associated with the creation of wealth and status of those distributing and consuming them. The first metal objects found in the Cyclades date to the Late Neolithic. The evidence is, however, much richer in later periods, especially during the later part of the Early Bronze Age, when a boost in metallurgical activities is observed (Renfrew 1972). The developments in trade, connections and power structures among the islands, together with the emergence of a more distinctive social stratification within their population during the Bronze Age, are believed to be accompanied by crafts specialisation or at least increasing intensity and organisation in craft production (Renfrew 1972; see also Whitelaw *et al.* 1997).

Furthermore, the period sees several significant changes in settlement patterns. In the earliest stages of occupation - the Cyclades appear to have been settled as late as the Late Neolithic period - small villages are the norm (Broodbank 2000, 146). A more dispersed pattern is observed in the start of the Early Bronze Age (Cherry 1980). The later part of this period witnesses the development (and by the end of the period the

⁵ Broodbank (2004, 46) defines the term 'minoanisation' as a 'modern term of sometimes deceptive convenience for a heterogeneous range of ancient material culture traits and practices that indicate the adoption in places beyond Crete, through whatever means, of ways of doing things that originated directly or indirectly within that island'.

abandonment) of some larger villages, presumably the centres of the long-distance maritime trade which was flourishing at the time (Broodbank 2000). The beginning of the Middle Cycladic period finally sees the first steps towards urbanisation with the nucleation of larger settlements (Cherry 1980). These would develop into important harbour towns during the succeeding periods (Doumas 1983, 25).⁶ The different crafts that had become defined more clearly during the preceding periods were now centralised in these proto-urban centres (Renfrew 1972, 402).

The main purpose of this chapter is to give the reader a short introduction to the Cyclades and more specifically to Akrotiri in the Bronze Age, in order to provide the context for the following case study. The first part of this chapter, therefore, presents some of the central aspects of Cycladic prehistory in chronological order. This is followed by a presentation of the sequence at the site of Akrotiri and by the description of the site's cooking ware assemblage.

3.1 The Cyclades throughout the Bronze Age

The Cyclades are an island group in the Aegean Sea. They lie close to mainland - Attica and the Peloponnese to the west, the Anatolian west coast to the east - and neighbour Crete in the south (Figure 3.1). The Cycladic islands are not ideal places for agriculture since arable areas are mostly restricted to few, small plains, but they have lithic (e.g. obsidian on Melos), and metallic (Siphnos, Seriphos and Kythnos) resources that were exploited early on (Torrence 1986; Stos-Gale and Macdonald 1991; Stos-Gale and Gale 2003; Carter and Kilikoglou 2007). Due to the constraints imposed by the lack of arable land and limited fresh water resources, it is believed that permanent settlement on the islands necessitated a system of exchange, which rendered the Cycladic islands thoroughly dependent on each other (Broodbank 2000).

The geography of the islands assigned a key role to seafaring in the history of the Cyclades, since the sea-route has been the only way to travel between islands and

⁶ Others, however, see urban development in the Cyclades from much earlier on (Televantou 2008).

was probably of importance for intra-island travel as well⁷. The presence of Melian obsidian at the Franchthi Cave on the Greek mainland from Palaeolithic times bears testimony to the existence of some sort of seacraft at an early point in time (Broodbank 2006). It is thought that the vessel type in use in the Aegean during the Neolithic and the Early Bronze Age periods was a rather small *canoe* with modest cargo capacity. At least for the later part of the Early Bronze Age, there is evidence for a larger *longboat*, which could hold a crew of perhaps 30 people. It is believed that while the canoes were the everyday craft more suited for short-range travel, these longboats were related to long-range voyaging and their use restricted to specialised, larger communities (Broodbank 2000). Finally, Broodbank argued that in the Middle Bronze Ages, a substantial advance in maritime technology was introduced into the Aegean, the much more efficient deep-hulled *sailing ship*.



Figure 3.1 Map of the Aegean. Regions and sites discussed in the text are indicated. The islands which belong to the Cyclades are marked in grey.

⁷ During the late Neolithic and the earlier Bronze Age, overland transportation of goods on the islands was probably carried out by human porters: it is believed that domesticated donkeys first appeared in the Aegean during the Early Bronze II (Brodie 2008).

3.1.1 Chronology

The chronological framework of the Neolithic and the Early Bronze Age periods in the Cyclades is largely based on the recognition of distinctive assemblages. The main groups became apparent relatively early (Renfrew 1972). They were - and still are - referred to as the Saliagos, Grotta-Pelos, Keros-Syros, and Phylakopi I cultures, and they are assigned to different phases of the earlier Cycladic periods (see Table 3.1), although it should be noted that in addition to their chronological dimension they more often than not also possess a spatial one. In addition to these cultures, pottery groups are used for chronological fine-tuning, these include the Kastri Group which indicates the later stage of the Keros-Syros culture, or the Kampos Group, which falls between Grotta-Pelos and Keros-Syros. From the Middle Cycladic periods onwards, the dating of assemblages is conveniently achieved by linking assemblages through imports with well-established Cretan or mainland sequences.

Period		Relates to	Crete	
Neolithic	Late Neolithic	Saliagos		4500 BC
	Final Neolithic	Kephala <i>(restricted to northern Cyclades?)</i>		
Early Bronze Age	ECI early	Grotta-Pelos <i>(goes back to end of the Neolithic, concentration in southern Cyclades)</i>	EMI	3000 BC
	ECI late	Kampos	EMI late	
	ECII early	Keros-Syros	early EMIIA	2500 BC
	ECII mature*		late EMIIA	
	ECII late	Kastri	EMIIIB	2200 BC
ECIII		EMIII		
Middle Bronze Age	Phase A	Phylakopi I	MMIA	1850 BC
	Phase B	Phylakopi II-ii	MMIB	
	Phase C (+D)	Phylakopi II-iii	MMII MMIIB-III MMIII	
Late Bronze Age	LCIA	LC destruction level at Akrotiri	LMIA	1650 BC

* The ECII period has been subdivided into an early and a late phase, with the Kastri Group horizon as a marker for ECII late, but see Day and Wilson in press for a possible tripartite phasing of ECII based on new material from Akrotiri.

Table 3.1 Overview of the chronology of the Cyclades, from the earliest settlements to the destruction of the site of Akrotiri at the start of the Late Bronze Age. Periods attested at Akrotiri are highlighted in grey. Relations to Cretan chronology, Melos (Phylakopi), as well as typical groups and 'cultures' of the respective periods are indicated. Calendar years are indicative and should not be taken too literally. The sub-divisions of the Early and Middle Bronze Age follow the system developed for the site of Akrotiri (Middle Bronze Age after Knappett and Nikolakopoulou 2008, Early Bronze Age after Kariotis *et al.* in press, Day and Wilson in press).

3.1.2 Late Neolithic (Saliagos) to Early Cycladic I (Grotta-Pelos)

The *Late Neolithic* settlement of Saliagos near Antiparos, a site which has produced evidence for farming, animal husbandry as well as fishing activities, provided the first evidence for permanent, long-lasting occupation in the Cyclades (Evans and Renfrew 1968). Contemporary villages of the Saliagos culture appear to have been all comparatively large. They are found exclusively on large and medium sized islands and are mostly restricted to one settlement per island (Broodbank 2000, 146). The earliest pottery remains found at Akrotiri have close affinities to the contemporary pottery from Saliagos (Sotirakopoulou 2008).

This settlement pattern is believed to change in the *Final Neolithic*, when in the Northern Cyclades more short-lived sites such as Kephala on Kea appear (Broodbank 2000, 149). These sites are significantly smaller and accompanied by many more or less contemporary sites. The recently excavated Final Neolithic settlement of Strofila on Andros, however, alters this picture: the large size of the settlement together with communal works points to a large society with proto-urban features (Televantou 2008). In the southeast Cyclades, the Final Neolithic is somehow obscure, possibly due to low visibility of remains. In the subsequent Grotta-Pelos period, however, a shift in settlement pattern has been suspected also there: while the overall population is estimated to be more or less that of the earlier periods, the number of sites increases significantly and their size decreases. Small short-lived farmsteads seem now the norm (Cherry 1980), rather than the villages of the Saliagos culture. The new settlement pattern indicates a revolution in the ways of life on the islands - possibly linked to an increase in stock breeding - which makes now also the more remote and hostile parts of the Cyclades accessible for settlement (Broodbank 2000, 154).

3.1.3 Early Cycladic I to Early Cycladic II: emergence of larger villages and intensification of trade and metallurgical activities

Although population increased during the Early Bronze Age in the Aegean, the main settlement pattern of small, dispersed sites remained largely unchanged in ECII, even

if the amount and permanence of settlements increased and small islands became settled for the first time (Broodbank 2000). Some exceptions from the main pattern are observed in the form of the emergence of larger, village-level settlements in ECII. Broodbank argues that, in the majority of cases, these 'atypical' villages represent major trading centres, associated with long-range trading activities.⁸ Together with an intensification in maritime trade, evidence for the longboat appears in the Cyclades during the ECII. Longboats require a crew of oarsmen to be operated; Broodbank therefore postulated that they were used by the larger communities only, a fact which presumably resulted in a differentiation of various areas and people. It should be noted, however, that recent excavations on the island of Andros brought to light evidence for extensive maritime activities within the Cyclades as early as the Final Neolithic period. Rock-art compositions were found which depicted a broad variety of ships and give evidence for a developed type of boat in use already in the Final Neolithic (Televantou 2008).

While short-range travel is very much independent of weather conditions, it has been argued that some long-range routes were travelled one-way only, based on the assumption that main weather patterns remained essentially unchanged over the last few millennia (Agouridis 1997). One example for such a directional route is Thera-Crete, which - due to prevailing wind conditions - is preferably travelled from north to south. Since the way back consequently involves island-hopping routes either to the west or to the east, this results in directional trading along cyclic routes, which has the potential to explain relative frequencies in the distribution of material remains along these routes observed in the periods in question (Broodbank 2000, 290).

Long-range interactions do appear to have taken off at the transition of ECI to ECII. From this time date the earliest Minoan imports in the Cyclades, recently found at Akrotiri (Day and Wilson in press). In the late ECI, a sizeable Cycladic presence is observed in Crete at a number of locations on the north coast of the island. At Aghia Photia, for example, this appears to be the result of a deliberate settlement of Cy-

⁸ The size of ECII *Akrotiri* cannot be assessed, since levelling activities for the foundations of the later Middle and Late Cycladic buildings destroyed most traces of earlier settlements. Due to its location in the Southern Cyclades, however, (*cf.* Figure 3.1) Akrotiri is a candidate for such a trading centre, possibly associated with long-range connections. Indeed, recent excavations have provided substantial amounts of transport jars in early ECII levels as well as impressive amounts of imported ware from EM I (IIA and B) (Kariotis *et al.* in press).

cladic people (Betancourt 2008). The location of the site on the east point of Crete before continuing eastwards in the direction of Kasos (*cf.* Figure 3.1) could be explained as a 'staging point', established on the directional cyclic trade-routes that have been suggested for the period (Broodbank 2000). The phenomenon of these 'Cycladic' settlements appears to be rather short-lived and restricted to the ECI late. Intriguingly, evidence for early metallurgy has come forward from most of these sites, with metal working believed to be dependent on off-island raw materials and possibly Cycladic expertise (Dimopoulou-Rethemiotaki *et al.* 2007; Doonan *et al.* 2007, see also below).

Trade within and beyond the islands is intensified during ECII, a period which based on the distribution of its material remains, has been thought to possess a distinctive 'international spirit' (Renfrew 1972, 451). In the earlier part of this period, Cycladic-based voyaging and trade is believed to be at its peak, leading to emulation of material culture at far-off Aegean sites, and maritime trade is considered to be a major source of social power in the Cyclades (Broodbank 2000). The export of finished goods and probably also raw materials from various parts of the Cyclades to Crete during the ECII is documented, amongst other things, by findings of great amounts of transport jars at the harbour site of Poros-Katsambas (Dimopoulou-Rethemiotaki *et al.* 2007; Wilson *et al.* 2008).

Metal objects have been connected frequently with the increasing trade observed in ECII, but are also associated with accruing of wealth and status, if not by the people producing, then at least of those distributing and consuming them (Renfrew 1972). Metal objects are not only supposed to play an important role in the symbolic display of status, wealth, and social affiliation, but the material probably also had some impact on a more practical level in the form of metal tools which could be utilised for a range of tasks including carpentry and shipbuilding (Renfrew 1972, 325). Metal procurement has been argued to have been controlled by the major trading centres (Broodbank 2000, 294). This possibly involved itinerant Cycladic metallurgists, as has been suspected for ECI late, when such mobile craftspeople are thought to have operated in an extensive area, including the North coast of Crete (Doonan *et al.* 2007). The first metal objects found in the Cyclades date to the Late Neolithic. The evidence becomes, however, much richer in later periods, especially during the ECII

(Renfrew 1972, 313). Alloying copper with tin, a non-Aegean metal, replaces the previous technique of alloying with arsenic in the course of the ECII and has recently been connected with an intensification of the production (Doonan *et al.* 2007).

3.1.4 Early Cycladic II late: Kastri Group phase

The Cyclades appear to have undergone profound changes in the course of ECII late. Radical transformations in trading systems and in the relations of the Cyclades with Crete are indicated by the fact that in late ECII levels there is very little material culture evidence for trade between the Cyclades and Crete (MacGillivray 1984), with the exception of EMIIB pottery recently found at Akrotiri in Kastri Group contexts (Wilson *et al.* 2008). Crete, however, was still consuming Cycladic obsidian and metals. This might be related to major changes in Crete itself and to a direct exploitation of the Cycladic mineral resources (Broodbank 2000, 317). It is around this time that an enclave of Minoan settlers appears to have been established on Kythera, a settlement which has been argued to lie on a cyclic route from western Crete to the metal-rich Cyclades (Broodbank and Kiriati 2007). While Crete appears to be largely cut out of the Cycladic long-range trading routes during the late ECII (with the exception of Akrotiri), increased contact of the Cyclades with coastal Anatolia is evidenced by material remains. While the number of actual imports is tiny, in the later ECII, besides an inflow of eastern metals (such as tin), many pottery assemblages of the Cyclades now contain distinctive, anatolianising drinking shapes, the so-called *Kastri Group* (e.g. Angelopoulou 2008). This Kastri Group pottery is a minor novel component in ECII assemblages (Davis 2001). The adaption of innovations and customs of Anatolian origin is thought to have spread through the existing long-range routes, from Anatolia through the southeast Aegean to the Cyclades (Şahoğlu 2005).

During ECII late, many sites in the Cyclades are fortified, and by the end of the Early Bronze Age, most of the sites occupied during the ECII are deserted (Rutter 1983). Since the abandonment episodes succeed the emergence of the Kastri Group in the pottery assemblages by what Rutter (1983, 71) refers to as an 'appreciable length of time', it has been argued that there appears to be no reason to connect the two events

and interpret the material remains as traces of an invasion from Anatolia. The Kastri Group was increasingly seen as an adaptation of Anatolian customs by Cycladic people resulting from increased interaction with the southeast Aegean (Davis 2001). In this reading, the fortifications might simply indicate a generally less secure period, perhaps caused by a rise in internal competition within the Cyclades. More recently the small fortified sites of ECII late, specifically Kastri on Syros, have been interpreted as trading posts established by Anatolian traders amongst local communities (Şahoğlu 2005). This view resumes the theme of movement of people; it differs, however, significantly from earlier scenarios featuring 'refugees' or 'intruders' that were subsequently expelled by the islanders (Gale and Stos-Gale 1984; Doulas 1988).

3.1.5 Disruption around the later Early Cycladic II horizon

There is considerable debate concerning the *Early Cycladic III* period, and whether or not there is a break in the sequence on the islands, a problematic which has been referred to as 'the ECIII gap' (Rutter 1984, 95). Numerous settlements are abandoned at the end of ECII late (Kastri Group phase) contemporary with a late phase of EHII on the mainland and the next identifiable horizon in the Cyclades, equivalent to Phylakopi I, has been argued to be contemporary to the earliest Middle Helladic phase(s). This, so has been reasoned, results in an apparent gap of a century or more in the culture sequence of the Cyclades at the end of the Early Bronze Age, corresponding to the EHIII on the Greek mainland, or to EMIII on Crete (Rutter 1983). Rutter points to significant differences between the ECII late and the Phylakopi I horizons, including innovations in pottery and changes in burial practices (but see Doulas 1988 who rejects Rutter's claims for changes in burial practices), but also a more nucleated settlement pattern which is observed on the islands from the Middle Cycladic period onwards. Although there is a lack of Cycladic imports in EMIII contexts in Crete (Wilson *et al.* 2008), some Cycladic pottery has been attested in contemporary EHIII contexts on the mainland. Rutter argued therefore that rather than marking a break in the human occupation of the islands, the 'ECIII gap' appears to indicate a major cultural discontinuity within the Cyclades (Rutter 1984). This view is, however, not shared by Barber and MacGillivray (Barber 1984; MacGillivray

1984). They insist that the Kastri Group should be attributed to ECIIIA and Phylakopi I to ECIIIB (Barber and MacGillivray 1980), and they maintain that there is no gap between the two phases. Likewise, Doulas (1988) expressed his disagreement with Rutter's position, and suggested that the two phases on either side of Rutter's gap would in fact be contemporary.

There are, however, undoubtedly many indications for change between the later ECII and the start of the Middle Bronze Age on the Cyclades. Admitting that the lack of material remains during the EC III in the Cyclades does indeed indicate some sort of collapse, attempts have been made at an explanation, ranging from short-term climatic change, over an epidemic originating from the Near Eastern urban centres, to localised collapse (see Broodbank, 326 for a detailed account). Looking beyond the Cyclades, severe disruptions are indeed observed in the Near East roughly around this time and settlement sizes do shrink on the Greek mainland. Some places in the Aegean, however, see a smooth transition from Early Bronze II to III, and in Crete, despite signs of disruption, the rapid emergence of palace states is observed by the beginning of the Middle Bronze Age (see also Manning 1994).

3.1.6 From Early Cycladic II late to the Middle Cycladic period

By the Middle Bronze Age, the settlement pattern on the islands had changed dramatically (Cherry 1983). Much in contrast to the preceding periods, nucleated villages or small towns are now the norm, and smaller islands are no longer settled. In many cases there is only one major settlement on any one island, commonly found close to the sea (Broodbank 2000, 325). In the later phases of the Middle Bronze Age many of these small coastal towns, which were long believed to mark the first stage of urbanisation in the Cyclades (but see Televantou 2008), become important harbours (Doulas 1983, 25).

Broodbank (2000, 341-347) connected the emergence of this very different settlement pattern, along with the apparent changes from the ECII trading centres network, with the advent of *deep-hulled sailing ships*, which were introduced in the Aegean around the Early Bronze III to Middle Bronze Age transition. He argues that these

new boats have greatly changed not only the conditions for trade but also the trade-routes themselves. Not only are sailing ships much faster, allowing to travel larger distances in less time, they are also much more flexible, overcoming the need for cyclical routes. Notably, the new ships can take the direct south to north route from Crete to the Cyclades. Broodbank believes that the new technology undermined the dominance of the longboat trading centres and led to restructuring in the Cycladic trading system. He observes that the newly nucleated Middle Cycladic settlements all possess excellent anchorage, a requirement for the unloading of sailing-ships.

3.1.7 Middle Cycladic to Late Cycladic early: increasing Minoan influence

At the end of Phylakopi I, the Cyclades appear to lose the dominance of their sea-routes to an up-and-coming Crete. A new dendritic trade-route system appears which reflects the acquisition of raw materials by the Cretans - such as obsidian from Melos (Carter and Kilikoglou 2007) and metal from Lavrion, the ore deposits of Siphnos and Kythnos not being exploited any longer (Gale and Stos-Gale 1984). In this new Cretan based trade system, Phylakopi and Akrotiri are the two access points to the Cyclades (Figure 3.1).

This change in geopolitical realities is reflected in an increased frequency of Cretan pottery imports in the Cyclades. From Phylakopi II onwards, local 'minoanising' pottery (emulating Cretan prototypes) appears at Cycladic sites, suggesting perhaps ideological adaptation of Cretan customs by the island communities (Broodbank 2000, 358). Throughout the Middle Bronze Age, Cretan influence grows and by the beginning of the Late Bronze Age it is substantial at a series of sites in the Aegean, such as Phylakopi, Aghia Irini and Akrotiri (Doumas 1983, 126-127; Knappett and Nikolakopoulou 2008).

There is considerable debate over the interpretation of this growing Cretan influence on the material culture of the Cyclades (Hägg and Marinatos 1984). The nature of, as well as the processes leading to, this 'Minoan presence' or minoanisation, are still subjects of discussion (Davis 2001). The views range from political control exerted by Crete (connected to the physical presence of Cretans on the islands, in the form of

some sort of colonialist activities) to cultural minoanisation by emulation of independent island communities, prompted by a strengthening of economic ties. Broodbank (2004) advocates that it is unlikely that a single process can account for the range of phenomena observed throughout the Aegean which are subsumed under the term minoanisation, and that each case must be examined individually. He recommends the use of ceramic petrology, which allows insight into the potters' technological choices as a potentially rewarding approach to address issues of population mobility through material culture. Cooking equipment and dietary remains were suggested to be amongst the candidates that could potentially provide the most reliable indications for Cretan emigrants (Schofield 1983). Surely, an analysis of the technological choices in the production of cooking ware is then an especially promising avenue to cast more light on processes of minoanisation. This must especially hold true for a site such as Akrotiri, which Davis (2001, 26) has categorised as having the strongest case for actual Cretan settlement of those islands that belong to the 'Westerns String' exchange route between Crete and mainland Greece (Thera, Melos and Kea).

3.2 Pottery production in the Aegean Bronze Age

One of the issues that have preoccupied scholarship on Cycladic and Aegean prehistory is *craft specialisation*. This is due to the fact that the emergence of specialisation has been linked to the appearance of wealth, social hierarchy and economic organisation and has been used to explain increased complexity of the social environment in the Aegean during the later Bronze Age periods (Renfrew 1972). Concerning pottery production, frequently no or only low levels of specialisation have been assumed for the Neolithic and Early Bronze Age societies of the Aegean. The production of pottery is thought to have taken place on a household-level (or perhaps on village-level, allowing for the possibility that a few people took over the task for the remainder of the settlement in some sort of part-time specialisation). As a consequence, Neolithic and Early Bronze Age communities were considered as being largely self-sufficient at least in regard to their ceramic consumption. The advent of craft specialisation, with pottery production becoming a full-time occupation was commonly dated to the Middle Bronze Age, with the emergence of the first proto-urban centres in the Cy-

clades and the first palaces on Crete. This view has been challenged more recently. On one hand the very nature of such a transition has been questioned, arguing that specialisation should be regarded as a continuum rather than a single phenomenon (Day *et al.* 1997), a plea which was coupled with a call to a more specific use of the term. Moreover, the authors pushed back the date for the emergence of pottery as a specialised craft, by making a case for specialisation in ceramic production on various levels already during the prepalatial Early Bronze Age on Crete. There is growing evidence that pottery has been traded from very early: the earliest pottery on Crete, for example, dated to the Early Neolithic, was exchanged fairly frequently and over substantial distances (Tomkins and Day 2001). It becomes therefore increasingly doubtful that there has been any time in the Aegean when pottery production was not specialised at least to some degree. Looking at the *intensification* and increasing organisation of the craft over the course of the Bronze Age, the case seems more unambiguous. Increasing standardisation in production is observed over the course of the Middle and the early Late Bronze Age in the Cyclades. This goes along with a trend towards investing less time and effort per unit of pottery produced, and has been interpreted as the producers' response to an increased exposition to competition, resulting from increased trade within the islands (Davis and Lewis 1985).

3.3 The site of Akrotiri

3.3.1 Final Neolithic and Early Cycladic periods

Despite the paucity of settlement remains from the early occupation phases of Akrotiri (many foundations of the Middle and Late Cycladic buildings rest directly on the bedrock and it is believed that much of the earlier settlement remains were destroyed when the Middle Cycladic town was built) the site is thought to have been settled as early as the Late Neolithic (Sotirakopoulou 1999). This assumption is based upon the fact that Late Neolithic pottery sherds are found occasionally in the Late Cycladic destruction layer; it is believed that soils which were used for construction purposes in the later periods are the source of this unstratified earliest material from the site (Sotirakopoulou 1990). Moreover, in the lowest levels of pits which were dug in the late 1960s for the pillars of the first generation of a protective roof

over the site, material attributed to the Keros-Syros and Phylakopi I cultures was found, sometimes associated with rock-cut chambers (Doumas 1978). More recently, the construction of a new roof over the site once more necessitated rescue excavations. During these, several such underground rock-cut chambers have been found, most of them with fills that were dated to the Early Bronze Age. The newly found rock-cut chambers provided for the first time stratified levels of pottery from sealed contexts. From these deposits, five phases of the early occupation at Akrotiri, belonging from the Final Neolithic to Early Bronze Age periods, could be identified (Kariotis *et al.* in press).

In the new excavations, the earliest well contexted material consists of *Final Neolithic* pottery which was found in pillar pit 35, chamber 1. Other material which can be attributed to the Grotta-Pelos culture and is dated to *ECI early* occurs in several contexts (Kariotis *et al.* in press). Furthermore, *ECI late* pottery which can be linked to the Kampos Group has been retrieved. Unlike most other *ECI late* assemblages in the Cyclades which derive from cemeteries, the *ECI late* pottery from Akrotiri is a domestic assemblage. It is from this period that the first Cretan import is attested at Akrotiri⁹. The *ECII early* material found at the site not only contains transport jars and a few Cretan imports dated to *EMIIA early*, but also domestic ware (Kariotis *et al.* in press). The material can be attributed to a Keros-Syros phase but does not show exact parallels in any other *ECII early* pottery assemblage in the Cyclades. Since it contains *EMIIA early* imports and appears earlier than the *ECII early* assemblage from Skarkos on the neighbouring island of Ios, which has close parallels in Cycladic imports in *late* *EMIIA* levels on Crete, a division of *ECII early* has been suggested into an early and a mature part, and *ECII early* sites such as Skarkos have been reallocated to a *mature ECII* (Day and Wilson in press; *cf.* also Table 3.1 - chronology). At Akrotiri itself, this mature *ECII* phase has not been found so far (Kariotis *et al.* in press). The latest phase of the Early Bronze Age which is attested at the site is *ECII late*. It contains Kastro Group pottery and an impressive amount of imports which come in a large variety of different fabrics (Kariotis *et al.* in press). These include transport jars, Talc Ware in large quantities and Cretan *EMIIB* pottery (Day and Wilson in press). Links with the western Cyclades appear to be much stronger in this

⁹ This is not only the earliest Cretan import found at the site, but also the first Cretan import which has been found in any Early Bronze Age context in the Cyclades.

phase than in the earlier ECII early. The next phase found at Akrotiri is considered to date to the beginning of the Middle Bronze Age. Judging from the pottery evidence, it appears that the Early Bronze Age was a period of change at Akrotiri, with trade playing a major role at least during the ECII and with transport jars that link the site to maritime trade appearing around ECI late (Kariotis *et al.* in press).

3.3.2 Middle to Late Cycladic periods

As with the early Cycladic material, it was not until the excavations for the pillars for a new roof that Middle Cycladic material from stratified deposits has been found at Akrotiri. The last layer in some of the rock-cut chambers which provided stratified Early Cycladic material produced also the earliest Middle Cycladic finds. Additional material attributed to an early Middle Cycladic phase at Akrotiri has been retrieved from layers on the bedrock, thought to have been created by levelling operations for the construction of the Middle Cycladic buildings. Deposits of the later Middle Cycladic phases were found mainly in indoor areas (Nikolakopoulou *et al.* 2008). The last phase of occupation at Akrotiri prior to the Bronze Age eruption, dated to an early phase of the Late Bronze Age, *LCIA*, is especially well documented due to the extraordinary circumstances that led to the burial and preservation of the settlement.

In contrast to the earlier periods, *architectural remains* dated to the Middle Cycladic period have survived in greater numbers: some of the later LCI buildings are built on top of or are additions to earlier buildings (Doumas 1983, 43). Akrotiri appears to have developed into a major, densely occupied settlement by the Middle Cycladic period, with smaller sites dispersed over the island. Middle Cycladic buildings, occasionally two-storied, have been excavated (Nikolakopoulou *et al.* 2008). The transition to the Late Cycladic is marked by a general destruction, probably caused by an earthquake (Doumas 1983, 44-43). The plan of the subsequent Late Cycladic harbour town is different from that of the Middle Cycladic settlement (Nikolakopoulou *et al.* 2008). By the Late Cycladic period, Akrotiri had developed into an urban community of considerable size. The exceptional preservation of the settlement allows for a detailed picture of housing conditions: the ground floors and basements of the multi-storey residences found in the excavated area were apparently used to store goods or

served as workshops. The upper storeys accommodated the living quarters and included lavatory installations, connected to the sewers beneath the paved streets with clay pipes (Doumas 1983).

The local *pottery* production of Akrotiri during the Middle Cycladic period finds close parallels in Phylakopi on Melos. In contrast to the Late Cycladic mass productions, the Middle Cycladic pottery of Akrotiri is characterised by a lack of standardisation in shape, size and decoration of the vessels (Nikolakopoulou *et al.* 2008). Initially, four phases of the Middle Cycladic period were recognised, with the later two, Phase C and D being more recently merged (Knappett and Nikolakopoulou 2008).

The earliest Middle Cycladic material found at Akrotiri, assigned to *Phase A*, follows the ECII late levels which contain Kastris Group pottery. Apart from featuring much less imported ware than the preceding phase, also the local pottery of Phase A appears very different from the ECII late material, both in terms of shapes and technology. Calcareous clays, which result in the distinctive light coloured buff fabrics characteristic for the Middle and Late Cycladic pottery of Akrotiri start being widely used, effectively replacing the darker fabrics typical for the Early Cycladic period (I. Nikolakopoulou pers. comm.). Cretan and mainland imports place Phase A at the beginning of the Middle Bronze Age. The subsequent *Phase B* can be correlated to the Cretan MMIB-IIA, while the local pottery has parallels in Phylakopi II-ii. Similarly, *Phase C* can be related to MMIIIA in Cretan and Phylakopi II-iii in Melian terms. Not only are Minoan imports now found in increased amounts, it is also the first time that Theraan potters appear to be receptive to Minoan influences (Nikolakopoulou *et al.* 2008). This is reflected in the appearance of imitations of Minoan vessel types using the distinctive local clays and in the first (albeit limited) use of the potters' wheel. By the beginning of the *Late Bronze Age*, the Minoan impact on the local pottery production has reached its maximum (Knappett and Nikolakopoulou 2008). As in the previous Phase C, however, LCI pottery (as well as wall paintings) from Akrotiri, keep their local character although sharing many traits with the Cretan prototypes. Finally, imports from various places imply considerable interaction between Akrotiri and other areas of the Aegean also in the last phase of occupation at the site (Davis 2001).

Considering the *process* of 'minoanisation', Knappett and Nikolakopoulou (2005, 2008) argue on the basis of the pottery evidence outlined above, that Cretan influence emerged gradually before culminating in LCI. They detect a fairly steady scenario at Akrotiri, which experiences a sudden shift in Phase C, when the 'weak ties of exchange' of the earlier phases of the Middle Bronze Age become much stronger and might be described as 'ties of affiliation' (when Minoan styles start being imitated and Minoan practices are adopted) (Knappett and Nikolakopoulou 2005, 181). The reasons and mechanisms for this shift, so they argue, might be linked to a fundamental change in the character of south Aegean networks, possibly connected with developments on Crete itself (*cf.* also above: 'emergence of Minoan dominance'). As to the *nature* of this 'minoanisation', Knappett and Nikolakopoulou (2008) argue against the establishment of a Minoan colony, for which they would expect a more fundamental shift¹⁰. Instead, they propose that Akrotiri opted to become more engaged in south Aegean networks once the possibility arose and that it was the inhabitants' response to novel forms of material culture which led to a gradual cultural colonisation of the community.

3.3.3 The cooking ware assemblage

As we have seen, the period covered by this study is one of continuity but also of wide-ranging changes in the Cyclades. These are also reflected in the Akrotiri cooking ware assemblage (*cf.* Figure 3.2). A major change in the production of cooking vessels is observed with the transition to the Middle Cycladic period, a time that has been connected with far-reaching disruptions on the islands (e.g. Rutter 1983; 1984). As is observed generally with the locally produced pottery at Akrotiri, a change to more calcareous clays is noticed also with the cooking ware. The discontinuation of the use of the non-calcareous clays, which were widely used in the production of the earlier pottery, is accompanied by the introduction of a new cooking pot shape. It is at the beginning of the Middle Cycladic period that the cooking jug with pedestal

¹⁰ They admit, however, that especially the adoption of the wheel technique (which had been in use in Crete from MMIB) points to a more intimate connection.

appears at Akrotiri (I. Nikolakopoulou pers. comm.).¹¹ From the same time stem the first examples of crêpière-shaped hearths. A second major change in cooking ware shapes is observed with the transition to the Middle Cycladic C, when tripod cooking vessels appear in the assemblage and the cooking jugs lose their pedestals. This change coincides with increased Minoan influence discernible at the site (Nikolakopoulou *et al.* 2008).

Cooking vessels

From the earliest Final Neolithic levels, only body sherds, which hint at the use of some sort of globular vessel, were retrieved. Similarly, also in the subsequent ECI early, sherds belonging to deep open bowls were sampled, in one instance providing evidence for lug handles. From this period, through to ECI late, there seems to be an additional type of cooking vessel in use, a pithoid jar. In ECI late, besides the pithoid jar type an additional shape appears: a deep ovoid bowl with out-turned collar (Kariotis *et al.* in press). This shape has, however, not been sampled as at the time of sampling the sequence had not yet been firmly established. In ECII early, besides the deep open bowl type with lug handles, the dominant shape is a deep globular jar with low vertical neck (S. Kariotis pers. comm.). From the same period is also an unusual globular jug with pedestal. Several changes seem to have taken place by ECII late; after a possible gap in the sequence corresponding to a mature phase of ECII, some of the cooking vessels now seem pedestalled (S. Kariotis pers. comm.). Also in Phase A of the Middle Cycladic, at least some of the deep globular vessels have pedestals (I. Nikolakopoulou pers. comm.). In addition, a new shape (not taking into account a unique ECII predecessor which apart from being more globular also is imported), the pedestalled cooking jug, appears. This apparently Cycladic cooking vessel is also known from Melos, Kea and Paros, where it is dated to Phylakopi I-iii (Sotirakopoulou 2008). From Phase C onwards, cooking jugs without pedestal are in use (I. Nikolakopoulou pers. comm.). In Phase C, pottery also includes local and imported tripod cooking vessels, an adaptation of a Cretan type, alongside the local cooking jugs. The first indications for tripod cooking ware come from Phase B contexts, in which a

¹¹ A unique earlier example of a similar shape, apart from being typologically slightly different, was in the course of this study confirmed to be imported.

very few examples of tripod legs have been found (I. Nikolakopoulou pers. comm.). On Crete, tripod cooking vessels are found in large quantities throughout the Middle and Late Minoan periods (Betancourt 1980; see also Haggis and Mook 1993). The evidence for tripod cooking vessels from EMII levels of Myrtos (Warren 1972, 124) is amongst the earliest for this type of cooking vessel on Crete. For Akrotiri, it has long been assumed that tripod cooking vessels which contain mica were imported from Naxos, based on the reddish-brown appearance of their paste (Doumas 1983). One could assume that these two shapes, the tripod cooking pot and the cooking jug, have sometimes been merged in the production of a hybrid-type cooking jug with tripod legs in the LCIA period. This type is, however, also found on Crete (see Martlew 1988, type E). Unfortunately, Martlew specifies neither temporal nor spatial extension of this type. Haggis and Mook (1993) list a cooking jug with tripod legs in MMI-II but not in the subsequent MMIII and LM periods. Betancourt (1980) in his account of cooking pottery from Minoan Kommos, finally, does not mention this type at all. Finally, there is evidence that cooking activities in LCIA took also place in an additional type of vessel, a funnel-mouthed jar.

Baking pans and plates / hearths

In addition to cooking vessels also baking plates/pans and hearths were sampled. These date mainly to the earlier periods, from the Final Neolithic to Phase A of the Middle Cycladic period. Baking pans of the LN and ECI early can feature holes below the rims ('cheese pots'), in ECI late this is not observed anymore. From MC Phase A stems a distinctive *crêpière*-shaped version (see Sotirakopoulou 2008, 128, Figure 14.15), a shape which appears to continue throughout the Middle Cycladic (I. Nikolakopoulou pers. comm.). Also found in Phase A deposits are hearth/pans with a rough rounded base (see also Sotirakopoulou 2008, 125, Figure 14.6). To the Late Cycladic IA date the large horse-shoe shaped hearth installations, which have been interpreted as descendants of the Early Bronze Age baking pans and are believed to have been intended for the cooking of diverse foodstuffs (Birtacha 2008)¹².

¹² Based on the large size of these installations which were apparently low- or non-fired, one could, however, argue that these vessels might rather have functioned as hearths.

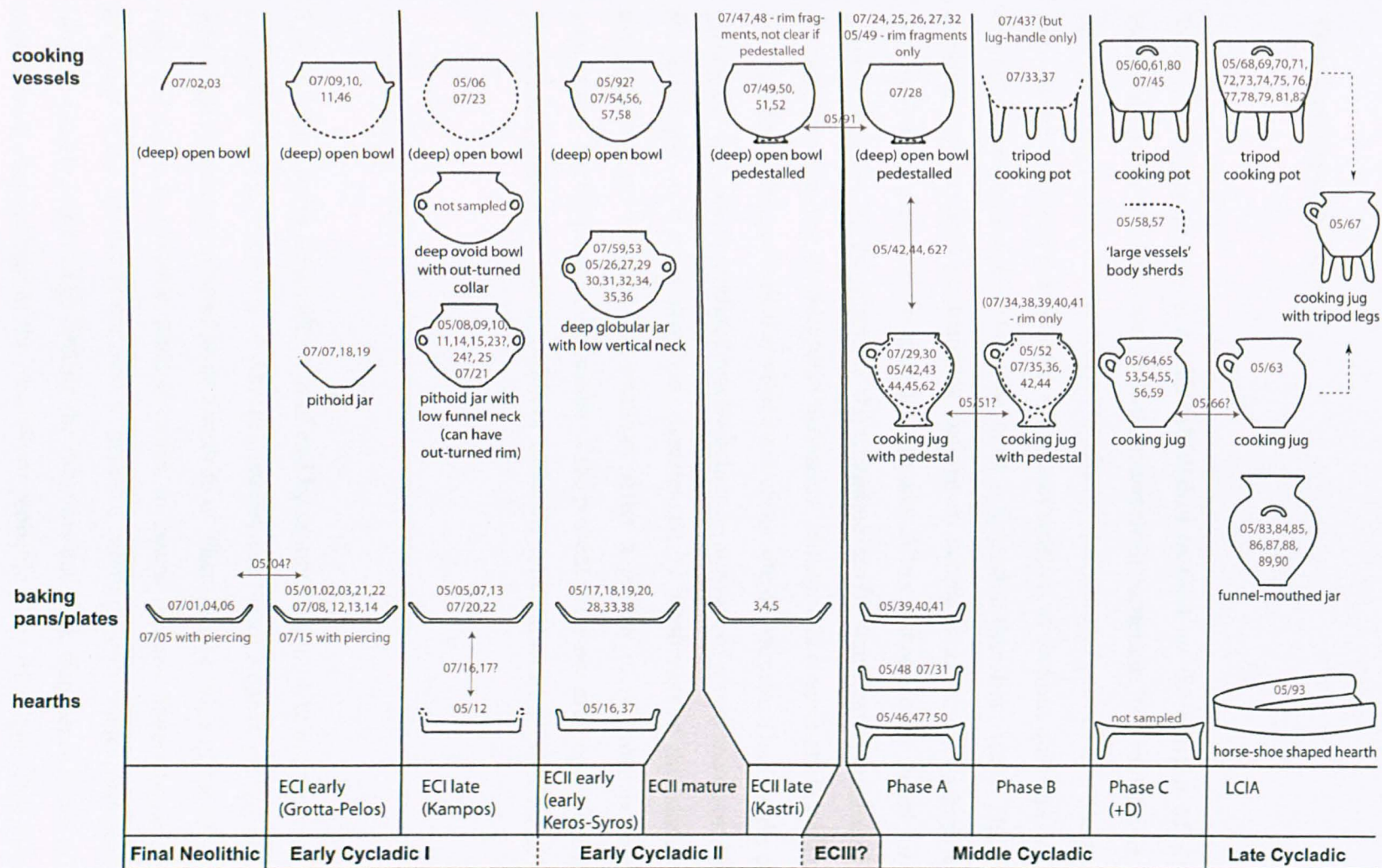


Figure 3.2 Development of cooking ware shapes at Akrotiri. The illustrations are neither to scale nor do they intend to represent exact typologies. The attribution of the analysed samples to the various shapes is indicated (cf. also Appendices I and II), except 07/55, which belongs to a unique, imported shape in ECII early.

Chapter 4

Thin section petrography

Thin section petrography is a well established method for the analysis of archaeological artefacts in general and ceramic materials in particular. Its popularity is due to its versatility, permitting the analyst to address questions of provenance and technology. As the method is based on the visual examination of sections cut from an object, coarse grained ceramics prove to be more informative than finer ware. The present cooking ware assemblage, featuring exclusively coarse ceramics with a high amount of non-plastic inclusions - in general more than 30% - is thus ideally suited for petrographic analysis. As the impact of the technique can be significantly increased when it is employed in a well-understood geological setting, this chapter starts with a brief introduction to the geological environment of the site of Akrotiri. The island's current geological features are outlined briefly before an account of recent reconstructions of the landscape, as it must have been experienced by inhabitants of the island before the massive Late Bronze Age eruption. After a review of previous petrographic analyses of Thera pottery, the results of the present study are presented, focusing on provenance and on the identification of variation in manufacturing procedures.

4.1 Geology of Thera

The following section provides a brief and by no means complete introduction to the geological setting of the site of Akrotiri, namely the South Aegean groups of islands which are commonly referred to as Santorini or Thera. Knowledge of the local geography of a site is valuable when it comes to assess the raw materials which were available to the ancient potter, and to gauge a ceramic's provenance prospects. The latter is usually achieved by linking the minerals and rock fragments found in a pottery sherd to the geology of the possible or probable place of origin. This, however, cannot be accomplished in a straightforward way in the present study, due to the rather vivid geological history of the island: Santorini is part of a volcanic complex which has erupted violently at the end of the Late Bronze Age, changing its topology

and covering it under thick layers of volcanic ash. The present-day relief of the island, including its soils, is therefore to a large part different to what has been experienced by and has been available to the people inhabiting the island before the Bronze Age eruption, making the sourcing of possible raw materials on the island a more challenging task than usual. The following paragraphs summarize attempts at reconstructing the pre-eruption environment, after a short overview of Santorini's modern geology and a brief account of the eruption that largely destroyed the island towards the end of the Bronze Age.

4.1.1 Present-day geology of Santorini

The name of Santorini, or Thera, commonly refers to a group of volcanic islands. Strictly speaking, the name of Thera is restricted to the main island of the archipelago, which is one of the two inhabited today (Figure 4.1).¹³ Santorini belongs to the



Figure 4.1 The island group of Santorini.

South Aegean volcanic arc, which emerged at a subduction zone: its islands mark the location where the Eurasian plate collides with the African, the latter being pushed beneath the former (Friedrich 1994). It is the southernmost of the Cycladic islands, situated some 120 kilometres to the North of Crete. Santorini is renowned for its spectacular appearance: it is dominated by a large caldera, a remnant of the Bronze Age eruption. Steep cliffs fall away, forming a natural bay that harbours the recent

Kameini islands, while on the other side gentler slopes lead to the outer perimeter of the island. Most of the island is covered by the ejections of the tremendous Bronze Age eruption: layers of volcanic ash and rocks, up to some 60 meters in thickness.

¹³ Additional confusion arises from the fact that many scholars use the terms Santorini and Thera to refer to the contemporary and to the pre-eruption island respectively. For ease of reference, this convention is followed in the present text, i.e. as long as not stated explicitly, 'Thera' refers to the archipelago as a whole.

However, this is only the last - at least for the time being - major eruption in a long history of volcanic activity that has formed the islands' geology and topography. Volcanic activity in the region started circa three million years ago. The oldest volcanic rocks on Santorini are exposed on the Akrotiri peninsula and are more than one million years old (Friedrich 1994). During Santorini's main period of activity, in the last two hundred thousand years, a series of volcanic centres operated on the island, the most active one being situated beneath the geologically relatively young Kameini islands (Higgins and Higgins 1996). Today, the geology of the archipelago is dominated by the products of those more than twelve different centres that have erupted in the course of the last couple of million years. Most of the rocks that are exposed on Santorini are either volcanic tuffs or lavas of basaltic to dacitic composition (Nicholls 1971; IGME 1980; Pichler and Kussmaul 1980; Vitaliano 1990; Friedrich 1994). They are described in more detail below, after a short account of the few outcrops of rocks of non-volcanic origin.

Non-volcanic rocks

Non-volcanic rock formations are relatively rare on the island. The prevolcanic basement, part of the Cycladic blueschist belt, is exposed only in the south-eastern part of Santorini: at and around Mt. Profitis Elias and in a couple of places at the inner side of the caldera. It consists mainly of metamorphosed sediments of the Tethys Sea (Triassic to Tertiary). The highest hills of the island, chiefly Mt. Profitis Elias, are composed of *limestone transitional to marble*. Underlying, and exposed in some ravines around the mountain and on the Sellada pass, but also in the lower caldera walls, are low grade *schists and phyllites* (Davis and Bastas 1978; Pichler and Kussmaul 1980). Around Mt. Profitis Elias, rather light coloured phyllites (containing muscovite/sericite, chlorite and quartz, occasionally stilpnomelane, and antigorite) and abundant calc-schists are found, while the darker blue schist (containing glaucophane, epidote and muscovite) seems restricted to a small outcrop at Athinios, at the inner side of the caldera. Here, the metamorphic rocks are cut by minor granite intrusions, a source of minerals such as magnetite, chalcopyrite and talc (Skarpelis and Liati 1990; Friedrich 1994).

Volcanic rocks

A complete description of the tuffs and lavas of Santorini goes beyond the scope of this introduction and for a more complete account the reader is referred to the relevant literature (e.g. geological map of Santorini (IGME 1980) together with Pichler and Kussmaul (1980) for a general overview, Nicholls (1971) for a detailed description of the lavas and Vitaliano *et al.* (1990) for an analysis of pumice deposits of the Thera series). For the purposes of this study it is sufficient to note that the *lavas* of all series are generally of basaltic to dacitic compositions, with the more basic lavas extruded first and the composition becoming more acid in the course of an emission event. They are commonly dominated by phenocrysts of plagioclase and pyroxenes (mainly augite and hypersthene). Hornblende is less common and restricted to the 'Lumaravi - Archangelo' series in the South of the island (*cf.* Figure 4.2, A₁ and A₂) (Fouqué 1879; Nicholls 1971) while olivine occurs predominantly in the more basaltic rocks of the other series. Modal quartz and orthoclase are almost entirely absent from the volcanic rocks of Santorini, even in the more siliceous lavas (Nicholls 1971). Generally, the lavas to the North of the island seem to be somewhat more basic than the southern ones. Analysing *pyroclastic rocks* of Santorini, Vitaliano *et al.* (1990) identified the presence of plagioclase, pyroxenes (mainly augite and hypersthene), opaques and rarely hornblende and olivine as phenocrysts in pumice deposits belonging to the Thera series. It is on the latest member of these series, which are commonly referred to as 'upper ignimbrites' or 'Cape Riva ignimbrites', that the ancient town of Akrotiri has been built.

Geological environment of the site of Akrotiri

The immediate geological environment of the site of Akrotiri is dominated by recent pyroclastics from the Late Bronze Age (frequently also referred to as 'Minoan') eruption. However, older volcanic rocks, predating the 17th century BC eruption, are exposed in the vicinity of the settlement. These are attributed to the oldest volcanic centre on the island, the Akrotiri volcanoes (Pichler and Kussmaul 1980). The A₁ tuffs and A₂ lavas (*cf.* Figure 4.2) represent the more acidic series of the Akrotiri volcanoes which have been extruded first, while the later volcanic rocks (A₅, A₆) are of

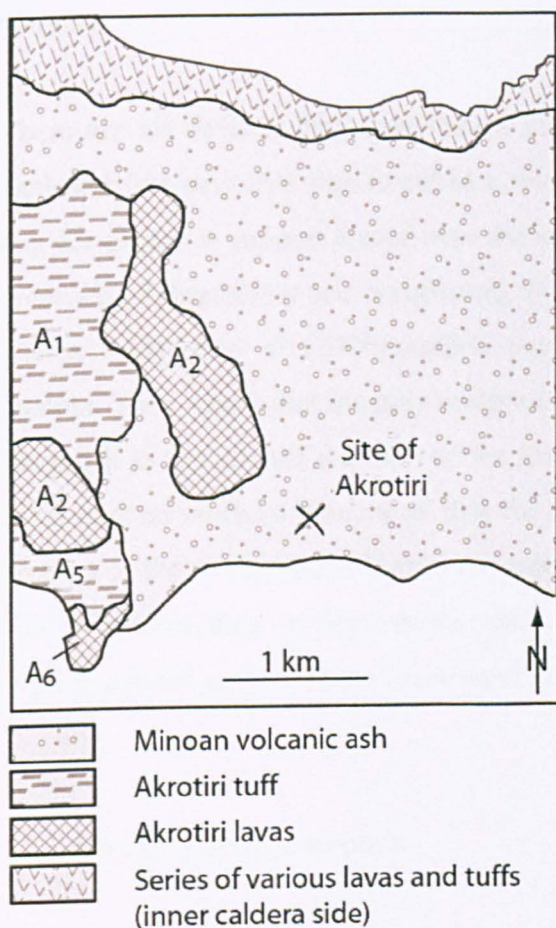


Figure 4.2 Immediate geological environment of the site of Akrotiri, after Higgins and Higgins (1996) and IGME (1980). A₁ - A₆ correspond to Pichler and Kussmaul's (1980) classification of the Akrotiri volcanic rocks (*cf.* text).

more basic composition. The 'lower series' (Pichler and Kussmaul 1980) or 'Lumavari-Archangelos' volcanics (Nicholls 1971), A₁ and A₂, consist of greenish white tuffs (A₁) and hornblende-dacite lavas (A₂) (Nicholls 1971). A₅ and A₆ belong to the 'upper series' (Pichler and Kussmaul 1980) or the 'Akrotiri' volcanics (Nicholls 1971) and are of andesitic composition. The A₁ tuffs of the lower series are of particular interest and will therefore be described in more detail. They are unique on the island, in that they contain Pliocene marine fossils, typically foraminifera (size: up to *c.* 1 mm). It is thought that the fossils' presence is caused by eruption into shallow water and subsequent uplift of 200 to 300 meters (Fouqué 1879). According to the original submarine pumice deposit levels, the species of the marine fossils present in the resulting tuffs vary: the foraminifera assemblage uphill at Mt. Archangelo is dominated by shallow water species, while the coastal tuffs are dominated by planktonic species and contain significant amounts of deep-water fossils (Friedrich *et al.* 2000). The sediments of the 'lower Akrotiri series' A₁ and A₂ are a mixture of clay, marl and pumice, with the highest clay and marl content found at the deeper water deposits - *i.e.* close to today's coastline - and higher pumice contents in the shallow water deposits which at present are on higher elevations further inland. Furthermore, postdepositional alteration of the Akrotiri tuffs resulted in sometimes extensive silicification (Fouqué 1879) and zeolitisation of the rocks, with clinoptilolite being the dominant zeolite phase (Kitsopoulos and Dunham 1996).

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Clays at Akrotiri

There are no obvious clay deposits on Santorini today. Vaughan (1990), however, analysed fine clay that was found in a rock cut structure at Akrotiri when pits were dug for pillars to support a roof over the site. Petrographic examination revealed the presence of plagioclase and hornblende, as well as andesitic lavas and polycrystalline quartz. Friedrich *et al.* (2000) studied clay from the same source for its foraminifera content. They found that the clay sample contained shallow- and deep-water species, linking it to the A₁ tuff deposits of the lower series of the Akrotiri volcanoes. Friedrich and co-workers concluded that the clay found at pillar 17 was an erosional product of the Archangelos-Lumavari updomed area, from where it had been washed out to be deposited in depressions, and suggested that such clays were probably available to the ancient potters at several locations.

4.1.2 Late Bronze Age eruption

The massive Plinian eruption of the 17th century BC abruptly ended a relatively long period of volcanic quiescence and covered Thera under thick layers of volcanic ash, thus conserving much of its Bronze Age settlements. The exact date of the Minoan eruption is the subject of ongoing debate: many archaeologists prefer a date around 1500 BC but virtually all evidence provided by natural sciences agrees on an earlier date of around 1630 BC (Kuniholm 1990; Manning *et al.* 2001; 2006; Friedrich *et al.* 2006).

It is thought that an earthquake preceded the Late Bronze Age eruption by a few months to a maximum of two years, probably caused by rising magma intruding an old vent or a fissure (Pichler and Friedrich 1980). There is evidence that, at the time of the eruption, the settlement was in the progress of being repaired from damages caused by an earlier seismic event (Doumas 1983, 134). Moreover, furniture and storage containers were found outside the houses. The fact that - unlike in the somewhat similar case of the 79 AD eruption of Vesuvius that buried the Roman city of Pompeii - no human remains and very few valuable objects have been found in the excavations at Akrotiri, suggests that the inhabitants had some warning and were

able to evacuate the site prior to the colossal eruption¹⁴. The eruption was long believed to be comparable to the 1883 AD Krakatoa eruption but is now thought to have been even more massive and dwarfing the latter. Recent estimates for the rock and magma emissions attain 61 km³ (Sigurdsson *et al.* 2006) thus doubling earlier volume estimates of ejecta material (Pichler and Friedrich 1980; Pyle 1990; Sigurdsson *et al.* 1990). Tephra was dispersed throughout the eastern Mediterranean; the deposits on Santorini itself consist of layers of white pumice and ash which reach a thickness of several tens of meters (Pichler and Friedrich 1980).

The eruption event is generally described as a sequence of a few distinctive main phases (Bond and Sparks 1976; Pichler and Friedrich 1980; Higgins and Higgins 1996). In a first Plinian phase, which is supposed to have lasted for a few hours only, the volcano erupted ashes and pumice blocks more than 30 kilometres into the atmosphere. After a while, seawater started to penetrate the vent and reacted with the magma so that the eruption became much more intense and violent, the so called base surge phase. The ring shaped explosive eruptions of this phase propagated mainly horizontally and lasted for a few days to a few weeks. The third phase is characterised by lateral mud and ash flows. Finally, the draining of the magma resulted in the collapse of the magma chamber producing much of the caldera that can be seen today.

4.1.3 Reconstruction of the pre-eruption landscape

Due to the great archaeological interest in the civilization that inhabited Thera at the time of the eruption - and possibly also owing to the fascination arising from connecting its destruction with the Atlantis saga - numerous scholars from a variety of fields have tried to reconstruct different aspects of the island's Bronze Age appearance. Although it had been believed initially (Pichler and Friedrich 1980; Pichler and Kussmaul 1980) that the island was circular before the eruption, it is now generally accepted that its shape was not so different from the one exhibited today. It is thought that already before the eruption, Thera featured a shallow, water filled cal-

¹⁴ But compare Fouqué's account on excavations on Therasia where he describes the discovery of human remains in a house that probably collapsed shortly before the eruption (Fouqué 1879, 99)

dera which contained a pre-Kameini islet and was connected to the open sea through a waterway in the South-East (Druitt and Francaviglia 1990; 1992).

Heiken *et al.* (1990), by 'stripping' the tuff from the Minoan eruption and noting the geology of the rocks underneath, attempted to establish the palaeogeology of Bronze Age Thera. Their map, at least in what concerns the Akrotiri peninsula, is very similar to the one presented by Nicholls (1971), which is based on a much earlier publication (Reck 1936, cited in Nicholls 1971). Figure 4.3 illustrates how the geology in the southern part of the island could have looked like in the Bronze Age. The main elevations, Mt. Profitis Elias and the Lumavari - Archangelo complex, which are not covered by the product of the late Bronze Age eruption today, must have appeared similar before the eruption, although the metamorphic basement was probably exposed to a somewhat bigger extent than it is nowadays. There is therefore no reason to assume that the phyllite outcrops at Sellada would not have been accessible in the past. Also the volcanic rocks of the Akrotiri series (see Figure 4.2 for a detailed map) which can be found immediately to the West of the settlement were equally accessible to the inhabitants of the Bronze Age settlement as they are today. As mentioned earlier, the ancient town of Akrotiri is built on weathered tuffs belonging to the Thera series (Pichler and Kussmaul 1980; Higgins and Higgins 1996), which are thought to have covered much of the island during the Bronze Age. They originate from the last volcanic event that took place before the Minoan eruption, *c.* 18 000 BC (Pichler and Kussmaul 1980). Most likely, much of the environment of the site was dominated by rocks attributed to the Thera series as was a great deal of the island's Bronze Age palaeosurface (Figure 4.3). As most of the surroundings of ancient Akrotiri are buried under Minoan pumice today, however, the exact relief and geology of these volcanic rocks is unclear. The topography might have been locally different, as small valleys and low hills would have completely disappeared under the blanket of Minoan pumice, leaving a modern ground surface with a relatively flat, featureless terrain (Aston and Hardy 1990). Some information has become available through ground-penetrating radar (GPR) mapping of the area around the site of Akrotiri: this revealed relatively flat land to the North of the site, but suggested the existence of (20 - 30 m) cliffs in the South onto which the settlement had been built (Russel and Stasiuk 2000). The soil conditions in the Bronze Age probably resembled the present-day situation: Thera seems to have been dominated by relatively poorly developed soils

which reflected the underlying geology and were low in organic matter and clay (Davidson 1978). It is thought that clay-rich matter, much as today, derived from the erosion of this paleosurface and accumulated in pits and sinks - natural or man made - where it could have been collected by the ancient potters (Friedrich *et al.* 2000).¹⁵

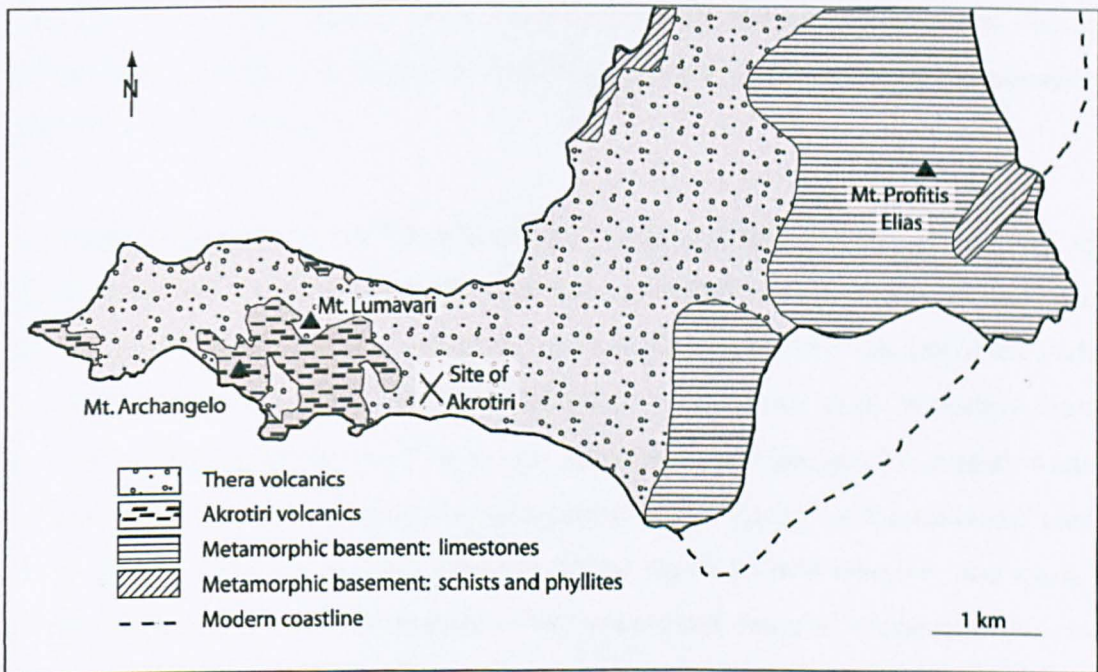


Figure 4.3 Possible palaeogeology of the southern part of pre-eruption Thera, adapted after Heiken *et al.* (1990), Nicholls (1971) and Higgins and Higgins (1996).

4.2 Ceramic thin section petrography: the method

Thin section petrography is a technique which finds wide application in geology when it comes to establish the mineralogical composition of rocks. Depending on their crystal structure and composition, minerals in thin section exhibit distinctive optical properties when polarized light is passed through them. These optical properties - such as relief, pleochroism or birefringence -, in conjunction with the examination of other characteristic properties, e.g. crystal habit, cleavages or twinning, permit the identification of a mineral by visual examination under a polarising microscope (Kerr 1977; Nesse 2004). To this end, a sample is cut from the specimen to be

¹⁵ It can be questioned, however, whether such a process would have provided enough clay resources for the sort of production which is attested at Akrotiri.

examined, mounted on a glass slide and ground very thin (typically 30 microns) so it becomes translucent. One advantage of thin section petrography over other techniques used for mineral identification, such as XRD, is the fact that besides allowing for the identification of the types of minerals present in a rock, the visual examination under the microscope also sheds light on their association with each other. This information in turn is crucial when it comes to assess the genesis of a rock, for example when establishing whether a rock is of igneous, sedimentary or metamorphic origin (Cox *et al.* 1988).

Although developed for the identification of rocks and minerals in geology, the application of thin section petrography has been extended to other materials and other subject areas early on in its development. It is interesting to note that one of the earliest examples of its application to archaeological ceramics is a study of pottery found on Thera, performed by the French geologist and petrographer Ferdinand André Fouqué (1879). Today, thin section petrography is a relatively well established technique also in those fields that embraced it later on in its development, and takes a prominent place in the examination of archaeological material. Ceramics, but also lithic objects, plasters, cements and others are studied in thin sections (Reedy 1994), for a variety of reasons. The main information thin section petrography can provide us with when applied to ceramic artefacts, regards two areas of considerable archaeological interest, namely provenance and technology (Freestone 1995).

The underlying principle of using thin section petrography for *provenance* purposes is the hypothesis that geographical variation in the mineralogy of the raw materials will be reflected in the finished product. By linking the rock and mineral types identified in a ceramic artefact with the geology of the assumed place of origin, therefore, it is possible to assess its provenance. The identification of the aplastic inclusions has long formed the core of ceramic petrography. This allows the sorting of ceramic objects into distinct fabric types, and in some cases to locate probable raw material sources and thus provenancing the pottery under examination. The success of such a petrographic study depends on a variety of factors such as variability of the geology in the study area or the coarseness of inclusions (Freestone 1995). Ideally, the petrographic analysis of a ceramic assemblage allows the analyst to distinguish between imported and locally produced ware, may hint at the origin of the imported vessels,

and, especially when combined with an analysis of possible raw materials, has the potential to reveal the sources of the materials used in local production.

In another line of inquiry, thin section petrography has been used to assess ceramic *technology*. In contrast to the study of provenance, which usually is confined to the characterisation of aplastic inclusions, the study of technology includes the examination of the plastic part of a ceramic, its voids and texture. This allows the identification and investigation of different stages in the *chaîne opératoire* followed in the production of ceramic vessels, e.g. raw material selection, paste preparation techniques, forming methods and firing parameters. This information is, in turn, a valuable contribution to the assessment of the technological choices made by ancient potters, and thus contributes to our understanding of past societies (Whitbread 2001).

Furthermore, the technique has the potential to be employed for an assessment of a ceramic's *performance characteristics*. Especially textural features such as the orientation of aplastics or pores or the size distribution of tempering material, provide important information pertaining to a ceramic's mechanical and thermal properties. Although this chapter focuses on technology and provenance and discusses the results of a 'traditional' approach, an important objective of the petrographic analysis in the present study was to collect also this information, which would subsequently allow assessment of the performance properties of the archaeological ceramics. Such an assessment, however, requires integration of the results with the outcome of the mechanical and thermal tests performed on replicates (Chapter 7 and 8) and is therefore left to chapter 10.

One of the main drawbacks of the technique is that describing a ceramic's fabric, i.e. the nature of inclusions, matrix, voids and their relative arrangement within a sample, is a subjective process. Also, much of the earlier publications on ceramic petrography provide only a little descriptive data. These difficulties led to attempts at standardising thin section description in order to facilitate comparison between different studies (Whitbread 1989; 1995). For the purposes of the present study, a modified version of the descriptive system introduced by Whitbread (1989; 1995) is used.

4.3 Previous petrographic studies of Thera pottery

Thera pottery, dating from all of the main Bronze Age phases, Early, Middle and Late Cycladic, has been examined previously by thin section petrography. The following section provides a short overview of these studies, which have dealt with the characterisation of local fabrics and their distinction from imported ware and - to a lesser extent - with the identification of ancient technologies in the manufacture of Thera Bronze Age pottery. The studies are discussed in order of their publication rather than according to the chronology of the pottery that was their subject. A summary at the end of this section lists the chronological evolution of the local fabrics, as assessed through the various studies, in table form.

As mentioned above, the earliest petrographic study that dealt with Thera pottery is also one of the very first instances where this technique is applied to archaeological material. More than a hundred years ago, Fouqué (1879) examined thin sections prepared from pottery sherds which he found in the course of his investigation of Thera's geology¹⁶. Intending to determine whether this pottery had been produced locally, he compared the mineralogy of the constituent rock fragments to the raw materials available on the island. Although he grouped the sherds macroscopically into several fabrics according to their body colour, when examined under the microscope, all samples contained the same rock components albeit in differing proportions. These components were tuff and amphibole andesite, which he assigned to southwest Thera, fragments of various types of lava and pyroclastic rocks, fragments of marble and mica schist which he thought were identical to those of Mt. Profitis Elias, various minerals, mainly derived from the volcanic rocks and, finally, a variety of microfossils (Fouqué 1879, 125). These observations led Fouqué to the conclusion that all the pottery he had found and analysed had been made on Santorini. He further believed that the clay source used for their production must have been at sea level, where detritus from all sorts of rocks would be brought in, in order to account for the simultaneous presence of rock fragments of metamorphic and volcanic origin in the pottery sherds.

¹⁶ The pottery fragments were retrieved from Therasia and the Akrotiri peninsula, either from surface layers directly under the Minoan pumice or from excavations of houses buried under this pumice and belonging almost certainly to the Late Bronze Age.

Nearly a hundred years later, Einfalt (1978) set out to answer exactly the same question anew, namely to assess whether pottery found at Akrotiri could have been produced locally. To this aim he analysed seven sherds recovered from the Late Bronze Age destruction level, each assigned to a different macroscopic group, with the petrographic microscope. He found that the composition of six out of the seven sherds was compatible with a local origin as they contained various minerals and rock fragments that fitted Santorini's geology. He identified - much like Fouqué in 1879 - metamorphic rock fragments, volcanic lava and pumice along with minerals of volcanic origin, and in some sherds carbonatic rock fragments or microfossils. Apparently unaware of the earlier petrographic study of Late Cycladic pottery, as well as of the fact that the Pliocene tuffs in the Akrotiri region are fossil-bearing (Fouqué 1879; Nicholls 1971), Einfalt struggled to account for the presence of microfossils much younger than the Triassic Mt Profitis Elias marbles. The presence of varied rock fragments in the ceramic sherds, however, led him to the conclusion that clays from different local sources, i.e. weathered phyllitic rock from the prevolcanic basement and altered volcanic material derived from the lavas and tuffs of the Akrotiri region, were mixed during manufacture. Einfalt's suggestion that raw material from different sources had been used in the production of pottery seems more likely than Fouqué's earlier theory of an all-encompassing sea-level clay source when it comes to account for the results of the petrographic analysis of the pottery, especially in view of the outcome of the present study, which will be discussed in detail later on.

At the same time as Einfalt, a slightly more comprehensive study was conducted by Williams (1978). He analysed forty sherds of Late Cycladic pottery, half of them thought to be local, the remainder supposedly imports. The aim of this study was to 'ascertain the mineralogical characteristics of the local wares of Thera, [...] so as to be able to distinguish the imported pottery' (Williams 1978, 508). The bulk of the assumed local samples indeed fell in a group which contained lava grains and in some cases additionally fragments of phyllite and foraminifera. Williams classified this group, which is compatible with the local pottery as described by Fouqué and Einfalt, as clearly local. He was also able to confirm a non-local origin for the vast majority of ware that had been classified as imports on macroscopic grounds.

A decade later, Vaughan (1990) studied the petrography of Early Cycladic wares with the declared intention to better understand Early Cycladic pottery and to assess contacts of the site with other settlements. She identified two fabrics which she assessed as being of local/Melian¹⁷ provenance. Both of her local fabrics (called A and B) contained pyroclastic rocks and argillaceous clasts, along with minerals derived from volcanic rocks, and seem to be derived from tuff deposits. Vaughan differentiated between the two fabric groups - which notably were more or less equally distributed in a series of macroscopic ware types - on the basis that fabric A, unlike B, was of obvious calcareous nature. Although she noted a substantial variation of carbonate content within her group A and allowed for the possibility that A and B represent a single type of clay with significant natural compositional variation, Vaughan concluded that the two fabrics represented two parallel material traditions.¹⁸ For another volcanic fabric she excluded a local origin altogether. This group is described as comprising mainly intermediate volcanic rocks and considerable amounts of zoned plagioclase. Seemingly based on the detection of hornblende in the sherds, she suggests a possible Aeginetan origin. It remains, however, unclear why Vaughan discounts a local origin for this fabric group, as hornblende-bearing lavas are well known in the Akrotiri series (Nicholls 1971). Possibly, her interpretation was affected by the fact that some of the corresponding pottery had been attributed to what she refers to as the Kastri and Amorgos cultures, i.e. is related to ware types that were thought to represent imports. In considering clearly non-local ware, Vaughan identified a coarse micaceous fabric which she believed represented imports from Naxos, while Talc Ware and glaucophane schist fabrics indicated that pottery was imported also from other Cycladic islands (see also Vaughan and Wilson 1993).

With the only published petrographic study of Middle Cycladic pottery from Thera (Vaughan *et al.* 1995), the focus shifts from the determination of provenance to the

¹⁷ On the basis that both fabric groups were attributed to ware that macroscopically had been identified as Melian as well as to material thought to be local, and taking into account the similarity of the local geologies of Milos and Santorini, Vaughan (1990) felt unable to distinguish between the two islands on petrographic grounds.

¹⁸ The interpretation offered by this study should be viewed with caution. The material analysed by Vaughan (1990) contained pottery dated to ECII and 'ECIII'. As discussed in chapter 3, the ECIII period appears rather problematic. Since the assemblage from which samples were chosen contained pottery attributed to the Kastri and Amorgos 'cultures', it is quite possible that the 'ECIII' sherds analysed would - in the notion employed in the present study - be attributed to either the ECII late or the early Middle Bronze Age instead. While the Kastri Group is dated to ECII late, the Amorgos group has been argued to be best seen in the early Middle Bronze Age (Rutter 1983, note 10).

assessment of the manufacture technology at ancient Akrotiri. The authors recognise continuity in the use of an earlier recipe as all samples were compatible with group A of the earlier ceramics (Vaughan 1990).¹⁹ The samples could, however, be subdivided according to the homogeneity (and ultimately to the size) of the carbonate inclusions. The difference is explained by the refinement - through crushing and grinding - of a common clay recipe. This procedure, together with the higher firing temperatures observed in samples of the more homogeneous fabric, so the authors suggest, is a prerequisite to obtain a white body colour with the specific raw materials. Accordingly, all dark-on-light ware, where such a white body is desirable in order to achieve maximum contrast with the decoration, fell into the subgroup characterised by homogenous distribution of the carbonate inclusions.

Table 4.1 summarizes the results of former petrographic studies on Thera pottery with reference to the fabrics identified as (probably) local.

PERIOD	FABRIC GROUPS	TECHNOLOGY
Early Cycladic (but includes 'ECIII' - see footnote 18)	Fabric A (Vaughan 1990) - <i>volcanic rock fragments</i> , mainly pumice - <i>various minerals</i> , derived from volcanic rocks - <i>calcareous</i> , fossils, carbonate fragments Fabric B (Vaughan 1990) - same as A but not obviously calcareous Intermediate volcanic rock ²⁰ (Vaughan 1990) - <i>volcanic rock fragments</i> : intermediate composition - <i>zoned plagioclase</i>	
Middle Cycladic	Fabric A (Vaughan <i>et al.</i> 1995) <i>as above</i> encompassing a more and a less homogeneous subgroup, based on the distribution/size of the carbonate inclusions	Finer fabric achieved by crushing and grinding (dry state) of raw materials, is consistently higher fired (Vaughan <i>et al.</i> 1995).
Late Cycladic	Non-subdivided fabric (Fouqué 1879; Einfalt 1978; Williams 1978) various amounts of: - <i>volcanic rock fragments</i> : volcanic lava and pumice - <i>metamorphic rock fragments</i> - <i>various minerals</i> , mainly derived from volcanic rocks - <i>carbonates/microfossils</i>	Mixing of material from different sources (Einfalt 1978).

Table 4.1 Summary of fabrics identified by former petrographic studies on Thera pottery as (probably) local.

¹⁹ but see footnote 18

²⁰ This fabric is included here as potentially local although referred to by Vaughan (1990) as imported, since a local origin cannot be excluded from the description of the fabric.

4.4 Results of the petrographic analyses of the Akrotiri cooking ware

The present study has produced results in terms of characterisation and grouping, the technology of production and the provenance of vessels found at Akrotiri. The petrographic analysis of the cooking ware assemblage reveals that, apart from locally manufactured vessels, also cooking ware imported from other Cycladic islands had been used by the people living on Thera during the Bronze Age. Besides identifying those imports, and - in some cases - pinpointing their probable location of origin, two substantial shifts that occurred in the local pottery production tradition could be identified within the time period studied. As the assemblage encompasses a relatively large timeframe, featuring samples dated to the Final Neolithic up to the Late Cycladic period, the results of the petrographic analyses are presented in chronological order. According to continuity and discontinuity of major fabric groups, the following temporal divisions were made for ease of presentation:

- Final Neolithic and Early Cycladic period
- Middle Cycladic Phases A and B
- Middle Cycladic Phase C and Late Cycladic IA period

For reasons of space and clarity, the following discussion identifies only the main characteristics of the fabric groups; for a detailed description of all petrographic groups identified within the cooking ware assemblage the reader is referred to Appendix III.

4.4.1 Fabric groups in the Final Neolithic and Early Cycladic periods

A rich variety of fabrics could be identified within the early material. A first division was made according to the geological origin of the dominant inclusions (volcanic or plutonic igneous rocks, and metamorphic rocks respectively). These main groups were then further subdivided according to mineralogical and textural variations, using criteria such as the relative abundance of rock fragments or minerals, or the presence of inclusions with unusual composition. Table 4.2 provides an overview of the fabric groups that were recognized within the Final Neolithic and Early Cycladic material.

Main character of inclusions	Fabric groups	Subgroups and related samples	Sample numbers	Time period	Inferred provenance	
Volcanic	1 - Volcanic rocks	1a - volcanic rocks	05/1, 5, 6, 7, 13, 16, 37, 07/1, 14, 17, 20, 22, 49	Final NL - ECII late	Thera	LOCAL
		1b - + coarse tuff → <i>very coarse dense tuff</i> → 07/51 (ECII late)	05/2, 3, 4, 19, 21, 22, 26, 28, 07/ 5, 10, 12, 13, 15, 54, 57			
		1c - + abundant zoned feldspar	05/8, 24, 07/4, 6			
	2 - Volcanic rocks + calc-schist	07/50	ECII late	Thera		
	3 - Volcanic rocks + phyllite/schist		07/08	ECI early	Thera	
Metamorphic	4 - Red phyllite		05/38	ECII early	Thera? (Amorgos?)	
Plutonic	5 - Granite/ granodiorite	5a - absent to few green amphibole → + <i>lava, metamorphic</i>	05/10, 12, 14, 15, 23, 25, 27, 29, 30, 31, 34, 36, 92, 07/2, 3, 7, 11, 16, 18, 19, 21, 23 → 05/11 (ECI late)	Final NL - ECII early	Naxos	IMPORTS
		5b - abundant green amphibole → + <i>phyllite</i>	05/09, 32, 07/09, 46, 53, 56, 58, 59 → 05/35 (ECII early)			
Metamorphic	6 - Talc		3,4,5, 07/47, 48, 52	ECII late	? Western Cyclades	
	7 - White mica schist + garnet ± daub		05/17, 18, without daub: 05/20	ECII early	Ios	
	8 - Schist/gneiss		05/33, 07/55	ECII early	Cyclades	

Table 4.2 Overview of fabric groups of Late Neolithic and Early Cycladic cooking ware from Akrotiri. The two main groups are marked in grey.

Local fabrics

Apart from two outliers, all samples that are thought to be of local origin fell into one large group, characterised by the presence of volcanic rocks and associated minerals (*group 1*). It is important to note that the subdivision of this group does *not* reflect compositional differences that could be related to different production centres or raw material origin; in fact all samples seem to derive from the same or at least from

petrographically indistinguishable sources. The reason for subdividing *group 1* lies in the possibility that the variations in the relative amounts of tuff, lava and plagioclase phenocrysts, which are highlighted through this division, may point to paste manipulation practices as will be explained below. The two outliers assigned to *group 2* and *group 3* respectively, are separated from the main group on grounds of the considerable number of metamorphic rock inclusions found in those samples. However, they still contain a significant amount of volcanic rocks and as the metamorphic rock fragments present are fully compatible with Thera's geology, there is no reason to discount local origin for those samples.

Group 1 - Volcanic rocks

This fabric group is characterised by the presence of lava fragments of intermediate to basic composition, along with fragments of phenocrysts, commonly zoned plagioclase and pyroxenes, and inclusions derived from tuffaceous deposits (Figure 4.4, a-c). Most samples contain predominantly basaltic andesites²¹ of rather trachytic structure with only rarely fragments of more basaltic composition, occasionally glassy and tuffaceous fragments, and abundant small mineral (phenocryst) fragments.

Provenance. The mineralogy of the inclusions seems compatible with lavas from the Akrotiri and Thera series. The presence of small amounts of hornblende fragments in several samples could indicate some sort of contribution of the Lumavari-Archangelos lavas (Figure 4.2, A₂), which are the only ones which are reported to bear hornblende phenocrysts (Nicholls 1971). The overall amount of amphibole in the fabrics, however, seems subordinate when compared to what is reported in literature for the lower series Akrotiri lavas which are exposed to the West of the settlement. Also, much in contrast to the later local fabrics, there is no contribution of the A₁ tuffs discernible in the samples as would be expected from an erosional product derived from the flanks of Mt. Lumavari. This, together with the fact that minor amounts of hornblende also occur in the Thera pumice series, which supposedly made up much of the local environment of Akrotiri (see above), could indicate that

²¹ Strictly speaking, the absence of modal quartz even in the more siliceous lavas of Santorini (Nicholls 1971) does not allow the use of a modal classification for Thera lava. The term 'basaltic andesites' as used here, therefore reflects the composition of the lava fragments as detectable under the petrographic microscope. Chemical analysis might well reveal an actual composition that is more acidic.

clay sources more to the East of the settlement were exploited for the production of cooking ware during the Late Neolithic and Early Cycladic periods. The presence of very rare occurrences of metamorphic rock fragments and, exceptionally, a granitic fragment, in some samples can readily be rationalised by the contribution of xenoliths derived from the volcanic basement whose presence in Santorini's pyroclastic rock deposits is well known (Skarpelis and Liati 1990). Alternatively, metamorphic rock fragments could enter the groundmass as erosional products derived from exposures in the elevations to the South-East of the island (Figure 4.3).²² It should be noted that this fabric does not match the local EC fabrics A and B reported by Vaughan (1990), but seems to fit much better with her intermediate volcanic rock fabric, for which she suggested an off-island origin. Moreover, none of the Early Cycladic cooking ware fabrics recognized in this study would correspond to the previously identified local fabrics A and B (see Table 4.1). As noted earlier, however, it should be kept in mind when comparing the two studies, that the material analysed by Vaughan (1990) comprised material dated to the somehow problematic 'ECIII', which in the notion used in the present study would be placed at the start of Middle Cycladic rather than at the end of the Early Cycladic period. Furthermore, although sampling a broad variety of ceramics, it is not quite clear whether cooking ware pottery had been included in her analytical programme; at least the samples falling in her fabric groups A and B, all derive from pottery sherds of clearly non-cooking ware.

Technology. The rather rounded character of the lava fragments gives the impression that an erosional product derived from lava flows has been used for paste preparation. The presence of some more angular fragments, especially prominent in the phenocryst population, might indicate that the clay-rich raw material had been crushed or ground prior to use. One might expect that gentle crushing of a clayey material would result in fracturing of the larger constituent aplastics along their weakest bonds - which are supposedly the interface between phenocrysts and groundmass and alongside the phenocrysts' crystal planes - while leaving smaller lava inclusions intact. The impression that the raw material has been broken up in some way is reinforced by the presence of textural features, present in a number of

²² The same holds for the rare metamorphic rock fragments identified in a few samples belonging to the later local fabric, *group 9*.

samples, which are of the same composition as the fabric containing the above mentioned rounded lava fragments. Accordingly, the generally finer appearance of *subgroup 1c*, containing abundant fragments of zoned plagioclase, possibly reflects a slightly more thorough crushing of the raw material. On the other hand, the subdivision of *group 1* in subgroups 1a and 1b reflects the presence of various amounts of coarse, mostly angular tuff/pumice fragments in some samples. Samples assigned to *subgroup 1a* contain generally less tuff/pumice fragments than those allocated to *subgroup 1b*. In contrast to the related sample 07/51, however, which clearly represents paste tempering with coarse tuff fragments, the amount of tuff/pumice inclusions in subgroup 1b seems generally too low and their abundance too varied to reflect tempering in the traditional sense of the word. Nevertheless, it is thought that the presence of pumice/tuff fragments in the ceramics might result from their intentional addition to the clay paste rather than from a natural variation of the source, based on the observation that they are present predominantly as coarse to very coarse fragments and underrepresented in the finer fraction. The fact that tuff or pumice deposits can easily be crumbled by hand along with their widespread availability in the environments of the site (see above) would account for their preferred use as tempering agent. An explanation for the addition of rather small and variable amounts could perhaps be provided by the water absorptive properties of the tuffaceous fragments: this volcanic rock type is highly porous and has therefore a high capacity to absorb water. For that reason, its admixture would potentially allow the regulation of a ceramic paste's plasticity through the binding of excess water to the pumice particles. The observation that clearly tuff/pumice tempered ware had been produced (sample 07/51) would suggest that potters probably were aware of such properties. While it is difficult to assess to which degree subgroups 1a-c are related to raw material variability, one could assume that they represent slightly different material or manufacturing traditions. Subgroups 1a and b might reflect a minor variation in the paste preparation, namely an optional step in the manufacturing sequence which is related to the regulation of paste workability. Finally, it should be noted that there is no distinguishable temporal evolution in the early cooking ware fabric, suggesting continuity in the selection of clay sources as well as in the procedures followed in the production of cooking ware through all of the Final Neolithic / Early Cycladic sequence.

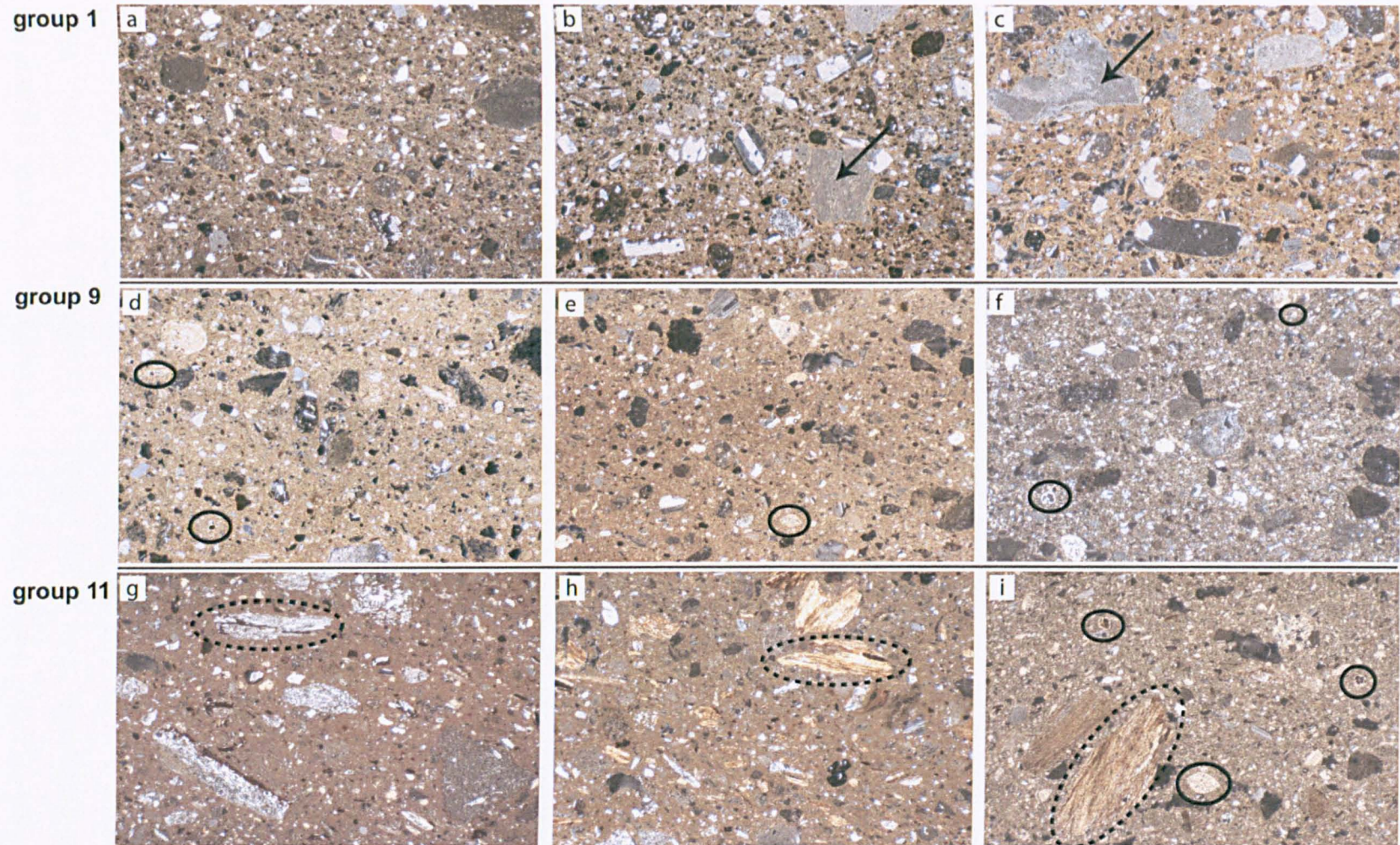


Figure 4.4 Main local fabric groups: *a-c*, group 1: volcanic rocks and tuff/pumice; *d-f*, group 9: volcanic rocks, calcareous, microfossils; *g-h*, group 11: volcanic rocks, calcareous, microfossils and phyllite. Arrows indicate examples of tuff/pumice fragments. Closed circles indicate examples of microfossils (in higher fired samples, these are discernible, if at all, in plane polarised light only). Open circles indicate examples of phyllite fragments. Field of view 7.4 mm.

Group 2 - Volcanic rocks and calc-schist

This sample is characterised by the presence of relatively coarse fragments of calc-schist along with somewhat finer grained rock fragments of volcanic origin (lavas and tuff), the latter similar to the extrusive rocks encountered in *group 1* (Figure 4.5, a). Calc-schists do occur in the pre-volcanic basement of Thera (see above), the composition of this sample is thus fully compatible with a local origin for the related vessel. The fact that the calc-schist fragments are restricted mainly to the coarse fraction indicates their addition to a groundmass which is probably derived from the same or similar deposits than those exploited for the manufacture of *group 1* ceramics.

Group 3 - Volcanic rocks and phyllite/schist

The one sample belonging to this group contains metamorphic rock fragments of phyllitic/schist-like nature together with volcanic lavas of intermediate(?) composition (Figure 4.5, b). Again, the composition of this sample is fully compatible with an on-island origin. However, unlike in *group 2*, the lava fragments present in this sample seem slightly different from what is encountered in the main *group 1*, in that they do not contain larger phenocrysts and are of a generally somewhat more uniform appearance. The fact that the metamorphic rock fragments and related minerals are not restricted to the coarse fraction suggests that plastic phyllitic material was mixed with material derived from a volcanic source. This sample's raw materials are possibly derived from sources in north-east Thera.

Group 4 - Red phyllite

Sample 05/38, which is the only representative of *group 4*, is dominated by low grade metamorphic rock fragments, mainly of a red phyllitic nature (Figure 4.4, c). An Amorgian origin could be suspected for this sample (*cf.* Vaughan's (2006) Red Shale fabric and Hilditch's (2008) 'shale and quartzite fabric'). The sample is, however, not compatible with later Amorgian imports in ECII late contexts at Akrotiri (P.M. Day pers. comm.). It should be noted the phyllites of Santorini are similar to those of Amorgos (Davis and Bastas 1978) and, indeed, the metamorphic rock fragments in this sample are compatible to those found in *group 3* as well as in the later *group 11*. A local provenance for sample 05/38 should therefore not be discounted. Also the presence of an - albeit lone - lava inclusion connects this sample to Thera,

although altered volcanics can be found on a variety of Cycladic islands, including Amorgos (Hilditch 2008). When assuming a Thera provenance, this would suggest, not unreasonably, that the weathered phyllitic clay that was mixed with volcanic earth in the production of *group 3* was also used on its own. As with *group 3*, we could perhaps envisage, based on the scarcity of the fabric within the assemblage and the slightly more distant raw material sources, some sort of connection with an alternate pottery centre. Although the provenance of this sample remains insecure, it has been grouped with the local fabrics since a local origin cannot be excluded.

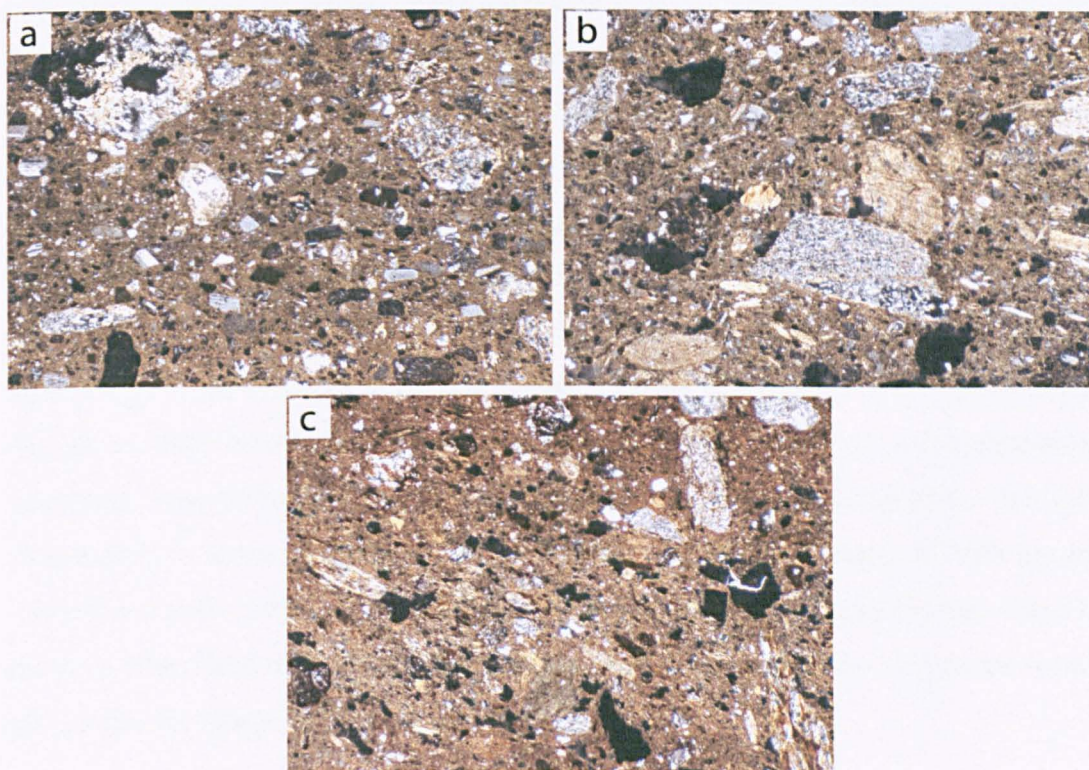


Figure 4.5 Local fabric groups 2-4: *a*, group 2: volcanic rocks and calc-schist; *b*, group 3: volcanic rock and phyllite/schist; *c*, Group 4: red phyllite. The field of view is 7.4 mm.

Imported fabrics

The vast majority of the samples that are believed to represent off-island imports fell into one main group, characterised by the presence of acid to intermediate plutonic rock fragments (*group 5*). The subdivision of this group according to hornblende content reflects the heterogeneous character of its inclusions. The remaining non-

local samples, which contained metamorphic rock fragments of various compositions, could readily be split up according to composition and texture of the inclusions and make up *groups 6 - 8*.

Group 5 - Granite / granodiorite with varying amounts of green amphibole

This group has been further subdivided according to the abundance of green amphibole: *group 5a* includes the samples with no to little green amphibole while the sections assigned to *group 5b* contain abundant amounts of this mineral (Figure 4.6). However, whether this compositional differentiation relates to slight differences in raw material origin or merely reveals the extent of intra-source variation is unclear. All samples contain abundant coarse igneous rock fragments, which may vary in composition from acid to intermediate. Overall, the impression is given that the more acid fragments, which are heavily altered (they frequently contain abundant iron oxides and chert and their shape is rather rounded), derive from some sort of sediment. On the other hand, many of the more basic rock fragments - although their constituent feldspars seem rather weathered - have a somewhat fresher appearance and are more angular. As most sections contain both of these types of rock fragments, although in very varied ratios, they could not be used as determinants for separating the group. Also the otherwise very similar mineralogical composition of the two subgroups (e.g. in terms of the presence of accessory sphene in samples of both groups and the occurrence of rare, rounded and heavily altered lava fragments that seem to come in with the plastic material) led to the decision that the two subgroups would not qualify for independent grouping.

The two related samples, 05/11 and 05/35 (related to subgroups 5a and 5b respectively), are similar in what concerns their constituent rock and mineral fragments. Sample 05/35 was separated from *group 5b* as it contains additionally frequent metamorphic rock fragments. Sample 05/11 does not seem to have much in common with *group 5a* at first sight; it contains a variety of fairly differing rock fragments, such as plenty of volcanic lava and low grade metamorphic rocks and chert fragments. However, its - tentative - allocation adjacent to group 5a is based on the presence of sphene, amphibole rich rock fragments and heavily altered feldspars.

Provenance. The mineralogical composition of the inclusions seems entirely compatible with a Naxian origin of the sherds. Although, seemingly, amphibole contents as high as found in the samples of *group 5b* have not before been identified in Naxian Bronze Age pottery (J. Hilditch pers. comm; P.M. Day pers. comm.), there is no reason to reject a Naxian origin for these samples just because of the lack of comparative material. In fact, the geology to the West of the island does seem to provide a near perfect match for the inclusions observed within the whole of *group 5*. The western part of the island is dominated by granodiorite intrusions of fitting mineralogy - especially the presence of sphene (IGME 1973), an accessory mineral which has been identified in virtually all ceramic samples of *group 5*, is noteworthy - and coarse grained silicified arkoses derived from these intrusions (see Hilditch 2008 for a brief outline of the geological landscape of Naxos with reference to pottery production). Also the heavily altered, in all probability fairly transported volcanic rock fragments, which are present in the ceramic groundmass, are compatible with, and have previously been identified in, pottery from Naxos.

Technology. As mentioned above, *group 5* encompasses a wide variation in terms of inclusions (rounded rather sedimentary versus more angular, acid to intermediate) as well as groundmass (very fine deep red to rather dull coloured with abundant fine mineral fragments), advocating caution when it comes to assess specific manufacturing techniques. It probably suffices to note at this point that - although almost certainly attained with varying methods (some samples seem quite clearly the result of tempering a very fine plastic material with what is probably a coarser sediment, while in other cases, higher angularity of the inclusions along with fine fragments of associated minerals in the groundmass might suggest crushing of raw materials) - the resulting compositions and textures of the finished ceramic products are very similar. In view of the non-local character of the sherds and subsequent lack of contextual information, a more in-depth discussion of raw material sourcing and/or technology seems ill-advised, at least without further information on contemporary cooking ware assemblages on Naxos itself.

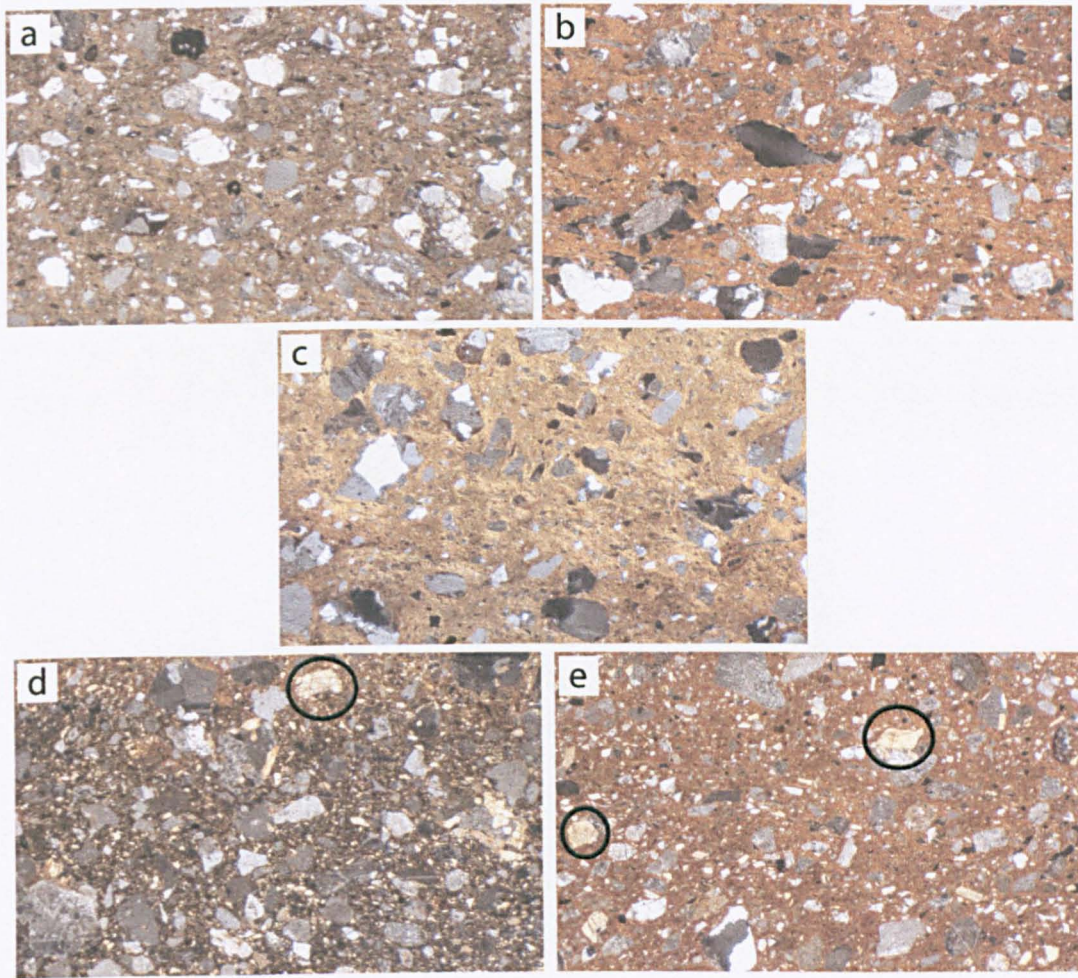


Figure 4.6 Imported fabric groups 5: *a-c*, group 5a: granite/granodiorite with no to little green amphibole; *d* and *e*, group 5b: granite/granodiorite with abundant green amphibole. Closed circles indicate examples of amphibole (these are in most cases easily distinguishable in plane polarised light due to their distinctive green colour). The field of view is 7.4 mm.

Group 6 - Talc

The samples that belong to this fabric group are dominated by inclusions derived from a talc deposit (Figure 4.7, a). This fabric is well known from EC II levels at Akrotiri and elsewhere, can easily be distinguished macroscopically by its soapy feel and is commonly referred to as Talc Ware. It is thought to derive from the western Cyclades although its exact origin remains unclear to date (Vaughan 1990; Vaughan and Wilson 1993; Hilditch 2008).

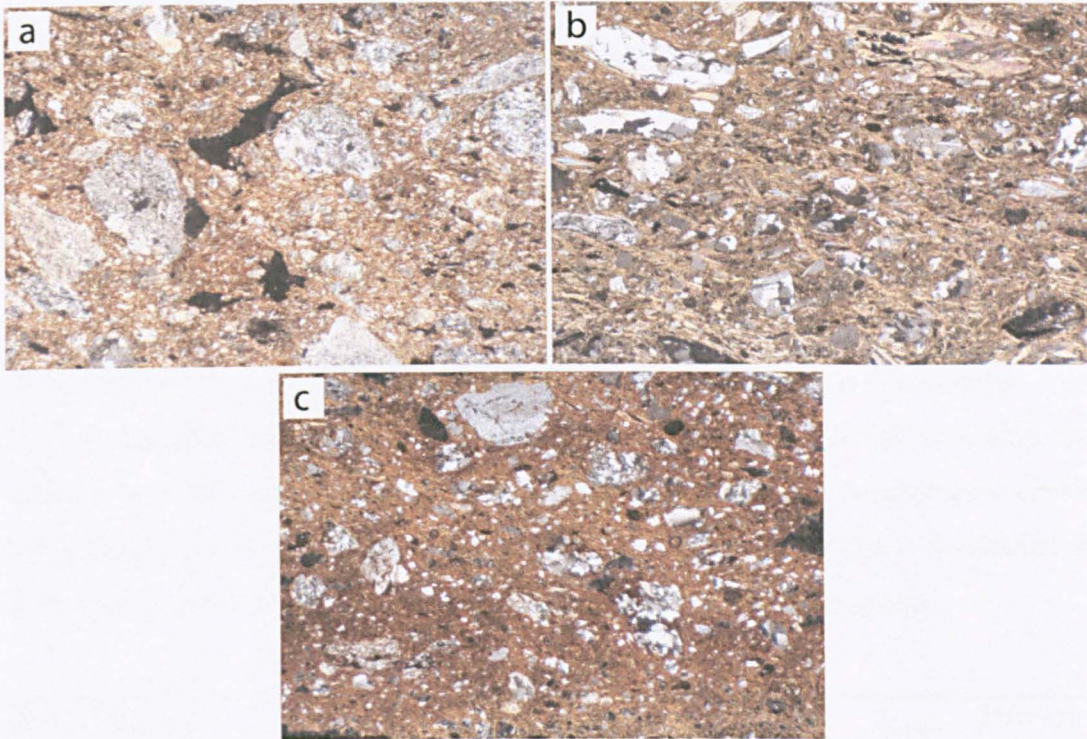


Figure 4.7 Imported fabric groups 6-8: *a*, group 6: talc; *b*, group 7: white mica schist with garnet \pm daub; *c*, group 8: schist/gneiss. The field of view is 7.4 mm.

Group 7 - White mica schist with garnet \pm daub

This fabric is dominated by metamorphic rock fragments characterised by tabular white mica and comparably rather high amounts of garnet (Figure 4.7, b), indicating an origin from the island of Ios (Hilditch 2008). The daub fragments which are present in samples 05/17 and 18 entered the paste possibly during forming and might not represent intentional tempering. Both samples are fragments of thin baking plates which probably have been mould made. Accordingly, the daub fragments could either derive from an original mould, or, in the alternative case of forming the plates directly on the ground, be merely pieces of some sort of building material that got accidentally incorporated in the ceramic paste. The mineral inclusions in the daub fragments are compatible to the rock fragments present in the ceramics, indicating a similar geographical origin for the ceramic and the incorporated building materials.

Group 8 - Schist/gneiss

This metamorphic fabric, characterised by fragments derived from metamorphic rocks (Figure 4.7, c), is not diagnostic as concerns its origin and seems compatible with many schist deposits across the Cyclades (Hilditch 2008).

4.4.2 Fabric groups of the Middle Cycladic Phases A and B

Relatively few fabric groups were identified for the cooking ware from Phases A and B of the Middle Cycladic period (Table 4.3). Most samples fell into one, quite heterogeneous fabric group, characterised by volcanic rocks and sometimes abundant microfossils. Only one sample not compatible with local origin - dominated by metamorphic rock fragments - could not be assigned to this main group.

Main character of inclusions	Fabric groups	Subgroups and related samples	Sample numbers	Time period	Inferred provenance	
Volcanic	9 - Volcanic rocks, calcareous and microfossils	→ rounded inclusions → coarse tuff	05/39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 50, 51, 52, 62, 07/24, 25, 26, 27, 28, 29, 30, 31, 32, 35, 36, 38, 39, 40, 41, 42, 43, 44 → 05/49(MCA) → 05/91(MCA?)	MC A and MC B	Thera	LOCAL
Metamorphic	10 - White mica-biotite-schist + rare volcanics		07/34	MC B	Naxos	IMPORTS

Table 4.3 Overview of fabric groups of Middle Cycladic cooking ware from Akrotiri belonging to Phases A and B. The main group is marked in grey.

Local fabric

All samples whose composition is compatible with local origin fell into one group (*group 9*), characterised by the presence of volcanic rocks in a predominantly calcareous groundmass which, although rather heterogeneous, was not further subdivided in the course of this study.

Group 9 - Volcanic rocks, calcareous and microfossils

This fabric group is characterised by the presence of volcanic rock fragments which consist, like in *group 1*, of lava fragments along with associated phenocrysts (commonly zoned plagioclase and pyroxenes, but also the occasional amphibole) and inclusions derived from pyroclastic deposits (Figure 4.4, d-f). Much in contrast to the earlier local fabric, though, the volcanic rock fraction of *group 9* is dominated by pumice/tuff derived inclusions, and contains in most cases fewer lava fragments, which are of a generally more weathered appearance. Another striking difference is the presence of sometimes abundant microfossils in the groundmass²³. Virtually all samples contain foraminifera or their remnants, albeit in highly varying amounts and sometimes detectable only in plane polarised light. The heterogeneous character of this group results from differences in the abundance of inclusions and in the appearance of the groundmass, the latter due to variations in firing conditions and calcite content.

Sample 05/49 differs from the other samples by the well rounded character exhibited by some of its inclusions, which seem rather heavily altered, possibly indicating the addition of a sandy material in this specific case. Sample 05/91 could be linked to sample 07/51 (a sample related to group 1) on account of the impression it has been tempered with tuff. The presence of microfossils, however, led to the assignment of this sample to group 9. It was obtained from a vessel whose assignment to either MC Phase A or ECII late is unclear (*cf.* Appendix I).

Provenance. The volcanic rock fragments in the coarse fraction of this group are very much compatible with the tuffs and lavas of the Lumavari-Archangelos massive to the West of the Akrotiri settlement (Figure 4.2, A₁ and A₂). The evidence is plentiful: a first indication is the occurrence of amphibole, which is present not only as phenocrysts but also, at least in one case, in a distinctive piece of hornblende lava,

²³ The species present in the ceramics seem to belong to both shallow and deep-water species. As shown by Friedrich *et al.* (2000), the composition of the fossil assemblages present on the slopes of the Lumavari-Archangelos complex varies according to elevation. A full analysis of the species present in the ceramics could therefore potentially shed light on questions related to raw material procurement and processing, as the characterisation of various species and their relative abundance within a sample potentially enable distinction between practices, such as the use of weathered erosional products or the admixture of specific fossil-bearing sediments to less calcareous material.

typical for the A₂ series. Also the chalcedony which is observed in a couple of samples is well known to occur in the A₁ tuffs (Fouqué 1879). But the most striking indication is the concomitant presence of microfossils, mostly foraminifera, since, as discussed in detail above, the A₁ tuffs are well known for being fossil-bearing. We might thus assume that the raw materials used from the Middle Cycladic period onwards were based on some sort of erosion product, derived from the immediate vicinity of the site. Such a product seems to be in many respects comparable to the clay sample analysed by Friedrich *et al.* (2000). In terms of raw material acquisition, the transition from the Early Cycladic lava-dominated non-calcareous fabric, to the Middle Cycladic, predominantly pumice-bearing and calcareous one, seems to represent a move westwards. In contrast to the earlier local fabric *group 1*, this fabric seems to correspond well to previously analysed, local Early and Middle Cycladic pottery (*cf.* Fabric A and B: Vaughan 1990; Vaughan *et al.* 1995).

Interestingly, the use of a calcareous paste at Akrotiri remains restricted to non-cooking vessels before the onset of the Middle Cycladic period (Vaughan 1990; P.M. Day and M. Relaki pers. comm.). For cooking ware, exclusively non-calcareous clays seem to have been employed invariably during the whole of the Early Cycladic period (*group 1*) and the adoption of the calcareous recipe did not take place until the transition to Middle Cycladic Phase A, at which point it was already established for other types of vessels, such as in the local production of dark-on-light ware.

Technology. This fabric encompasses a fairly heterogeneous group of samples. The presence of textural features in some sections, frequently argillaceous clasts of roughly the same composition as the surrounding groundmass, might indicate that the clay-rich raw material had been crushed or ground prior to use, as has been suggested by Vaughan *et al.* (1995). This would point to a continuity of raw material preparation practices from the previous periods (*cf.* discussion to *group 1*) and their adoption to the new set of material. On the other hand, some more marl-like textural features, together with colour variations that are observed in the groundmass of various samples, might indicate the admixture of a marl-rich sediment - such as can be found in coastal regions of the Lumavari-Archangelo complex (Friedrich *et al.* 2000) - to a less calcareous material. It cannot, however, be determined conclusively, whether the variability exhibited by the samples in *group 9* is due to raw material

heterogeneity or reflects differences in manufacturing techniques (i.e. the deliberate addition of calcite rich sediments). A further variation exhibited by some samples of this group is the relative amount of coarse pumice/tuff fragments. As argued in the discussion of *group 1*, one possible explanation for the occurrence of coarse tuff/pumice temper might be their intentional addition to the clay paste, possibly as a plasticity controlling agent.

While within the Early Cycladic material of *group 1*, no temporal development was distinguishable, one could perhaps identify a tendency exhibited by a number of the earlier Middle Cycladic sherds, to what appears to be fairly dense tempering with coarse tuff/pumice fragments, exceptionally high firing temperatures, lesser amounts of microfossils and increased amounts of opaques in the groundmass. The other early Middle Cycladic samples, like most of the Middle Cycladic Phase B sections, feature inclusions which are more openly spaced, generally lower firing temperatures and a more calcareous matrix. The significance of this variation, however, remains open to speculation. The interpretation of the higher variability observed in the earliest Phase of the Middle Cycladic as reflecting an initial 'trial phase' with the new raw materials, which proceeds the establishment of a more consistent production process as observed later, seems - although tempting - unlikely, as a certain expertise with the calcareous recipe can be assumed since it had been used beforehand in the production of decorated ware (Vaughan 1995; P.M. Day and M. Relaki pers. comm.).

Imported fabrics

Only one non-local sample was attested for the earlier Middle Cycladic periods. It did not group with any other sections and makes up its own metamorphic fabric (*group 10*).

Group 10 - White mica-biotite-schist and rare volcanics

The presence of mica schist containing only very infrequent garnet, in conjunction with rare volcanic rock fragments (Figure 4.8, a), suggests a Naxian origin for this sample. Contrary to what has been said earlier for *group 5*, the mineralogy of this sample, which, besides the few lava fragments, contains exclusively metamorphic

inclusions, seems to fit better with the eastern part of Naxos (Hilditch 2008), perhaps indicating a different workshop on Naxos.

4.4.3 Fabric groups of the Middle Cycladic Phase C and the Late Cycladic IA

Most of the samples that belong to the Middle Cycladic C and Late Cycladic period fell into one, again rather heterogeneous, fabric group, which is thought to be of local origin. The samples of *group 11* are, as the earlier Middle Cycladic ceramics, characterised by volcanic rocks and microfossils, but contain, in addition, phyllitic and schistic metamorphic rock fragments. Three samples could be allocated to the previously described *group 5a*, of probable Naxian origin, and another one is related to this fabric. The three remaining samples did not group with any other sections and represent their own metamorphic fabric.

Main character of inclusions	Fabric groups	Subgroups and related samples	Sample numbers	Time period	Inferred provenance	
Volcanic	11 - Volcanic rocks, calcareous, microfossils + phyllite/schist	→ <i>very calcareous, very open</i>	05/53, 54, 55, 56, 57, 58, 59, 60, 61, 63, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 80, 81, 83, 84, 85, 86, 87, 88, 89, 90, 07/33*, 37* → 05/93 (LC)	MC C and LC	Thera	LOCAL
Plutonic	5 - Granite-granodiorite	5a - absent to few green amphibole → + <i>metam.</i>	05/64, 65, 82 → 05/66 (MC C - LC)	MC C and LC	Naxos	IMPORTS
Metamorphic	12 - White mica schist + very altered feldspars	→	05/78, 79 → 07/45 (MC C)	LC	Naxos	

Table 4.4 Overview of fabric groups of Middle Cycladic Phase C and Late Cycladic cooking ware from Akrotiri. The main group is marked in grey. Samples marked with * are dated to the Middle Cycladic Phase B but are included in this table for reasons stated in the text.

Local fabric

As with the earlier material of *group 9*, all samples with a composition compatible to local origin fell into a fairly heterogeneous group, which was not further subdivided in the course of this study.

Group 11 - Volcanic rocks, calcareous and microfossils with phyllite/schist fragments

This fabric group is characterised by volcanic rock fragments and microfossils but, unlike the earlier local fabric *group 9*, contains additionally significant amounts of phyllitic inclusions (Figure 4.4, g-i). Apart from the additional phyllitic material, the paste seems essentially unchanged from the local recipe identified in the first two phases of the Middle Cycladic period. Much as with *group 9*, the volcanic rock fragments are accompanied by associated phenocrysts and the tuff/pumice fragments exceed the lava-related inclusions. Also the presence of very varying amount of microfossils in the groundmass is reminiscent of *group 9*, as are the argillaceous and marl-like clasts which are present in some samples. The relative amount of the metamorphic rock fragments varies, but is in all cases comparable to or exceeding the amount of volcanic inclusions. Again, there seems to be considerable variation within this group in what concerns firing conditions as reflected by the wide-ranging appearance of the samples' groundmass.

Sample 05/93 differs from the other samples by the scarcity of its inclusions, together with an exceptionally calcareous groundmass.

Provenance. As already mentioned, if we disregard the metamorphic component, the ceramic recipe seems to be identical to what has been employed earlier, and therefore most likely represents continuing use of sources immediately to the West of the settlement (*cf.* *group 9*). The case is, however, somewhat different for the phyllitic constituents of the ceramics belonging to *group 11*. It is assumed that the metamorphic rock fragments are derived from the area around Mt. Profitis Elias to the East of Akrotiri, which is made up of limestone transitional to marble, overthrust on some phyl-

lite/schist deposits.²⁴ The latter are exposed in the valleys around the massif, and in particular at the Sellada pass (Figure 4.3). The presence of phyllitic inclusions in a material clearly derived from the West of Akrotiri therefore implies that raw materials from different locations were brought together at the settlement in the production of cooking vessels in the Late Middle and Early Late Cycladic periods. The possible incentives for the drastic change which occurs in the paste recipe employed for cooking ware at the transition to Middle Cycladic Phase C at Akrotiri, i.e. the emergence of a novel recipe involving the addition of phyllitic material, will be discussed in Chapter 10. When compared to earlier petrographic analyses, the findings of this study seem to fit well with the previous descriptions of Late Cycladic pottery from Thera (Fouqué 1879; Einfalt 1978; Williams 1978).

Technology. Besides what has been said for *group 9*, which is equally valid for this group, the additional presence of metamorphic rock fragments in all samples clearly reflects the intentional admixture of a different material from a distinct source as has been suggested by Einfalt (1978). The significance of this drastic and widespread change in manufacturing techniques, which seems to have been implemented on a general level by the Middle Cycladic Phase C, will be discussed in detail later on (Chapter 10). At this point it should only be noted that the temporal framework, as sketched in Table 4.4 is a slight simplification, as, in fact, two of the samples belonging to fabric *group 11* are of an earlier date than the remainder, deriving from levels dated to the Middle Cycladic Phase B. It is perhaps significant that these two 'pioneering' samples are both obtained from tripod legs, and, moreover, represent the earliest examples of this typically Cretan shape. Tripod cooking pots are not known from earlier phases, but, from Phase C of the Middle Cycladic period onwards, are a firmly established component of the ceramic repertoire at Akrotiri.

²⁴ Metamorphic rocks are also exposed at certain places in the inner caldera walls, alongside granitic intrusions (see above). It seems more probable that the phyllitic material used in the production of cooking ware had been procured from around Mt. Profitis Elias, not so much because of accessibility considerations but more on grounds of the mineralogical composition of the fragments. An acquisition from the inner caldera walls possibly by sea, however, does remain an option which cannot be excluded.

Imported fabrics

The samples which are characterised by the presence of plutonic rock fragments of acid to intermediate composition, belonging to *group 5* (see above), argue for a continuation of the connection with western(?) Naxos, established already during the early Cycladic periods at the site. The three remaining samples did not group with any other sections and represent their own metamorphic fabric (*group 12*).

Group 12 - White mica schist and very altered feldspars

Also for the samples assigned to the metamorphic fabric *group 12*, which is characterised by fragments derived from mica schists and by the occasional occurrence of heavily altered feldspars (Figure 4.8, b), a Naxian origin may be considered. As has been argued previously for *group 10*, the presence of exclusively metamorphic rock fragments points to an origin more to the East of the island. Consequently multiple connections with this island could be suspected.

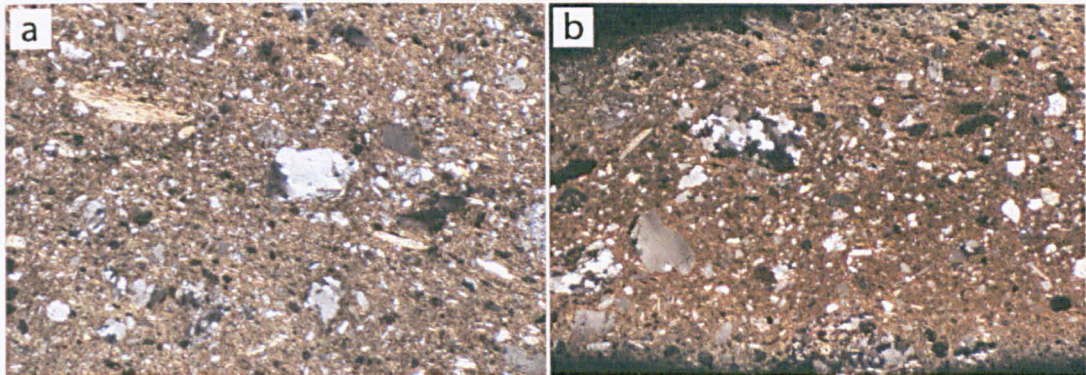


Figure 4.8 Imported fabric groups 10 and 12: *a*, group 10: white mica-biotite-schist + rare volcanics; *b*, group 12: white mica-schist + altered feldspars. The field of view is 7.4 mm.

4.4.4 Summary

Besides confirming continuing importation from other Cycladic islands during the Bronze Age, with Naxos seemingly a main player, the petrographic analysis of the cooking ware assemblage at Akrotiri revealed a clear tripartite division of the locally produced ware in terms of paste recipe. In the Late Neolithic and during the whole of the Early Cycladic period, the production of cooking ware was based on a non-

calcareous recipe. This seems to have been abandoned in favour of a novel - at least in what concerns its application to the manufacture of cooking vessels - calcareous formula with the transition to the Middle Cycladic period. The second drastic shift in production procedures is the addition of phyllitic material to this, by then established, calcareous paste, a practice which first manifests itself in a few rare examples of the Middle Cycladic Phase B, but is generally adopted by the Middle Cycladic Phase C. These changes which occur in paste preparation throughout the Bronze Age at Akrotiri will be assessed in view of their technological aspects in Chapter 10, taking into account the requirements put on cooking ware pottery and the resulting differences in performance properties. Additionally, the importance and implications of the latter change in manufacturing technique will be examined in view of the ongoing discussion of minoanisation processes in the region and on Akrotiri itself.

As mentioned earlier, the above presentation and discussion of the petrographic analyses has focussed on the identification of the vessels' origin and the assessment of manufacturing procedures. Some features that will become essential when it comes to evaluate the ceramics' performance characteristics have not been referred to in the present chapter. These include, besides the obvious firing temperatures, characteristics for whose identification thin section petrography proves ideally suited, such as distinct debonding of inclusions - arguably playing a vital role in fracture toughness - or preferred orientation of elongated voids - important when it comes to infer a material's heat transfer properties.²⁵ These issues are left to be discussed in Chapter 10, when the results of the analyses on the archaeological material will be integrated with the archaeological evidence and interpreted taking into account the outcome of the mechanical and thermal tests performed on replicates.

²⁵ Essential parameters are the nature, size, shape, amount and orientation of inclusions, but equally important are size, shape and orientation of pores as well as debonding of inclusions. Petrographic analyses, especially those preoccupied with provenance assessment, frequently neglect these factors, not allowing the data gathered to be employed for later performance assessments. Especially for utilitarian assemblages, it would be desirable to tap the full potential of the technique and record information which will enable a performance assessment of the pottery more systematically when a programme of petrographic analysis is run.

Chapter 5

X-ray diffraction, infrared spectroscopy and scanning electron microscopy

Powder XRD, FT-IR and SEM were used in addition to thin section petrography to further analyse the archaeological assemblage. They were employed mainly for the identification of the samples' mineralogical composition and for firing temperature estimations. This additional data allows further refinement of the differing techniques of manufacture which have been identified by thin section petrography, as well as validating conclusions reached in the last chapter. This chapter presents these complementary methods and their results and integrates the newly obtained data with the findings of the petrographic analysis. It is divided into three sections, one for each analytical technique.

The results of the analyses of samples belonging to the four main petrographic fabric groups will be discussed in this chapter. These are the three main local groups, group 1 - *volcanic rocks*, group 9 - *volcanic rock, calcareous and microfossils* and group 11 - *volcanic rock, calcareous, microfossils and phyllite/schist*, as well as the largest imported one, group 5 - *granite/granodiorite with green amphibole*, which is thought to be of Naxian origin (*cf.* Chapter 4). Due to reasons of space and clarity, the discussion of the results is generally restricted to overall group characteristics and refers only exceptionally to specific samples. For a detailed listing of all results, including several additional samples from minor fabric groups, the reader is referred to Appendix IV.

5.1 X-ray diffraction

X-ray diffraction has found wide application to inorganic as well as to organic compounds (a famous example being the solution of the DNA structure), as it is a powerful tool to determine the structure of solid, crystalline substances, with a resolution down to the atomic level.

Much more important for its application to archaeological material, however, is the use of powder XRD as a routine method to identify the crystalline phase(s) present in a sample of unknown composition. This can be achieved through comparison with diffraction patterns from reference collections and allows the identification of the crystalline phases in a sample. It should be emphasised that only the *crystalline* compounds, such as minerals derived from rock temper or thermally unchanged clay minerals, as well as crystalline high temperature phases cause interference patterns and become visible in an XRD diagram. Poorly crystalline or amorphous phases, such as the unstructured glassy matrix of high-fired samples or volcanic glass inclusions, elude identification²⁶.

5.1.1 The use of X-ray diffraction in the analysis of archaeological ceramics

X-ray diffraction is used widely to identify mineralogical phases in archaeological pottery. These crystalline phases can be assigned to different stages in the life-cycle of a vessel, including origin, production and burial (Maggetti 1982). Accordingly, they can be classified as *raw materials* (such as clay minerals and minerals derived from temper material), *firing products* (newly formed high temperature phases, or thermally changed raw materials), and minerals formed during *burial*. Their identification therefore potentially reveals information on one or more of the corresponding stages in the life cycle of the ceramics.²⁷

X-ray diffraction has been used, together with other methods, to determine and distinguish between different *paste recipes* (e.g. Maggetti and Schwab 1982). Attempts at establishing the technique as a stand-alone tool for such purposes (Eiland and Williams 2001), however, must be viewed with a great deal of caution. When coupled with a comparison to the geographical environment of a site, XRD analyses might

²⁶ In cases where the glassy phase makes up a substantial part of the sample volume, this is commonly reflected in a broad hill at low 2θ values in the resulting diagrams.

²⁷ In reality, however, such a classification is problematic, as many of the minerals can occur in several of those categories, and in most cases it is not possible to decide conclusively on a mineral's origin by XRD analysis alone. Some of those ambiguous phases include *anorthite* and the *pyroxenes* (both frequent minerals in rock-temper but also the main high temperature phases that are formed in calcareous clays), the clay mineral smectite (either present from the original clay paste or neo-formed from a glassy phase during burial) and zeolites (usually referred as a secondary mineral, but see this study for incorporation of a zeolite in the ceramic body clearly during manufacture).

potentially provide information regarding provenance. However, due to the ubiquity of the commonly identifiable minerals, the technique can be of assistance for the provenancing of ceramic artefacts only in exceptional cases. An example of such a case will be presented in detail below.

More widespread is the use of the method to estimate *firing temperatures* of archaeological pottery. When assessing the ancient firing temperatures, the presence or absence of certain mineral phases is compared to their respective stability ranges, sometimes in conjunction with refiring experiments on unfired or low-fired samples (Maggetti 1982). Furthermore, the identification of specific minerals may hint at the prevailing firing atmosphere (Edwards and Segnit 1984). In general, however, the use of a 'mineralogical temperature scale' (Heimann 1982, 90), is problematic when dealing with archaeological ceramics, as the nature of the raw clays is unknown in the majority of cases. Since it is not possible to determine in retrospective whether a mineral has been present in a paste prior to firing, the absence of a phase in a diffraction pattern by itself is in the majority of cases not sufficient for estimating a firing temperature range. Also, several minerals that form upon firing (e.g. the feldspar anorthite) are often already constituents of the raw paste. Other complications involve the formation of minerals outside their stability ranges and the rehydroxylation and structural reconstitution of thermally altered clay minerals during burial and their neoformation from amorphous matter (Maggetti 1982). All these factors may lead to either under- or overestimation of the actual firing temperature.

Finally, the method has been used to determine *alteration* products. Poorly defined, thermally unstable smectite is thought to have been formed during burial (Maggetti 1982), as is the zeolite analcime (Buxeda 1999; Buxeda *et al.* 2001).

When analysing ancient pottery with XRD methods, the limitations of the technique have to be borne in mind. Firstly, as already mentioned, amorphous phases will not be detected. Secondly, archaeological ceramics are often complex mixtures of various minerals and the resulting patterns, especially those of coarse pottery, can become rather complex. Also, many minerals, such as the feldspars, form complex solid substitution series, of which databases usually only provide the endpoint patterns. This makes an analysis that goes beyond the mere identification of the preva-

lent minerals families in most cases unfeasible. Thirdly, especially with coarse ceramics, it cannot safely be assumed that representative patterns are recorded, because minerals may be over- or underrepresented in the powder mixture analysed, since in most cases only a small piece of a sherd is available for analysis. Finally, powder XRD analysis is a bulk method and does not allow the retrieval of textural information. These restrictions make thin section petrography the method of choice when it comes to determine the mineralogy of a ceramic's *temper material*. X-ray powder diffraction, however, does provide additional information that cannot be obtained by petrographic methods. In particular, it facilitates the identification of crystals which are too small to be identified under the polarising microscope ($<30\mu\text{m}$), such as *clay minerals* and neo-formed *high-temperature phases*.

5.1.2 Results of the X-ray diffraction analyses of the Akrotiri cooking ware

X-ray diffraction patterns were obtained from randomly orientated powder samples. A small piece was broken from a sherd, thoroughly cleaned by removing the surface with a tungsten carbide drill head, and then ground in an agate mortar. All samples were measured with a Siemens D 500 diffractometer with $\text{Cu-K}\alpha$ radiation. Data were collected from $4\text{-}50^\circ 2\theta$, using a step width of $0.03^\circ 2\theta$ and a count time of 4 seconds.

In the following section, the results of the XRD analyses on the archaeological samples is presented and compared to the petrographic data. From each of the main groups, several samples were chosen for subsequent XRD analyses, primarily to identify clay minerals and to refine the firing temperature ranges. As stated at the beginning of this chapter, the discussion is restricted to the four main petrographic groups: the local groups *1*, *9* and *11* and the imported *group 5* (*cf.* Chapter 4) and focuses on the general traits of a group, rather than on the individual results of single samples. For those detailed results the reader is referred to Appendix IV, section A.

Group 1 - Volcanic rocks

Group 1 is the predominant local cooking ware fabric in the Final Neolithic and Early Cycladic periods at Akrotiri. The XRD diagrams of all samples of this group are dominated by reflections that were compatible with the typical pattern produced by anorthite (*cf.* Figure 5.1). This indicates that the prevailing crystalline phase is a calcium-rich plagioclase. Indeed, plagioclase has been identified by petrographic analysis as phenocrysts and as groundmass laths in lava fragments, but is also present as isolated minerals. Quartz, which could not be identified as macroscopic grains by petrographic analysis, was detected in variable amounts, from negligible to substantial, but never exceeding the plagioclase content. The pyroxene augite was detected in almost all samples; this mineral is a phenocryst phase of the constituent lava fragments and has been identified in all petrographic thin sections. Similarly, the exceptional determination of traces of hornblende in one sample is not surprising, since the results of the petrographic analysis account for rare occurrences of this mineral. Iron oxide was found in several cases in subordinate amounts, while calcite was not detected in any of the samples, confirming the earlier impression that a non-calcareous volcanic earth was used in the production of the local cooking ware during the earlier phases of the Bronze Age at Akrotiri. Illite/muscovite²⁸ was the main clay mineral that could be detected, although apparently rather poorly crystallised. In most cases, only the 110 reflection was clearly identifiable in the XRD patterns, a phenomenon which has been related to high firing temperatures (Maggetti 1982). In this study, however, very poorly developed basal reflections are also observed in samples belonging to the later local group 9 where they do not seem to correlate to firing conditions. For the present case study therefore, it must be assumed that the effect is due to poorly developed crystallinity of the raw material - present from the outset - rather than reflecting a loss of structure during firing.

Finally, traces of the zeolite clinoptilolite were found in two samples and suspected in three others. This mineral, a common post-depositional alteration product of pyroclastic rocks, is a well-known component of the A₁-tuffs near Akrotiri (see Chapter 4). Clinoptilolite is indeed found in substantial amounts in most of the samples

²⁸ Illite/muscovite cannot be distinguished by powder XRD and are therefore referred to together.

analysed in group 9 and 11 (see below), which are thought to derive from those rocks. It seems therefore worthwhile to discuss the occurrence of this mineral, which is a rather unusual component of archaeological ceramics, in some more detail.

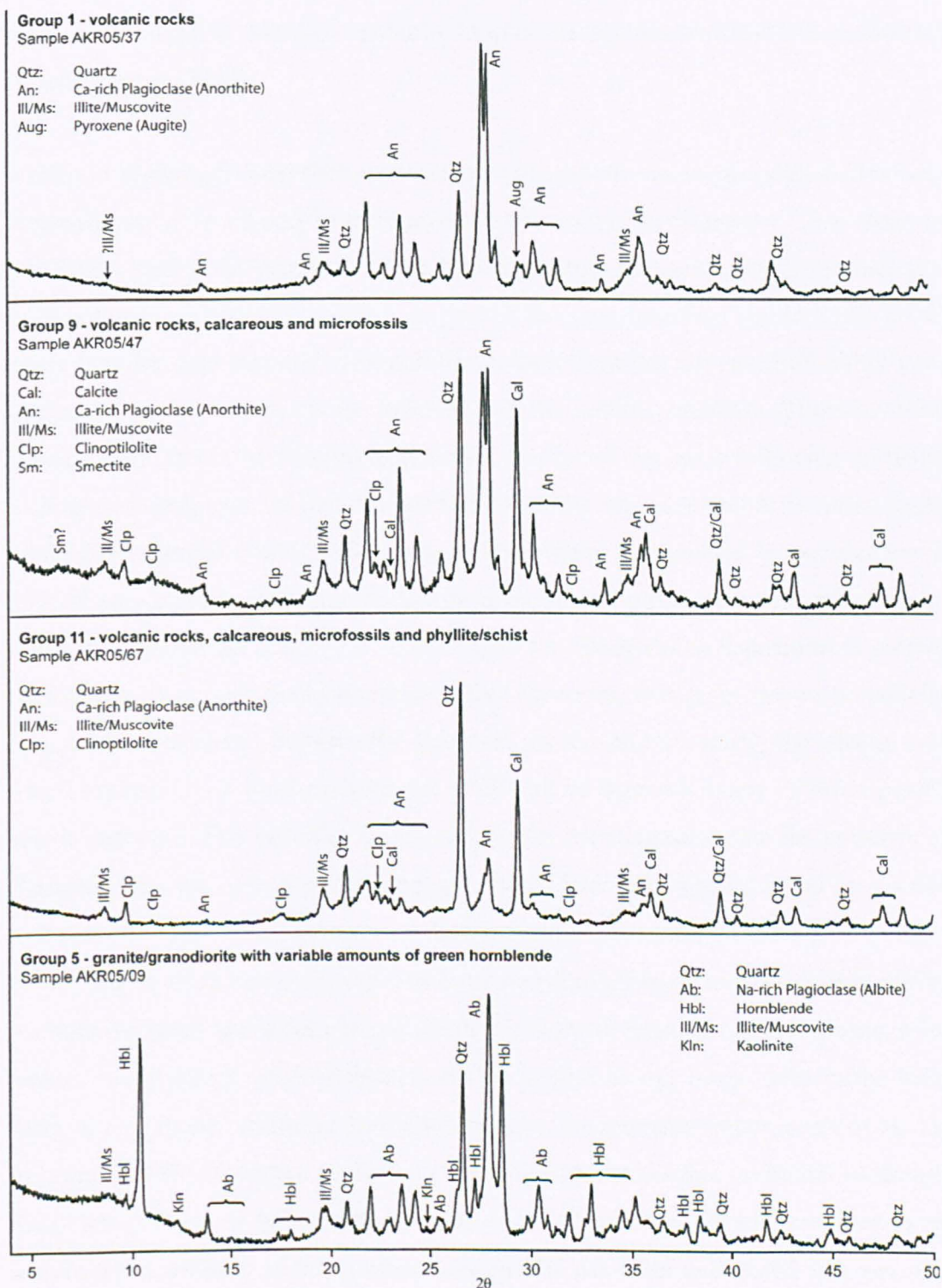


Figure 5.1 X-ray diffraction patterns of representative samples for each main fabric group. The measurements were performed on randomly orientated samples. The assignment of the reflections is indicated.

In the later local fabrics of group 9 and 11 (discussed below), microfossils, another common component of the A₁-tuffs, accompany the zeolite. It can be safely assumed for those samples that clinoptilolite is incorporated into the ceramics as part of the raw materials. This impression is reinforced by the fact that erosional products of these tuffs, found at Akrotiri, contain clinoptilolite besides clay and other minerals (Friedrich *et al.* 2000).

Unlike in these later local fabrics, however, clinoptilolite is not accompanied by microfossils and is found only in trace levels in a few samples of group 1. This observation could lead to the rejection of the hypothesis that the zeolite had been incorporated into the ceramics of group 1 as part of the raw materials. Instead, one could argue that the occurrence of clinoptilolite in these samples derives from either neoformation during burial, as is observed for the zeolite analcime (Buxeda 1999; Buxeda *et al.* 2001), or from precipitation in the buried ceramics following diffusion from the environment. In fact, this particular zeolite was detected in Permian fossil bones from Zambia (Davis 1981), where its presence is explained by penetration of mineralising thermal water into porous bone tissue and subsequent deposition. Theoretically, a similar process could be envisaged for clinoptilolite deposition in pottery buried in a place with volcanic activity, like Santorini, that gives rise to potentially favourable conditions. Importantly, however, in the present study, the zeolite was found exclusively in local samples and could not be detected in any of the imported sherds analysed. This provides strong support for the suggestion that the presence of clinoptilolite - not only in group 1 but also in the later local groups 9 and 11 - is due to its incorporation as a raw material during production (either with tempering material or as part of the groundmass) and is neither formed nor deposited during burial. As both imported and local pottery sherds are derived from the same deposits, a selective incorporation or neoformation of the zeolite during burial only in the local fabric seems highly unlikely. An explanation for the arguably lower levels of zeolite in group 1 when compared to the later groups (with the notable exception of sample 05/02 which contains rather high amounts of clinoptilolite), might be provided by an assumption expressed in the previous chapter. It has been postulated that volcanic earth from a geological distinct source, probably to the East of the settlement and buried today under the pumice layers of the Minoan eruption, has been used in the production of the ceramics assigned to group 1. Either this source contained rela-

tively lower amounts of clinoptilolite, or the tuff temper which was assumedly added to the paste (*cf.* Chapter 4) was obtained from non-fossiliferous tuffitic layers of the Akrotiri series. The examination of the thin sections of those samples of group 1 which contain clinoptilolite indicates that the mineral enters the ceramics of this group alongside the tuff/pumice fragments: all these sections feature tuffs/pumice fragments, usually with a speckled appearance (caused by the zeolite?). Indeed, exceptionally high amounts of tuff/pumice fragments along with tiny granules of micrite-like appearance are observed in sample 05/02. In contrast, it must be assumed that clinoptilolite enters the ceramics assigned to groups 9 and 11 as part of the groundmass (see below).

The XRD analyses of this group proved unhelpful for estimating firing temperatures. The only restricting statement that can be made, is that the samples containing illite/muscovite have probably been fired to temperatures not exceeding 1000°C (Brown and Brindley 1980).

Group 9 - Volcanic rocks, calcareous and microfossils

Group 9 encompasses all locally produced pottery dated to the Middle Cycladic Phases A and B. Similar to the earlier local ware, the dominant feldspar phase is a calcium-rich plagioclase. The increased quartz content of this group, which is thought to derive from the A₁-tuff deposits to the West of Akrotiri, can readily be explained by the silicification processes which are observed in those tuffs (Fouqué 1879) and which are manifested by the presence of chalcedony in several of the sherds (see petrographic analysis, Chapter 4 and Appendix III). Also the presence of hornblende in a few and the presence of augite in most of the samples analysed is accounted for by the petrographic analysis. As above, iron oxides were detected in some patterns.²⁹ Unlike in group 1, however, and as expected from the petrographic analyses, calcite is present in highly variable amounts. This variation is due on the

²⁹ The intensity of the main hematite peak could potentially be linked to firing temperatures, as it is observed that it increases significantly with increasing firing temperatures (see Chapter 6). Unfortunately, iron oxides also enter the fabric along with temper material (as seems to be the case for sample 05/91 of this group which features exceptionally high amounts) so that the prominence of reflections attributed to iron oxides in a pattern is not very informative. There seems to be some correlation, however, between firing temperatures and hematite content in group 11 (*cf.* Appendix IV, section A).

one hand to the decomposition of this mineral at higher firing temperatures and on the other to its irregular distribution throughout the samples of this group. In addition to illite/muscovite, traces of the clay mineral smectite could be detected in a few samples. This result is in good agreement with XRD analyses of erosional products derived from the A₁ tuff deposits, which revealed illite, smectite and subordinate amounts of kaolinite as constituent clay minerals (Friedrich *et al.* 2000). The fact that clinoptilolite is detected in nearly all samples analysed of this group - in notably higher amounts than the trace levels observed in group 1 - reinforces the assumption phrased in Chapter 4, namely that the raw materials for the Middle (and Late, see below) Cycladic local pottery derive from sources to the West of the settlement. The zeolite clinoptilolite is a well-known component of the A₁-tuffs (Kitsopoulos and Dunham 1996; Stamatakis *et al.* 1996) and has, tellingly, been identified in a clay sample taken from the Akrotiri settlement (Friedrich *et al.* 2000) (see also discussion for group 1, above).

The estimated firing temperatures for each analysed sample are listed in Appendix IV. The estimations are based on the following considerations: the structure of smectites is usually conserved up to firing temperatures in the range of 800-900°C (Grim 1968, 318). The presence of smectite thus probably indicates temperatures not in excess of 900°C for the samples concerned. Illite is the most stable of all clay minerals and is frequently detected after firing up to 1000°C (Brown and Brindley 1980). For samples in which calcite is determined, in general, a firing temperature lower than 750-800°C is postulated (Noll 1991). Similarly, in this study, the firing of a calcareous clay to 850°C resulted in the disappearance of the corresponding reflections from the XRD pattern (see Chapter 6). When using the presence (or absence) of calcite for the estimation of firing temperature, it must be kept in mind, however, that a variety of factors influence the mineral's exact decomposition temperature. The chemical composition of the mineral plays an important role: for pure calcite and related carbonates, decomposition temperatures around 900°C are reported (Smykatz-Kloss 2002). Furthermore, in unfavourable conditions (e.g. reducing atmosphere), decomposition may be delayed to higher temperatures. Also grain size is a factor: finely distributed calcite in a calcareous base clay will react differently from large crystals in a calcite tempered ceramic paste.

Group 11 - Volcanic rocks, calcareous, microfossils and phyllite/schist

Group 11 is the predominant local cooking ware fabric in the Middle Cycladic Phase C and the Late Cycladic IA. The mineralogical composition of this group, as determined by XRD analysis, is very similar to the previous one and most comments for group 9 are equally applicable to group 11. For this reason, only a few peculiarities will be discussed here. Firstly, the amount of quartz is clearly increased, an observation which can readily be explained since this mineral enters the fabric alongside the metamorphic rock fragments which characterise the samples of this group. Also the illite/muscovite reflections seem more prominent and better resolved than in the previous local groups, undoubtedly due to the additional presence of micas from the phyllite/schist fragments. Secondly, the broadening of the reflections attributed to anorthite, a phenomenon which is observed in a couple of samples, is an indication of the very high firing temperatures achieved in the manufacture of the respective vessels. This is confirmed by the very glassy appearance of their groundmass as observed under the petrographic microscope.³⁰ Broad reflections are an indication of poorly-developed tiny crystallites, which are typical for a firing product such as neo-formed anorthite, well-known to form from calcareous clays at elevated temperatures (see also Chapter 6). It must be assumed, therefore, that these reflections are caused by neo-formed anorthite, in addition to the contribution arising from the lava fragments' phenocryst population. The concomitant absence of illite/muscovite in those samples confirms a firing temperature probably well in excess of 1000°C. Other typical high temperature phases of calcareous clays, such as gehlenite or diopside, were not detected in any of the samples, either because the relevant peaks are obscured by other minerals or because these phases are altogether absent. Finally, the presence of kaolinite in sample 05/93 points towards a firing temperature lower than 550°C for the respective object. Kaolinite is the most unstable of the clay minerals;

³⁰ It should be noted here that in both samples abundant microfossils are observed under the petrographic microscope, these were in one case rather altered but in the other well-preserved. This does not refute firing at high temperatures, but probably indicates either fast firing rates (i.e. vitrification of the surrounding matrix before burning out and subsequent 'trapping' of the microfossils) or reducing conditions (le Châtelier's principle, i.e. delayed decomposition due to shift in equilibrium following increased CO₂ pressure), or a combination of both. This illustrates the difficulties of using microfossils for firing temperature estimations of ceramic materials (Quinn and Day 2007; Quinn 2008), be they obtained by examining the presence/absence (due to burning out) of microfossils or their state of preservation.

hydroxyl loss and accompanying structural change is usually complete by 525°C (Grim 1968), a property which is used for its identification in clay samples (Braun and Brindley 1980). In fact, the particular sample (05/93) is taken from a large horse-shoe-shaped hearth structure which seems to have been constructed *in situ* from a clayey material.

As with the previous sections, firing temperature estimations for all analysed samples are listed in Appendix IV.

Group 5 - Granite/granodiorite

The last group to be discussed is the main non-local group, dominated by acid to intermediate rock fragments and thought to be imported from the island of Naxos. The identification of quartz and feldspar in the XRD diagrams of the samples belonging to this group was expected from the results of the petrographic analysis. Unlike in the local ware, however, the reflections of the dominant feldspar phase in group 5 fit well with those of albite, the sodium-rich end member of the plagioclase series. In a few cases, XRD detected the additional presence of a potassium feldspar, microcline. This mineral was also identified in some samples by petrographic examination. Similarly, the identification of hornblende in very varied amounts was expected as considerable variations in this mineral's abundance had been noted under the petrographic microscope. The fact that not even traces of clinoptilolite were found in any of the clearly imported samples provides a strong argument against a post-burial deposition of this zeolite in the pottery, as has been discussed above. In contrast, a reflection at *c.* 25.9°2θ which is observed in three samples of this group, possibly indicates the presence of another zeolite, such as analcime (although the reflection which is usually observed at around 16°2θ is absent from the diffraction patterns). Analcime is observed to form from highly vitrified, calcareous ceramics (Buxeda 1999; Buxeda *et al.* 2001). Fabric group five is clearly non-calcareous, arguing against the presence of this particular zeolite, which is believed to form from gehlenite, a firing product in calcareous clays. The conspicuous reflection is, however, present only in the diagrams of the very high-fired samples which have a glassy appearance under the microscope, suggesting that it is caused by a post-depositional

alteration product formed from a glassy phase. Calcite was not detected in any of the samples of group 5, confirming its non-calcareous character. The clay minerals present in this group are illite/muscovite and, found in a couple of samples, kaolinite, which indicates exceptionally low (if any) firing temperatures for the related vessels (see Appendix IV). A final remark should be made on sample 05/11 which, by petrographic analysis, has been tentatively classified as related to group 5. The fact that in this sample, unlike in all other samples of group 5, anorthite instead of albite was found to be the dominant feldspar constituent, accentuates its different character, and probably results from the prominent lava component observed in this sample.

Summary

Concerning the *mineralogical composition* of the cooking ware ceramics, XRD was able to provide additional information on raw materials - clinoptilolite and various clay minerals - which could not be detected under the petrographic microscope due to their small particle size. The presence of clinoptilolite exclusively in the locally produced pottery and predominantly in the ware dated to the Middle and Late Cycladic periods (group 9 and 11), confirms the earlier suspicion that the raw materials of the later local groups are derived from tuff deposits to the West of the settlement (*cf.* Chapter 4). In addition, XRD analysis confirmed the non-calcareous character of the earlier local ware as well as of the imported group, while it corroborated the use of a more calcareous paste for the production of the local cooking ware in the Middle and Late Cycladic periods. It also revealed that the main feldspar phase in all locally produced fabrics is a calcium-rich plagioclase while in the Naxian fabric a sodium-rich plagioclase together with potassium feldspar prevails. The detection of different amounts of quartz in the various groups could be rationalised by various frequencies of different quartz bearing inclusions, (chalcedony for group 9, phyllite/schist fragments in group 11). An overview over the main mineral phases found by XRD in the four principal fabric groups is given in Table 5.1.

	Prove-nance	Time period	Calcite	Feldspar	Clinoptilolite
Group 1	Local (Thera)	Late Neolithic and Early Cycladic	no	Anorthite (Ca-rich plagioclase)	rarely traces
Group 9	Local (Thera)	Middle Cycladic Phase A & B	in some samples	Anorthite (Ca-rich plagioclase)	in most samples
Group 11	Local (Thera)	Middle Cycladic C and Late Cycladic	in some samples	Anorthite (Ca-rich plagioclase)	in many samples
Group 5	Imported (Naxos)	Final Neolithic to Late Cycladic	no	Albite (Na-rich plagioclase) & Microcline (K-Feldspar)	no

Table 5.1 Main variations in mineral content of the four main fabric groups as detected by XRD.

Furthermore, XRD analysis provided information on the *temperature* ranges attained during firing. Since, when doing so, it is advisable to exercise caution for a variety of reasons that have been discussed above, the XRD results were integrated with the results obtained by the other analytical methods which were applied on the samples. For several samples the presence of certain minerals allowed a restriction of the range of firing temperatures (Appendix IV).

5.2 Fourier transform infrared spectroscopy

Infrared spectroscopy is employed widely for the identification and analysis of organic and inorganic compounds. The method is based on the interaction of electromagnetic radiation of the infrared region (i.e. with frequencies between 4000 and 400 cm^{-1}) with atomic bonds. Electromagnetic radiation of this range is absorbed by atomic bonds at characteristic frequencies and induces different vibrational motions, depending on the local symmetry. As the frequencies absorbed depend on the constituent atoms and the vibrational mode induced, the associated absorption bands in an IR spectrum can be correlated to bonds and functional groups and utilised for structure determination and phase identification.

IR spectroscopy provides useful information especially for poorly crystalline or amorphous samples, and has found extensive application in the study of soils and

clays. The IR spectra of clayey materials are usually divided into two main areas of interest: the 4000-3000 cm^{-1} region which features the OH stretching modes of the clay bound hydroxyls, and the 1600 to 400 cm^{-1} region, comprising the main Si-O stretching band (around 1000-1100 cm^{-1}), Al-O and Si-O deformation bands (400-600 cm^{-1}) and, in the case of calcareous clays, a C-O stretching band around 1400 cm^{-1} .

5.2.1 The use of FT-IR in the analysis of archaeological ceramics

Unlike thin section petrography or XRD, IR spectroscopy is not used very widely in the analysis of ancient ceramics, but the technique has been employed occasionally to assess ancient firing temperatures and infrequently for characterisation purposes. Fourier transform infrared spectroscopy has a high sensitivity, requiring only a few milligrams of sample for an analysis, and, since it provides complimentary information, it supplements the other techniques employed in the analysis of archaeological ceramics.

The firing temperatures of *moderate to very high-fired* ceramic materials have been estimated by IR spectroscopy combined with other analytical techniques (Shoval 1993; 1994; 2003). To this aim, IR spectra of archaeological material were compared to spectra of a supposedly similar clay which had been fired to a series of different temperatures and rehydrated before examination. Comparison with reference spectra was deemed necessary since the structural and compositional changes upon exposure to heat, which are reflected in the IR spectra, are dependent not only on firing temperatures but also on the nature of the raw material. Several phenomena were employed in these studies to estimate ancient firing temperature, amongst others the occurrence of high temperature phases and the shifting of the main Si-O stretching band. IR spectroscopy has also been used to estimate firing temperatures of *low-fired* archaeological ceramics (Maniatis *et al.* 1982; 2002). The presence of clay-bound hydroxyl bands was interpreted as an indication of incomplete dehydroxylation and, accordingly, low firing temperature. Maniatis *et al.* (2002) correlated the intensity of the clay hydroxyl peaks to the firing temperature, through comparison to reference spectra which were obtained by refiring apparently low-fired specimens. While the

presence or absence of clay-bound hydroxyls may be employed - within certain restrictions - for rough firing estimations, more exact estimations, including the use of the hydroxyl peaks' intensity as a low temperature mineral thermometer, is problematic, since various complications arise through de- and rehydroxylation processes. When a ceramic is exposed to moisture during use and burial, this can result in the rehydroxylation of clay minerals which did not completely and irreversibly lose their structure in the firing process. Such rehydroxylated species usually dehydroxylate at a lower temperature. Additional complications occur in the case of 2:1 layer silicates, when hydroxyl sites different than the original are occupied in the rehydroxylated species, resulting in a differing dehydroxylation temperature for the rehydroxylated species (Muller *et al.* 2000). Moreover, the temperature a clay mineral has been exposed to during firing can influence its dehydroxylation temperature (Emmerich 2000). All these factors hamper the use of the presence and especially of the intensity of clay-bound hydroxyls, as determined by IR methods, for temperature estimations that go beyond a more general level.

Exceptionally, infrared spectroscopy has been applied with a view to study *provenance*. De Benedetto *et al.* (2002) attempted to group pottery according to their spectra with the aim ultimately to use the technique as a tool for provenancing. It seems rather doubtful though that IR spectroscopy will gain wider popularity when it comes to provenance studies. This is due primarily to the ubiquity of the unambiguously identifiable minerals, to the fact that the method does not allow identifying the spatial relation of minerals with each other, and the strong influence of firing and post-depositional alteration processes on the spectra.

From what has been discussed above, it seems clear that the applicability of IR spectroscopy to the study of ancient ceramics is subject to some restrictions, and that care must be taken when interpreting the results of such measurements. First, the characterisation of clays used in the manufacture of ceramics is not always straightforward, since natural occurring clays are usually a mixture of different clay and other minerals. Furthermore, the identification of constituent clay minerals is restricted to low-fired ceramics. In what concerns firing temperature estimations, especially de- and rehydroxylation phenomena must be taken into account when applying the technique to low-fired ceramics. The method can, however, provide additional information

when used in tandem with another technique such as thin section petrography or XRD.

5.2.2 Results of the FT-IR analyses of the Akrotiri cooking ware

IR spectra were measured on KBr pellets. A small piece was broken from a pottery sherd, thoroughly cleaned and powdered in an agate mortar, to be added to previously dried KBr in the ratio of 1:100. This mixture was ground and dried at 115° C for at least 24 hours. Approximately 170 mg were transferred directly from the oven to a die and pressed to disks. The resulting KBr pellets were measured without delay on a Bruker FT-IR Spectrometer. Spectra were recorded in the range of 4000 to 400 cm^{-1} with a spectral resolution of 4 cm^{-1} , against air as background, by adding and averaging 30 scans before Fourier transformation.

For the analysis of clays it is usually recommended to record two spectra with different sample concentrations (Farmer 1979; Russell 1987): one with a relatively high concentration to ensure a good resolution of the region of OH stretching bands between 3000 and 4000 cm^{-1} (1-2 mg sample/170 mg KBr) and a more diluted sample for the region of intense silica absorption (0.025-0.5 mg sample/170 mg KBr). As the chosen concentration of 1.7 mg sample/170 mg KBr resulted in spectra with a reasonably good resolution in both regions, however, it was considered sufficient to record only one spectrum per sample.

In the following the results of the FT-IR analyses are presented, taking into consideration the previously discussed XRD and petrographic data. IR spectra were recorded in order to identify clay minerals, but mainly to detect and assess low firing temperatures. For this reason, a high proportion of measurements were made on samples whose groundmass was optically active in thin section and therefore thought to be low-fired. Comparatively fewer samples were measured of higher fired, optically inactive or even glassy sherds. As with the previous section on XRD, the following discussion is restricted to the main petrographic groups. Since FT-IR is not frequently applied to archaeological ceramics, the following discussion will take place on a more detailed level: the presentation of the results includes the interpreta-

tion of the resulting spectra, explaining the way firing temperature estimations were obtained and the assignment of different absorption bands.

Some features are common to most spectra and will therefore not be discussed in the single sections. These include the characteristic doublet of ubiquitous quartz at 799 / 779 cm^{-1} , which can be found in virtually all spectra, usually accompanied by a band at 693 cm^{-1} . C-H absorption bands at 2850-2960 cm^{-1} are caused by organic contaminants (Russell 1987), the broad bands at 3400 cm^{-1} and 1630 cm^{-1} by adsorbed water. Furthermore, peaks and shoulders around 760, 723, 650 and 590 cm^{-1} are thought to be caused by the presence of feldspars (Moenke 1974; Russell 1987). Generally, the mineral constituents of a clay based ceramic are more readily and more reliably identified by XRD and thin section petrography, the results of which have been discussed at length earlier on. For this reason the presentation of the results from the FT-IR analyses will be restricted to the detection of carbonates, the nature of clay minerals - if identifiable - and firing temperature estimates. The detailed assignment of the spectra's absorption bands can be found in Appendix IV, section B.

Group 1 - Volcanic rocks

The constituent clay minerals of this group are difficult to determine by FT-IR. The broad peaks around 3630 cm^{-1} which are observed in a few spectra are caused by clay-bound hydroxyls probably of illite and/or smectite. That a mixture of clay minerals (including a kaolinitic component?) is present in the samples of this group could also be suspected from the relatively broad frequency distribution of the Al-O and Si-O deformation bands.

Group 1 has been characterised by XRD and thin section petrography as non-calcareous. Yet, typical C-O stretching bands of CaCO_3 were found in two samples, 05/01 and 05/03 (Table 5.2). These bands are rather weak, though, and micrite was determined in the related samples as lining on the sherds' surface and in a few pores (*cf.* Appendix III - petrographic analysis: fabric descriptions). The fact that no calcite peaks were found in the respective XRD diagrams, reinforces the impression that the

calcium carbonate present in those samples is poorly crystalline and of secondary nature.

Sample	Clay OH stretching bands	Main Si-O stretching band	Estimated firing temperature	CaCO ₃
AKR05/01	-	1042	700-850°C	traces
AKR05/02	weak	1047	700-800°C	-
AKR05/03	-	1045	700-850°C	traces
AKR05/04	-	1051	700-850°C	-
AKR05/05	weak	1047	700-800°C	-
AKR05/06	v. weak	1049	700-800°C	-
AKR05/13	v. weak	1049	700-800°C	-
AKR05/16	weak	1049	700-800°C	-
AKR05/21	-	1053	700-850°C	-

Table 5.2 Summary of the results of the FT-IR analyses for samples of group 1.

The fact that bands between 3700 and 3600 cm⁻¹ are either absent or only weakly present, indicates that all samples have been fired. Where OH stretching bands from the clay-bound hydroxyls are absent from a spectrum, it must be assumed that the firing temperature exceeded the dehydroxylation temperatures of the constituent clay minerals. Additionally, the main Si-O stretching band, which in unfired clays is expected to occur around 1030 cm⁻¹, is shifted to higher frequencies in all samples (Table 5.2). This can be used to estimate the firing temperatures of the sherds (Shoval 1994; 2003) and indicates that the samples have been fired above 700°C. It seems therefore quite probable that the weak and rather broad hydroxyl bands which are observed in a few spectra of this group are caused by rehydroxylated clay minerals rather than by unchanged raw materials. For smectites and illites, rehydroxylation is known to occur after firing to up to 800°C (Shoval *et al.* 1991).

Group 9 - Volcanic rocks, calcareous and microfossils

Calcium carbonate was detected in moderate amounts or traces in several of the samples that were analysed from group 9 (Table 5.3). This result was expected, as a more or less calcareous clay has been used for the manufacture of pottery assigned to this group, and calcite was found in thin sections as well as by XRD analysis³¹. Much like in the spectra of samples belonging to the earlier local group 1, the clay-bound

³¹ Calcite is present in the samples as part of the groundmass but also in the form of microfossils. In a few samples, the mineral was found additionally in the form of micritic aggregates or as sparry calcite.

hydroxyl bands are - if present - broad and very weak. In combination with the rather high frequencies that are observed for the main Si-O stretching band, this probably indicates rehydroxylated material. A direct identification of the clay constituents is not possible, but previous XRD analyses indicated that the later local pastes (fabric 9 and 11) contain a mixture of different clay minerals, namely illite, smectite and kaolinite, as do locally available raw materials (Friedrich *et al.* 2000).

Sample	Clay OH stretching bands	Main Si-O stretching band	Estimated firing temperature	CaCO ₃
AKR05/39	v. weak	1044	700-850°C	yes
AKR05/40	v. weak	1041	700-850°C	yes
AKR05/43	v. weak	1048	700-850°C	-
AKR05/44	-	1054	750-900°C	yes
AKR05/45	-	1050	750-900°C	-
AKR05/46	v. weak	1048	700-850°C	-
AKR05/49	-	1048	700-850°C	-
AKR05/50	-	1089	>900°C	-
AKR05/52	-	1039	700-850°C	traces
AKR05/91	-	1090	>900°C	-

Table 5.3 Summary of the results of the FT-IR analyses for samples of group 9.

The majority of the analysed samples seem to have been fired to temperatures between 700-850°C. Firing temperatures in excess of 900°C are assumed only for samples 05/50 and 05/91, due to the distinctively higher frequencies of the Si-O stretching band in their spectra. This interpretation is confirmed by the fact that the groundmass of those samples appears inactive to glassy in thin section (*cf.* Appendices III and IV).

Group 11 - Volcanic rocks, calcareous and microfossils

The absence of the characteristic OH stretching bands in all but the related sample 05/93 does not allow the identification of the constituent clay minerals of group 11 (Table 5.4). As we know from the petrographic analysis, however, this group is based on the same raw materials as the earlier local group 9, so that it seems probable that a clay mixture containing kaolinite and illite/smectite characterises this group as well (*cf.* also Appendix IV, section A). The typical bands of CaCO₃ were detected in most samples. The main carbonate stretching band is shifted to higher frequencies in

the case of AKR05/88 (1438 cm^{-1} vs. 1424-1430 cm^{-1}). This shift is thought to be indicative of recrystallised calcite and caused by the presence of impurities, e.g. magnesium which are incorporated into the mineral structure upon recrystallisation (Shoval 2003; Shoval *et al.* 2003). The extremely high frequency of the carbonate band (1485 cm^{-1}) together with an additional band at 855 cm^{-1} which are observed for sample AKR05/76, on the other hand, possibly indicate the presence of amorphous calcite³² (Russell 1987).

Sample	Clay OH stretching bands	Main Si-O stretching band	Estimated firing temperature	CaCO ₃
AKR05/57	-	1073	>900°C	-
AKR05/61	-	1039	700-850°C	yes
AKR05/63	-	1043	700-850°C	-
AKR05/68	-	1045	700-850°C	-
AKR05/67	-	1045	700-850°C	yes
AKR05/74	-	1041	700-850°C	traces
AKR05/76	-	1083	>900°C	traces (shifted to 1485)
AKR05/83	-	1045	700-850°C	yes
AKR05/84	-	1041	700-850°C	yes
AKR05/85	-	1084	>900°C	-
AKR05/87	-	1048	700-850°C	traces
AKR05/88	-	1044	700-850°C	yes (shifted to 1438)
AKR05/89	-	1042	700-850°C	yes
AKR05/90	-	1042	700-850°C	yes
AKR05/93	yes	1031	<550°C	yes

Table 5.4 Summary of the results of the FT-IR analyses for samples of group 11.

All samples seem to have been fired to at least moderate temperatures. Dehydroxylation occurred in all samples: none of the spectra exhibits the characteristic bands of clay-bound hydroxyls. Additionally, the Al-O and Si-O deformation bands are collapsed to one band in most cases, another effect which is observed after firing (Shoval 2003). The shift of the main Si-O stretching band to distinctively higher frequencies in the spectra of samples AKR05/57, AKR05/76 and AKR05/85 is thought to be caused by firing to temperatures probably well in excess of 900°C.

³² The absorption bands would also fit those of aragonite, a common component of the shell of marine organisms. It seems unlikely, though, that this mineral is present in a highly fired sherd, despite the fact that sample 05/76 contains microfossils; the aragonite modification of calcium carbonate is thermodynamically unstable and known to revert upon firing to calcite (Feathers 1989).

The related sample 05/93 contains kaolinite (sharp bands at 3697 and 3622 cm^{-1}). In addition, the broad OH band at around 3620 cm^{-1} together with Al-O and Si-O deformation bands at 519 and 469 cm^{-1} probably indicate a smectite as would be suspected from the XRD analyses (Russell 1987). Also a substantial amount of calcium carbonate was detected. The presence of kaolinite as well as the relatively low frequency of the main Si-O stretching band and the fact that the Al-O, Si-O deformation bands are well separated, suggest that this sample has been fired, if at all, to a temperature not exceeding 550°C.

Group 5 - Granite/granodiorite

The predominant clay mineral in the main imported fabric group seems to be of kaolinitic nature. This notion is supported by the presence of the characteristic hydroxyl bands in the spectra of some low-fired specimens and by the frequencies of the Al-O and Si-O deformation bands. The weak and fairly broad hydroxyl band around 3619 cm^{-1} in sample 05/09 is possibly caused by traces of smectite/illite. These may either be present in subordinate amounts in the clay mixture (and not obscured by kaolinite peaks in this sample; smectites and illites dehydroxylate later than kaolinite: roughly 600-750°C vs. 450-600°C, see e.g. Smykatz-Kloss 2002) or be of secondary nature (Maggetti 1982). Calcite is not normally detected in the samples of this group. The weak C-O stretching bands, attributed to CaCO_3 , which were found in a couple of spectra are most probably due to contamination with calcite from the burial environment. No calcite minerals were detected by XRD in the samples belonging to group 5, and their groundmass seems distinctively non-calcareous under the petrographic microscope. The same seems to be the case for sample 05/09, where somewhat higher amounts of calcite were found: this may originate from contamination from the sherd's outer crust in sample preparation.

Also the related sample 05/11 contains substantial amounts of CaCO_3 . As no calcite was found by XRD or in thin section, it could be assumed that its clay matrix contains finely dispersed, poorly or non-crystalline calcium carbonate. The sample, however, seems to have been fired to a rather high temperature (*cf.* Table 5.5 - frequency of Si-O stretching band) so that it seems more probable that the CaCO_3 detected in

this sample is caused by contamination. Also in the spectrum of the other related sample 05/66, traces of calcite were found. In this case, though, the mineral was also detected in rare occurrences in thin section.

Sample	Clay OH stretching bands	Main Si-O stretching band	Estimated firing temperature	CaCO ₃
AKR05/09	traces?	1036	600-700°C	yes
AKR05/10	-	1077	>900°C	-
AKR05/12	-	1034	600-700°C	traces
AKR05/14	traces	1035	400-600°C	-
AKR05/15	traces	1035	400-600°C	-
AKR05/23	-	1039	600-800°C	-
AKR05/25	yes	1034	<550°C	-
AKR05/27	-	1043	700-800°C	-
AKR05/29	-	1042	700-800°C	-
AKR05/31	traces	1035	400-600°C	-
AKR05/32	-	1077	>900°C	-
AKR05/64	-	1043	700-800°C	traces
AKR05/92	-	1039	600-800°C	-
AKR05/66	-	1036	600-700°C	traces?
AKR05/11	-	1080	>900°C	yes

Table 5.5 Summary of the results of the FT-IR analyses for samples of group 5.

The firing temperatures observed in the samples of this group are rather varied. The spectrum of sample 05/25 shows the typical features of a kaolinitic clay, with the diagnostic OH stretching bands at 3696, 3653 and 3621 cm⁻¹ and OH deformation bands at 939 and 914 cm⁻¹ (Russell 1987). Furthermore, the Si-O and Al-O deformation bands at 537, 471 and 432 cm⁻¹ are well separated as is the case in an unfired kaolinitic clay. It must therefore be assumed that this sample has been barely fired, if at all. Kaolinite has also been found in a few other spectra, although in much smaller amounts. The corresponding ceramics seem to have been fired in excess of 400°C, but most probably below 600°C. For the remaining samples, the shift of the main Si-O stretching band can be used for firing temperature estimations (Shoval 1994). The rather high frequencies of this band along with the collapse of the Si-O and Al-O deformation bands into a single band around 460 cm⁻¹, observed in samples 05/10, 05/32 and the related sample 05/11, indicate firing probably in excess of 900°C. This is consistent with the inactive to glassy appearance of these samples' groundmass under the petrographic microscope.

Summary

Fourier transform infrared spectroscopy was employed to obtain information on the *firing temperatures* of the archaeological samples. The technique allowed estimations for low as well as for moderately to high-fired samples, and thus narrowing the range of possible firing temperatures for individual specimens. A list of the estimated firing temperatures for each analysed sample, integrating the results obtained by infrared spectroscopy with the other analytical techniques, is given in Appendix IV, section C. When estimations are based on the presence/absence and intensity of clay-bound hydroxyls, it must be kept in mind that it is not only the nature of the clay minerals and their firing history but also the burial conditions which dictate the hydroxylation state and the dehydroxylation temperature and ultimately the appearance of characteristic bands in the relevant IR spectra. For this reason, taking into account data obtained with other analytical methods seems preferable in order to avoid erroneous conclusions. The technique also provided information on the *mineralogical composition* of the samples. Fourier transform infrared spectroscopy confirmed previous results obtained by thin section petrography and XRD - mainly regarding the presence of calcium carbonate and specific clay minerals - but failed to provide any additional information. Only relatively few phases could be detected, and an unambiguous identification of single phases proved difficult in most cases.

5.3 Scanning electron microscopy

Scanning electron microscopy allows us to obtain high magnification images of a sample and is used in a variety of fields, ranging from materials science to biology. Commonly, the instruments allow simultaneous determination of the chemical composition of a specimen.

Scanning electron microscopes are based on similar principles to optical instruments. They use, however, a focused beam of electrons for imaging instead of light. When this beam is scanned across a sample's surface, the electrons interact with the atoms they impinge upon and give rise to different emission signals. According to the kind of beam-sample interaction detected, different information can be retrieved (Froh

2004). *Secondary electrons*, which are produced near the sample surface from a small area around the beam tip, are collected to obtain high resolution images. Images built up by *backscattered electrons* bear qualitative information on the composition of the sample, as the emission intensity of backscattered electrons is a function of the interacting atoms' atomic number. The resolution achieved with back scattered electrons is, however, inferior to the one that can be realised with secondary electrons. Finally, the detection of the characteristic *X-ray radiation* allows the determination of quantitative information on the composition of a sample. Since every element emits characteristic X-rays, constituent elements can be identified and, upon calibration, the absolute concentrations of individual elements can be determined.

5.3.1 The use of scanning electron microscopy in the analysis of archaeological ceramics

The SEM can be used to obtain high magnification topographical images of a ceramic; additionally the composition of its groundmass and/or inclusions can be determined with the EDX-unit (energy dispersive x-ray spectrometer). The first feature is commonly employed to detect changes in microstructure which are indicative of firing temperature, while the second allows the analysis of bulk, clay body, and inclusion compositions. Scanning electron microscopy can thus provide information on aspects relating to technology and, in some cases, to the provenance of ancient ceramics.

The microstructure of a ceramic body changes upon firing: increasing temperatures result in increasing vitrification of the matrix, with the precise behaviour of a ceramic matrix depending on clay composition and firing atmosphere (Tite and Maniatis 1975; Tite *et al.* 1982a; 1982b). Examining the clay matrix's degree of vitrification therefore allows an *estimation of the original firing temperature*. This is usually carried out on a freshly fractured sample, as the fracture tends to occur through the glass phases so that they are clearly visible under the SEM as smooth, flat areas, if present. This method has become a standard procedure for firing temperature estimations in archaeological ceramics. It must be kept in mind, however, that it is not suited for low-fired ceramics, as up to *c.* 850°C, no changes occur in microstructure

which could be observed under the SEM.³³ It is for this reason that, in the present study, firing temperature estimations were obtained to a large part by other techniques, such as FT-IR, which are sensitive also to lower firing temperatures.

In contrast to the morphological examinations discussed above, the determination of the *composition* of the clay matrix or inclusions by the EDX-unit of a microscope is usually performed on polished samples. Chemical analysis by energy dispersive X-ray spectroscopy (EDX) of the *fine grained matrix* of ceramics can distinguish between refractory and non-refractory ceramics (Freestone 1982). When it comes to the identification of mineral *temper*, EDX analysis cannot compete with thin section petrography, but may provide additional information on the chemical composition, which in turn may help solving provenance questions. The chemical composition of feldspars and pyroxenes, but also of other minerals, can be related to their geological formation process (Freestone 1982; Freestone and Middleton 1987; Dorais and Shriner 2002). Similarly, the chemistry of volcanic glass inclusions may be employed for pinpointing the region of origin.

Finally, although this is only of minor interest for the present study, the SEM is frequently used in the analysis of surface treatments, including the determination of texture and composition of slips, glazes and paint layers applied to ceramics.

5.3.2 Results of the SEM analyses of the Akrotiri cooking ware

While SEM on fresh fractures is well suited to the microstructural analysis of fine ceramics, it is more problematic to assess the degree of vitrification in coarse fabrics. Fracture occurs usually along the weakest bonds, which, in coarse ceramics, are given by the boundaries between inclusion and matrix. For tempered ceramics, this results in high relief surfaces, which are dominated by protruding inclusions and their impressions. With higher temper grades it becomes therefore increasingly difficult to

³³ Morphological changes do occur before the onset of vitrification, but other methods are required to detect these. It is, for example, possible to monitor dehydration and dehydroxylation processes which cause voids and the collapse of the clays' layer structure by transmission electron microscopy (TEM) (Mata *et al.* 2002).

find patches of fractured groundmass that can be examined for their degree of vitrification in order to achieve firing temperature estimations. It is for this reason that the coarse cooking ware pottery of the present study is not ideally suited for examination by SEM. Also, many of the samples were apparently fired to temperatures below the onset of vitrification, so that SEM analysis would not provide additional information on the firing temperature estimates obtained by other techniques (degree of birefringence under the petrographic microscope, XRD, FT-IR). Additionally, the petrographic analysis of the assemblage did not call for further chemical analysis of specific minerals.

Nevertheless, a few fresh fractures of group 11, which contains several high-fired samples, were examined in order to confirm and corroborate the firing temperature estimates obtained by other methods. The result of the examination of those fresh fractures by SEM are presented in the following section and compared to firing estimates obtained by other methods.

Freshly fractured surfaces were mounted on a stub, and carbon-coated to be examined under a SEM (FEI - Quanta Inspect), coupled with an energy dispersive X-ray spectrometer (SEM/EDX).

Based on the appearance of their groundmass under the petrographic microscope, eight samples of group 11 were chosen to be examined under the SEM. They were selected so as to cover the range of firing temperature which is observed in this group: three samples were characterised as slightly active, two as inactive and three as glassy, based on the birefringence of the matrix in thin section. Semi-quantitative analysis by the EDX-unit revealed a calcium content around 8 weight% CaO for the samples, with considerable inter- and intra-sample variation (up to +/- 4% deviation from the mean), reflecting the heterogeneous character of the groundmass. The samples can, however, be considered calcareous, so that for assessing the degree of vitrification the four morphological stages identified by Tite and Maniatis (1975) were employed (see Table 5.6). Calcareous clays develop a cellular structure shortly after the onset of vitrification which remains essentially unchanged from 850-1050°C; in excess of these temperatures, the cellular structure collapses and a continuous vitrified layer, containing bloating pores is formed.

Vitrification stage	Description of microstructure	Temperature
NV - no vitrification	no signs of vitrification	<850°C
IV - initial vitrification	isolated, smooth-surfaced areas of glass	~850°C
V - intermediate vitrification	glass filaments are separated by pores building a vitrified layer with cellular structure,	850-1050°C
CV - continuous vitrification	continuous, smooth, vitrified layer containing unconnected bloating pores	>1050°C

Table 5.6 Vitrification stages in calcareous clays, indicating the associated temperature ranges (after Tite and Maniatis 1975).

A very good correlation was found between the vitrification stage as observed under the SEM and the appearance of the micromass as determined by thin section petrography (Figure 5.2). Table 5.7 lists vitrification stages and the appearance of the groundmass in thin section for all samples examined, along with the results of the FT-IR and XRD analyses. It is apparent that the appearance of the matrix in thin section is indeed a good indicator for its microstructure as observed under the SEM and can be used unambiguously for firing temperature estimates.

Sample	Vitrification stage (SEM)	Birefringence (PE)	XRD (Temperature, Phase)	FT-IR (Temperature)	Final temperature estimates
AKR05/53	IV	inactive	< 800°C (calcite)	n.d.	800-850°C
AKR05/54	V	inactive	< 800°C (calcite)	n.d.	850-900°C
AKR05/57	V	glassy	< 1000°C (Illite)	>900°C	950-1050°C
AKR05/61	NV	slightly active	< 800°C (calcite)	700-850°C	700-800°C
AKR05/76	V-CV	glassy	> 1000°C	>900°C	1050-1100°C
AKR05/84	NV	slightly active	< 800°C (calcite)	700-850°C	700-800°C
AKR05/85	V-CV	glassy	< 1000°C (illite)	>900°C	1000-1100°C
AKR05/86	NV	slightly active	< 800°C (calcite)	700 - 850°C	700-800°C

Table 5.7 Comparison of vitrification stages to the appearance of the groundmass in thin section for selected samples of group 11. The firing temperature estimates obtained by other methods (PE, XRD, FT-IR) are also indicated, as are the final firing temperature estimates for the particular samples.

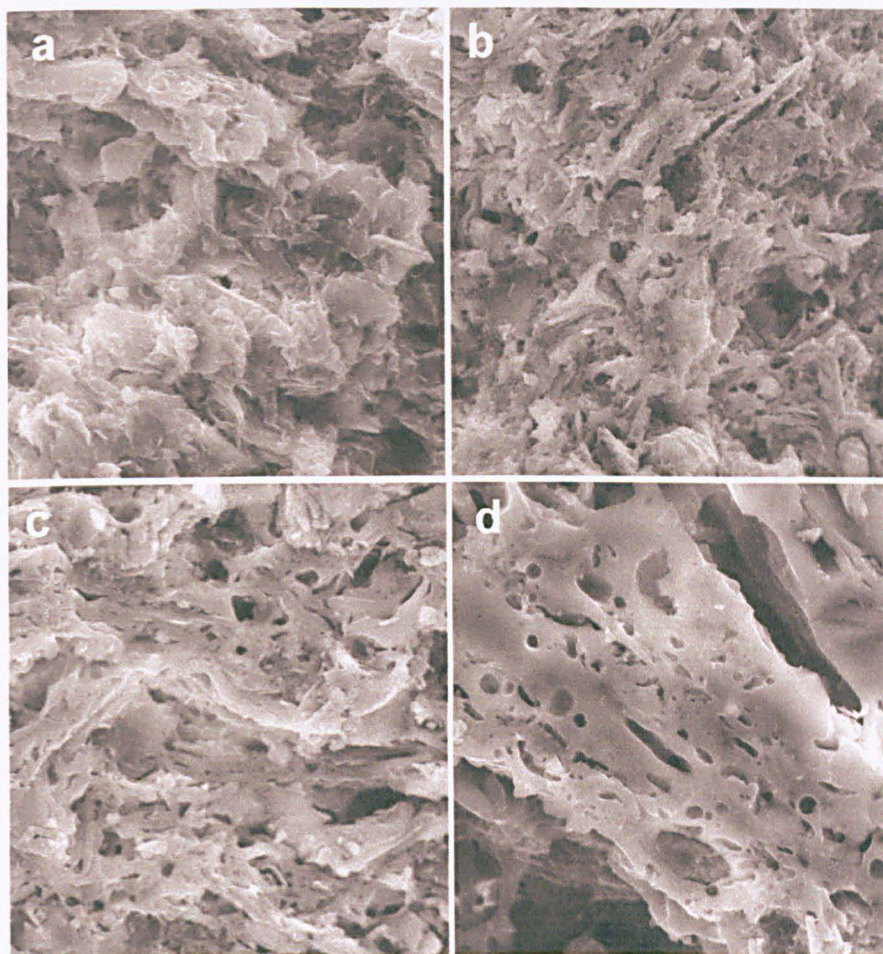


Figure 5.2 Microstructures of several samples as observed under the SEM and vitrification stage after Tite and Maniatis (1975) (*cf.* Table 5.6): *a*, no vitrification (but firing is indicated by smoothed edges) - NV (sample 05/84); *b*, initial vitrification - IV (sample 05/53); *c*, intermediate vitrification - V (sample 05/54); *d*, intermediate to continuous vitrification V-CV (sample 05/76). The field of view is 50 μm .

None of the samples with an optically active groundmass showed signs of vitrification under the SEM. In combination with the results of the FT-IR analyses, this resulted in a final firing temperature estimate of 700-800°C for those samples that are described as slightly active by petrographic analysis. All samples with a glassy appearance in thin section, on the other hand, showed a rather highly vitrified groundmass, in some cases featuring bloating pores that indicate firing temperatures well in excess of 1000°C for the related samples. The overall firing temperature estimates indicate a firing temperature range of 950-1100°C for the glassy samples. The inactive samples, finally, showed initial vitrification in one case and a more advanced vitrification stage in the other. The presence of calcite detected by XRD, however,

suggests that also in the latter case firing temperature most probably did not exceed 900°C. These results indicate firing temperatures between 800 and 900°C for the samples with an inactive groundmass. It should be emphasised here - especially in view of a discussion of material properties - that it is the microstructure of the ceramics samples which is of importance, while the actual firing temperatures are secondary, since it is the microstructure which influences the behaviour of a material, and not the firing regime that led to its formation.

To sum up, the assessment of firing temperatures through the micromass' birefringence as established in petrographic analysis could be validated and temperature ranges were assigned to the different appearances of the matrix (Table 5.8). Not surprisingly, it seems that the different stages of vitrification as

Appearance of groundmass	Firing temperature
(slightly) active	<800°C
inactive	800-900°C
glassy	950-1100°C

Table 5.8 Correlation of the groundmass' appearance, as determined in the petrographic analysis, with firing temperature ranges for calcareous ceramics belonging to group 11.

commonly assessed by SEM, are directly reflected in the groundmass' appearance in thin section. While the temperature-appearance correlation might not be transferable to samples outside group 11 (and the related group 9, which is based on the same clay raw materials) on a one-to-one basis, the results obtained do confirm that petrographic analysis can be used reliably to ascertain firing temperature ranges.

The results also illustrated that caution must be exercised when using the presence or absence of certain phases for the assessment of firing temperatures. The presence of calcite (determined by XRD) in sample 05/54 whose matrix shows vitrification, indicates that calcite may be detected in a ceramic even after firing to temperatures beyond 800-850°C. On the other hand, illite/muscovite may be more stable under certain circumstances than has sometimes been assumed for the estimation of firing temperatures by XRD. Its presence in sample 05/85, whose microstructure is highly vitrified and shows some bloating, points towards stability of the mineral well in excess of 1000°C in the particular case.

5.4 Summary

This section outlines the main results of the complimentary analyses performed on the archaeological material and provides a brief assessment of the usefulness of the techniques employed - FT-IR, XRD and SEM - in particular for the analysis of coarse cooking ware ceramics. For a comprehensive discussion of the findings from the analyses on the archaeological material, taking into account the impact of the observed technological choices on the performance characteristics of the related vessels, the reader is referred to Chapter 10.

In order to obtain meaningful results, the choice of the analytical techniques that are applied to a ceramic assemblage must be based on the kind of information that is sought as well as on the nature of the ceramic material. For coarse ceramics, *thin section petrography* is usually the most versatile stand-alone technique, as it enables a discussion of questions regarding both technology and provenance. A petrographic study also provides the basis for a further application of complementary techniques, such as those discussed in the present chapter. Regarding those additional techniques, *infrared spectroscopy* can be of assistance when determining firing temperatures for both, high and low-fired specimens. *Powder XRD*, on the other hand, is better suited to fine rather than coarse ceramics if more information on firing regimes is required. This is because the diagrams obtained of coarse ceramics are usually dominated by the reflections of temper minerals. In order to facilitate a meaningful interpretation of the XRD patterns, in what regards the nature and origin of the detected minerals and their variation within a fabric group, concurrent petrographic analysis is required. X-ray diffraction allows for the identification of mineral phases that are not visible under the petrographic microscope. Apart from high temperature phases these are usually clay minerals and alteration products. The detection of a mineral such as clinoptilolite which can be linked to a specific origin of the raw material, however, is the exception rather than the rule. *Scanning electron microscopy*, finally, does not generally provide additional compositional information in the case of coarse fabrics. Also, changes in microstructure provide information only for firing temperatures in the upper end of those observed for earthenware ceramics. Unless warranted by a specific problem, e.g. if the exact chemical composition of a constituent mineral can

potentially answer provenance questions, SEM seems therefore not ideally suited to a broad application to coarse and frequently low-fired cooking ware ceramics.

In the present study, *FT-IR* proved helpful to refine the firing temperature ranges, for low as well as for high-fired samples. A series of changes which occur in the relevant spectra were evaluated, in order to avoid the shortcomings of basing estimations solely on the presence or absence of clay-bound hydroxyls. *X-ray diffraction* notably revealed the presence of significant amounts of the zeolite clinoptilolite in local samples. This provides further support for the hypothesis that the raw materials derive from a relatively small area in the immediate vicinity of the Bronze Age settlement of Akrotiri. As this mineral is a rather unusual component of archaeological ceramics, it might potentially be used - in combination with other characteristics - as a geological provenance marker.³⁴ While XRD measurements successfully identified phases that eluded detection by other methods, the technique did not provide further information regarding the firing regimes of the ceramics studied. *Scanning electron microscopy*, finally, allowed the confirmation of the firing temperature estimations obtained by other methods, specifically thin section petrography, by linking the degree of vitrification to the appearance and the birefringence of the groundmass under the petrographic microscope. In general, the cooking ware seems to have been fired to intermediate temperatures, with sometimes considerable variations within a group. The amount of exceptionally high-fired samples in the latest local fabric is striking, not least since cooking ware is not normally associated with high-fired fabrics. The implications of this phenomenon and possible interpretations will be discussed in Chapter 10.

³⁴ This might be especially useful, since Melian and Theran ware cannot conclusively be distinguished by other methods (e.g. Vaughan 1990; Kilikoglou *et al.* 1990). The zeolite might be of assistance to assist in provenance assessments of the buff ware, which is typical for the Middle and Late Cycladic periods at both sites, if it can be confirmed that its presence is restricted to Theran pottery. The discrimination of pottery produced on the two islands is of great value in the reconstruction of exchange patterns in the Aegean during the Bronze Age. So is for example Bichrome ware which is widely distributed over the Aegean, commonly assigned to Melian workshops, and its distribution has been employed to trace trading patterns. The finding of locally produced Bichrome ware at Akrotiri, however, led to calls for a re-examination of this ceramic material at Aegean sites (Nikolakopoulou *et al.* 2005).

Chapter 6

Manufacture of experimental briquettes

Ceramic briquettes were prepared in order to evaluate the influence of a set of parameters on the performance characteristics of the resulting fabrics. This chapter specifies the experimental procedures followed in the manufacture of these ceramic briquettes. Furthermore, the choice of the parameters that were varied in manufacture is explained and a specification of the raw materials as well as of the fired ceramic briquettes is provided.

For the manufacture of the experimental briquettes, it was decided to select parameters that reflect choices available to the potter in different stages of the production process - namely raw material selection, paste preparation and firing. Additionally, the parameters chosen would have to allow an assessment of the fabrics which are observed in the Bronze Age cooking ware of Akrotiri. There are several reasons that the mechanical and thermal properties were determined on replicates rather than on the archaeological sherds. Besides requiring a substantial amount of material and the emergence of problems caused by geometrical restraints posed by the testing methods, measurements on archaeological material are problematic because the material has undergone alteration through use and subsequent burial. Also, to assess the influence of individual parameters on mechanical and thermal properties, it is imperative to work under controlled conditions.

The rationale for selecting the particular parameters as specified below, is based on concerns related to the material properties of the raw materials used in the production of traditional pottery, as well as on considerations relevant to the archaeological case study. However, it was felt necessary to restrict the factors to be varied in the manufacture of the replica briquettes to a few relevant ones. Archaeological pottery comes with a huge variety of fabrics and firing conditions, the same is true even for the restricted case of the Akrotiri cooking ware assemblage. A full coverage of all possible or actually encountered varieties might not be feasible - at least within a sensible timeframe and without an army of helping hands. Also, the effort involved might not

be justified by the potential results, as, theoretically, the effect of a specific parameter value can be estimated by extrapolating measured reference data. It is, therefore, essential to restrict the variables to a few from which a *significant* influence on the performance properties can be expected, and thus determine reference points for the assessment of the performance characteristics. Aside from establishing a relationship between a ceramic's microstructure and its performance properties, which is applicable to pottery in general, it is an immediate aim of this study to determine whether and how the changes in manufacturing techniques and ceramic fabrics that are observed in the assemblage at Akrotiri, influence the performance characteristics of the respective cooking ware. For this reason, when selecting the manufacture parameters, care was taken to cover the diachronic change and synchronic variation that is observed in the assemblage. On these grounds, it was decided to study the influence of the following four parameters on the performance characteristics of the resulting fabrics: type of clay, type (shape) of temper, amount of temper and firing temperature.

Two different *clays* were used for the manufacture of the briquettes, a calcareous and a non-calcareous one. Calcareous clays are known to behave differently from non-calcareous ones due to the decomposition of calcite at elevated temperatures in the former. This results in a differing development of vitrification in the two types of clay (Tite and Maniatis 1975). With regard to the specific case study, pottery thought to be local to Thera is commonly described as calcareous (Maniatis and Tite 1978; Noll 1978; Aloupi and Maniatis 1990) and is easily distinguishable by its buff fabric (Doumas 1983, 110). In this study, the analysis of sherds of presumably local production revealed a high calcium content for Theran pottery dated to the Middle Cycladic period and later, whereas the imported fabrics are predominantly non-calcareous, as are the earlier local fabrics (see Chapter 4 and 5).

The shape of temper is known to influence the Young's modulus of a ceramic (Rossi *et al.* 1972) and is also expected to affect thermal properties. The main reason for choosing two different *temper types* with distinctively different shapes, however, is the observation that in Akrotiri, from the late Middle Cycladic onwards, platy phyllite is added to all locally produced cooking ware, a temper that is absent in the earlier local fabrics. Granite has been chosen as a second temper material not only because of the angularity of broken pieces of the latter (as opposed to the flaky phyllitic

material), but also because of the potential of comparing those results to earlier measurements made on quartz tempered briquettes (Kilikoglou *et al.* 1998), as the major component of granite is quartz. Furthermore, the main fabric in the Akrotiri cooking ware assemblage that is not compatible with local origin is tempered with granite and is thought to be of Naxian origin.

The *amount of temper* is known to influence performance properties significantly (Kilikoglou *et al.* 1998). To study the influence of the amount of temper material, therefore, each clay-temper mixture was prepared with 10 and with 40 weight% temper (see Table 7.2 for correlation weight% and volume%).

The fourth variable in the production of the briquettes is *firing temperature*. Three different temperatures were selected: 550°C, 850°C and 1050°C. The lowest temperature, 550°C, has been chosen, as at this temperature many clay minerals have not yet dehydroxylated (with the notable exception of kaolinite). Calcite has not decomposed yet. At 850°C, the clay minerals have dehydroxylated and mostly lost their mineral structure. Significant changes in the microstructure of the ceramic that can be detected under the SEM, however, are just about to, or have not occurred yet. The onset temperature for vitrification is considered to be *c.* 850°C (Tite *et al.* 1975; 1982a; 1982b). At 1050°C, finally, the microstructure of the ceramic body has significantly changed. The clay particles have coalesced, resulting in a structure that is completely vitrified. In addition, high temperature phases such as calcium aluminium silicates have started to form. In the cooking ware assemblage at Akrotiri the whole spectrum of firing temperatures from virtually unfired to highly vitrified is represented.

The above considerations led to the following manufacturing schedule with ten different clay mixtures, fired to three different temperatures each, resulting in 30 different briquette types:

Mixture	Temper type	Clay	Amount of temper	Temperatures
1	no (control)	non-calcareous	no	550 / 850 / 1050°C
2		calcareous	no	550 / 850 / 1050°C
3	granitic temper	non-calcareous	10 %	550 / 850 / 1050°C
4			40 %	550 / 850 / 1050°C
5		calcareous	10 %	550 / 850 / 1050°C
6			40 %	550 / 850 / 1050°C
7	phyllitic temper	non-calcareous	10 %	550 / 850 / 1050°C
8			40 %	550 / 850 / 1050°C
9		calcareous	10 %	550 / 850 / 1050°C
10			40 %	550 / 850 / 1050°C

Table 6.1 Clay mixtures used in the manufacture of ceramic briquettes.

6.1 Manufacturing procedure

The following section describes the protocol followed for the manufacture of the ceramic briquettes. The raw materials - clays and temper materials - could not be employed directly; they needed to be refined prior to the preparation of ceramic pastes as is illustrated in Figure 6.1.

6.1.1 Preparation of the raw materials

The lumps of raw clay were broken down to smaller pieces which were then transferred to a wooden mortar and ground to a fine powder. The use of a wooden mortar ensured that pieces of hard rock would not be crushed and could subsequently be removed by sieving. The powdered clay was passed through sieves of consecutively smaller mesh size so that a fraction with particle size of $<63 \mu\text{m}$ was obtained. From this, the fraction with grain size $<30 \mu\text{m}$ was separated through levigation by applying Stokes' law (assumed particle density: 2.65 g/cm^3), a method commonly used in soil analysis (Kilmer and Alexander 1949). The resulting clay-water suspension was left for a few days in order to allow the clay particles to settle, and, after removal of the water layer, left to dry. The dried clay plates were crushed and ground to a fine powder.

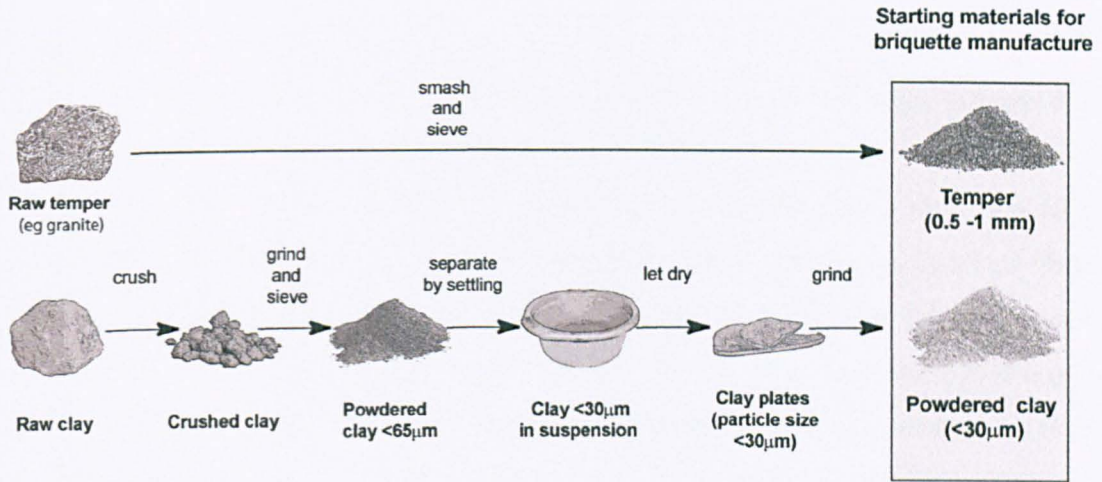


Figure 6.1 Procedure for the preparation of the starting materials for the briquettes' manufacture.

The granite chunks were crushed with a geological hammer and then sieved, separating the fraction with particle sizes between 0.5 and 1 mm to be used as temper material (Figure 6.2). The phyllite required a slightly different treatment: first, it was manually separated in thin sheets, taking care to remove any quartzite layers that would result in non platy particles. The layers were then very gently crushed, either by hand or with mortar and pestle, and sieved. As with the granite, the fraction with particle sizes in between 0.5 and 1 mm was used for tempering the briquettes.

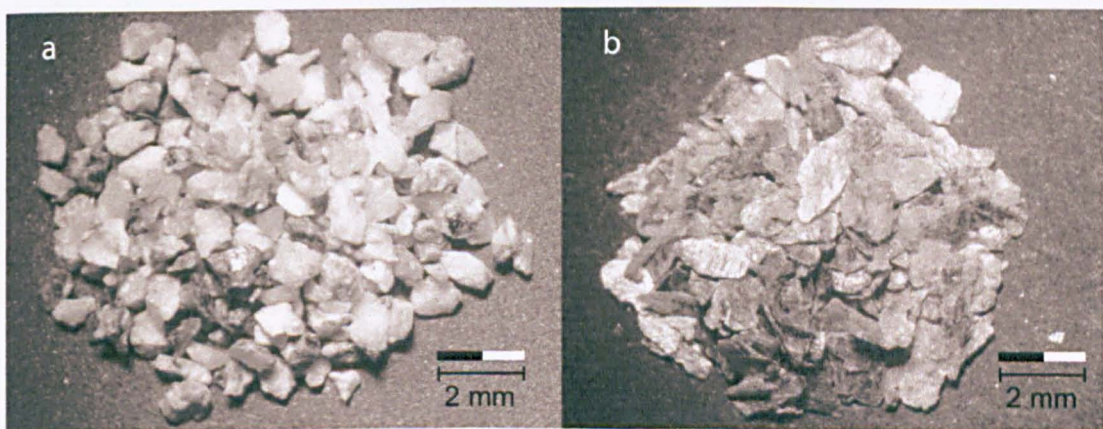


Figure 6.2 Photograph of granitic (a) and phyllitic (b) temper material as used in the production of the experimental briquettes, fraction with particle size 0.5-1 mm. The difference in shape is clearly visible.

6.1.2 Forming and firing of briquettes

The manufacture of the ceramic briquettes involved a series of steps (Figure 6.3). First, both components, clay and temper, were weighted. Then water was added, and the clay-temper mixture was stirred until it was homogeneous. This paste was filled in moulds made of plaster of Paris and matured for about one day, in order to obtain a workable clay mixture. The paste was thoroughly kneaded and briquettes were formed with the aid of a Perspex mould. Where the mixtures contained phyllite temper, the clay was repeatedly folded and flattened applying uniaxial pressure, in order to obtain an alignment of the platy particles parallel to the larger surfaces of the briquettes. The briquettes were left to dry for at least three weeks and subsequently fired in an oxidising atmosphere. The heating rate was kept constant at $3.3^{\circ}\text{C}/\text{min}$ (*c.* $200^{\circ}\text{C}/\text{h}$) for all firings and the maximum temperature was kept for one hour, after which the oven was switched off and the briquettes were left to cool down. The rectangular (*c.* $12 \times 7 \times 1$ cm) briquettes from which the test bars for the mechanical tests and for the determination of thermal shock resistance would be cut, were ground parallel. One of the large surfaces was ground even by hand; the briquette was then ground parallel. Subsequently, the briquettes were cut with a diamond blade, mounted on a Struers Accutom, into test bars of $1 \times 1 \times 7$ cm approximately.

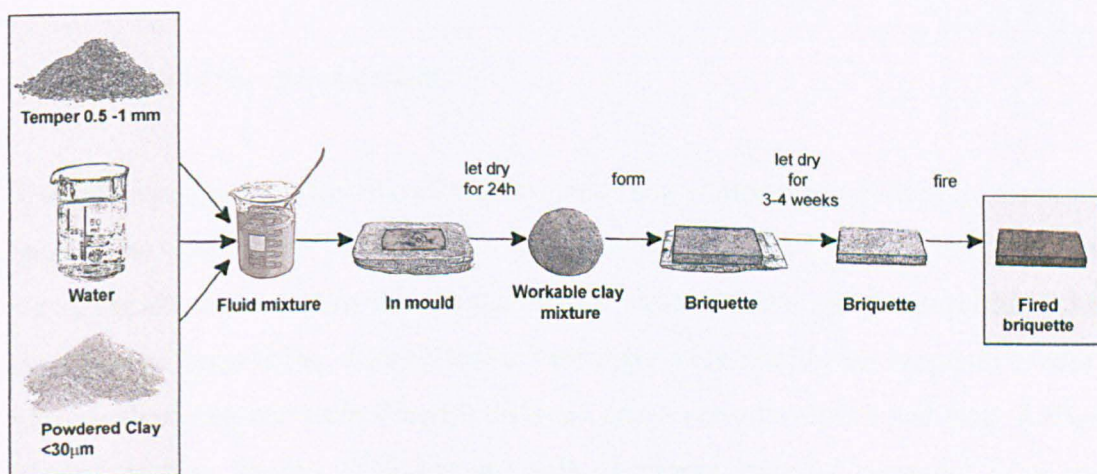


Figure 6.3 Procedure for the manufacture of ceramic briquettes from the starting materials.

6.1.3 Resulting fabrics

All mixtures resulted in pastes exhibiting good workability that would survive firing to all temperatures. The Kalami clay showed - in contrast to the calcareous Pikermi clay - pronounced shrinkage when fired at 1050°C. These briquettes were difficult to process, due to their tendency to warp during firing, combined with an exceedingly

high hardness. At the other end of the spectrum, the very low-fired briquettes of both clays that contain 40% granite temper resulted in very crumbly briquettes, which had to be handled with utmost care in order to avoid failure before actual testing. Of those two very fragile fabrics, the one based on the Pikermi clay seemed comparably more resistant. What regards the phyllite tempered briquettes, the procedure of multiple folding resulted in a good alignment of the platy particles, parallel to the large surfaces of the briquettes. This can be seen when examining their cross sections (Figure 6.4).

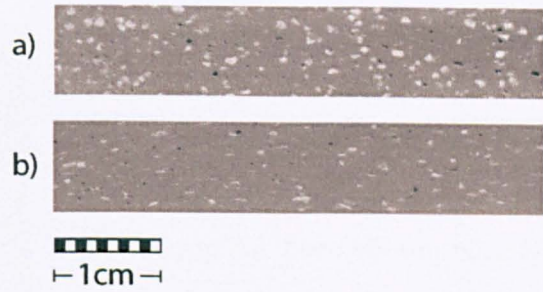


Figure 6.4 Cross section of fabrics containing 10% of granite (a) and 10% of phyllite temper (b) respectively.

6.2 Analyses of the raw materials

The following section describes the provenance and composition of the raw materials used in the manufacture of the replica briquettes, namely the base clays and the temper materials, and explains the changes in the clays' mineralogical composition that are observed upon firing. Two different base clays were used in the briquette production, a calcareous one from Pikermi (Attica), and a non-calcareous one from Kalami (Crete), both in Greece. Different amounts of temper material, prepared from two different rock types, were added to these clays. To achieve angular inclusions, weathered granite from the island of Naxos was crushed while platy inclusions were prepared from weathered phyllite procured from the Peloponnese.

6.2.1 Phyllite

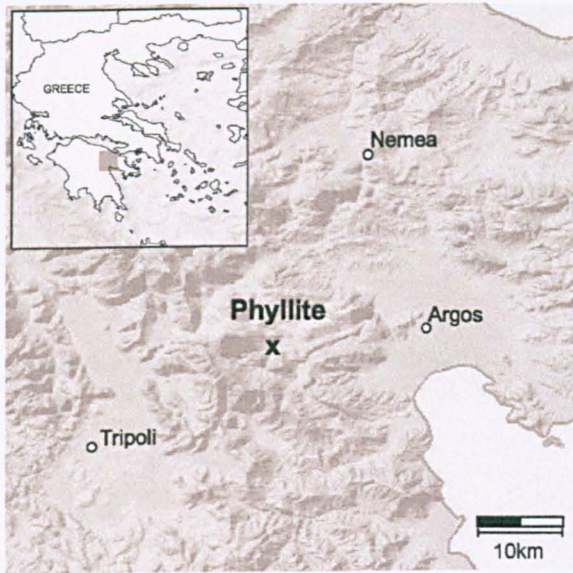


Figure 6.5 Origin of the phyllite used in the manufacture of the experimental briquettes.

phyllite can easily be collected after a few hundred meters, when it is exposed on the right side (GPS position N 37° 36,75', E 22° 34,16'). When sampling the phyllite, care was taken to select the flaky, dark grey material and to avoid very crumbly pieces that were rich in quartz and iron oxides, as the latter would disintegrate into crumbs rather than break into the desired flakes. The nature of the outcrop has been described as muscovitic schists and phyllites of sericitic (i.e. containing fine grained muscovite), graphitic, and chloritosericitic nature (IGME 1970). In accordance, XRD measurements on a powdered phyllite sample revealed the following constituents: quartz, muscovite, chlorite and traces of hematite (Figure 6.6). Graphite was not detected in the X-ray diffractograms, but this may be due to the poor crystallinity of the mineral; the dark colour of the phyllite as well as its grey streak indicates the presence of graphite.

The phyllite used in the manufacture of the ceramic briquettes was collected in the northeast Peloponnese, in the region of Argos, Greece. The specific outcrop has been chosen because of its relatively easy accessibility. Weathered phyllite was collected approximately 20 kilometres to the west of the town of Argos (Figure 6.5). En route from Argos to Merkouri there is a junction just before entering the village of Spilia. Leaving the main road to follow the small road to the right,

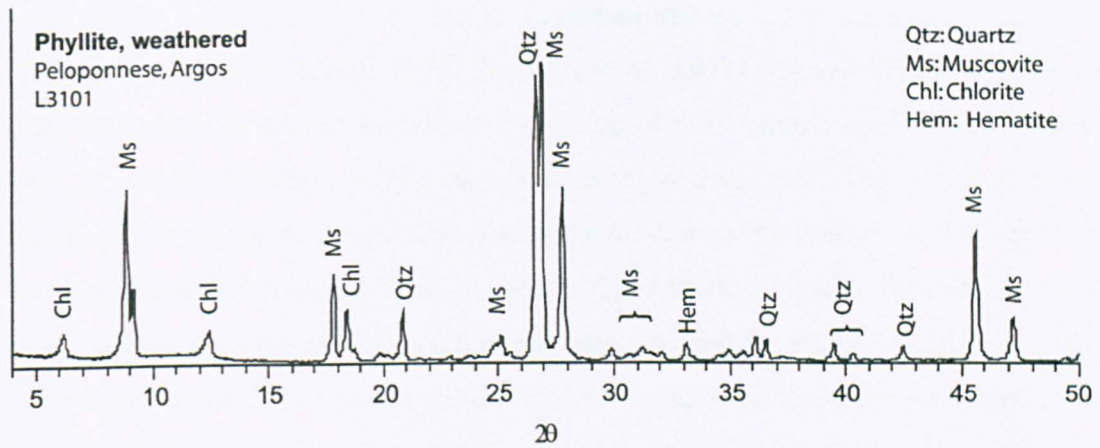


Figure 6.6 X-ray diffraction pattern of phyllite from northeast Peloponnese (Greece). The assignment of the peaks is indicated. Abbreviations of mineral names according to Kretz (1983).

6.2.2 Granite

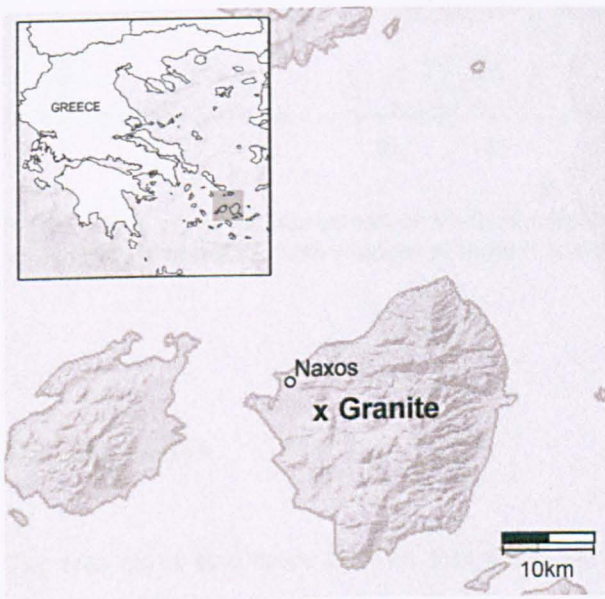


Figure 6.7 Origin of the granite used in the manufacture of the experimental briquettes.

Additionally, rock of granitic composition from the island of Naxos in the Cyclades, Greece, was used to temper the ceramic briquettes. The main imported fabric that is found within the cooking ware assemblage at Akrotiri, which is characterised by the presence of acid to intermediate igneous rock fragments, is thought to derive from Naxos (see Chapter 4). For this reason, it was decided to procure granitic rock from the western pluton of Naxos

to be used as temper material in the replication experiments, rather than rock from a random source. Weathered rock fragments have been collected at an outcrop alongside the road connecting Biblos with Glinadon, where the igneous intrusion has been exposed due to road construction (Figure 6.7). The granodiorite-granite intrusion in the west of the island is referred to as hornblende-biotite granite and contains quartz, alkali feldspars, plagioclase, biotite and hornblende, in addition clinopyroxene, and

occasionally sphene. Where the granite is metamorphosed, it is associated with secondary chloritisation (IGME 1973; Pe-Piper *et al.* 1997). X-ray diffraction analysis performed on a powdered sample of the collected rock sample confirmed the presence of quartz, feldspars (albite and orthoclase) and chlorite. The peaks of hornblende and biotite were absent from the diagram. A possible reason for this could be that the amount of those minerals is below the detection limit or because they are altogether absent from the sample that has been crushed for analysis. This is not too improbable as the hornblende-biotite granites are reported to be inhomogeneous on an outcrop scale (Pe-Piper *et al.* 1997).

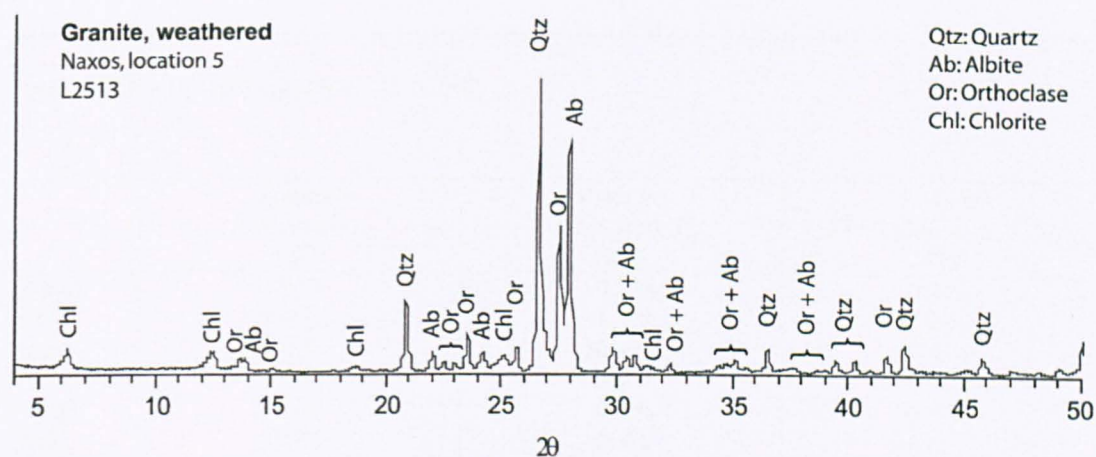


Figure 6.8 X-ray diffraction pattern of weathered granite from the island of Naxos. The assignment of the peaks is indicated. Abbreviations of mineral names according to Kretz (1983).

6.2.3 Base clays

The two clays that were used in this study were taken from the warehouse at the Institute of Materials Science at NCSR Demokritos as they are part of the Institute's clay collection. The calcareous clay from Pikermi (Attika, Greece) has been used in previous studies on mechanical properties of ceramics (Kilikoglou *et al.* 1998; Kilikoglou *et al.* 1995) while the non-calcareous clay from Kalami (Crete, Greece) had originally been sampled to be used in environmental stability laboratory tests. It is known from former analyses, and could be confirmed by acid test³⁵, that the clay from Pikermi is calcareous, while the Kalami clay does not show any reaction when

³⁵ A few drops of dilute hydrochloric acid (HCl) applied to a clay sample is widely used as a quick test to confirm the presence of carbonates. They effervesce when coming in contact with hydrochloric acid, as gaseous carbon dioxide is formed.

coming into contact with hydrochloric acid and can be regarded as non-calcareous. Prior to employing the clays in the manufacture of the replica briquettes, both were characterised using an array of analytical techniques. Chemical and mineralogical analyses were performed on the clay fraction (particle size <30 µm) that was separated from the raw clays as described above. The chemical composition of the two clays has been obtained by EDX, while XRD was used to study their mineralogical composition.

The chemical analyses by EDX were performed on polished sections of untempered briquettes that were fired to 1050°C. Table 6.2 lists the results of the element analyses and compares them to a former analysis of the Pikermi clay by X-ray fluorescence (XRF) (Kilikoglou *et al.* 1998).

	Kalami (this study) EDX	Pikermi (this study) EDX	Pikermi (Kilikoglou <i>et al.</i> 1998) XRF
Na ₂ O	1.0 %	0.9 %	0.4 %
MgO	1.0 %	1.9 %	2.2 %
Al ₂ O ₃	19.8 %	20.3 %	22.6 %
SiO ₂	65.0 %	50.3 %	49.1 %
P ₂ O ₅	0.6 %	0.9 %	0.2 %
SO ₃	0.2 %	0.4%	n.m.
Cl ₂ O	<0.1 %	<0.1%	n.m.
K ₂ O	2.5 %	2.6 %	3.1 %
CaO	0.5 %	14.0 %	11.2 %
TiO ₂	1.2 %	0.7 %	0.9 %
MnO	n.d.	0.1 %	0.1 %
Fe ₂ O ₃	8.3 %	8.0 %	10.1 %

Table 6.2 Chemical composition of the two clays used in the manufacture of the replica briquettes (in weight% oxides). The values taken from the literature, which have been measured by XRF, have been normalised to 100% in order to facilitate comparison with the data obtained in this study.

The results of the chemical analyses by EDX confirm that the Kalami clay is a typical non-calcareous clay with a calcium content of less than 1% CaO, while the clay from Pikermi is fairly calcareous, containing well above 10% CaO. The iron content of the two clays is comparable, as is the content in fluxes other than calcium oxide. The amount of calcium oxide in the Pikermi clay, measured by EDX, is higher than what has been previously measured for clay from the same outcrop (Kilikoglou *et al.* 1998). The results of this study are, however, in reasonable agreement with the published values, taking into account intra deposit variation, a phenomenon which is commonly observed in clay deposits (Hein *et al.* 2004).

X-ray diffraction patterns were obtained from randomly orientated powder samples of the <30 µm fraction of the respective clays. To facilitate the identification of ambiguous clay minerals, orientated specimens were prepared additionally. Orientation of the clay minerals was obtained by pipetting a few drops of a clay-water suspension onto a glass slide and letting it dry in air. Three such slides were prepared per base clay. One of the slides was saturated in an ethylene glycol atmosphere, thus shifting selectively the smectite peaks. The second slide was exposed for one hour to 550°C, breaking down the kaolinite's structure and removing its peaks from the diagram, while the third one was measured as it was (see Brown and Brindley 1980, 322-328).

	Pikermi	Kalami
Clay minerals		
Kaolinite	x	x
Illite/Muscovite	x	x
Chlorite	x	
Smectite	x	
Accessory minerals		
Quartz	x	x
Calcite	x	
Feldspar	x	x
Hematite	traces	traces

Table 6.3 Mineral phases detected by XRD in the two clays used in the manufacture of the replica briquettes.

Table 6.3 lists the mineral phases, clay and accessory, that could be identified by XRD. Both, the Pikermi and the Kalami clay, contain kaolinite and illite/muscovite³⁶ as clay minerals. Additionally, traces of chlorite and smectite were identified in the clay from Pikermi. With regard to accessory minerals, ubiquitous quartz and feldspar, together with traces of hematite, could be

ascertained in both clays. As expected, calcite was found in the Pikermi clay only. The relative amounts of the mineral phases that were detected by XRD were estimated with the reference intensity method. The diffractograms obtained from the randomly orientated samples were evaluated, following the procedure described by Hein *et al.* (2004); the resulting pie diagrams are shown together with the respective XRD diagrams in Figure 6.9. This quantification method is sensitive to factors such as sample preparation, mineral and amorphous phases not considered, and the accuracy of the k-factors used in the calculation. The pie diagrams must thus be regarded as a rough guide to the composition of the base clays rather than reflecting an accurate analysis of the amount of the constituent minerals. As the following example illustrates, however, the quantitative results inferred from the diffractograms were found to be in good agreement with the findings of the chemical analysis (EDX). For

³⁶ Illite and muscovite cannot be distinguished by XRD methods and are therefore referred to together.

the Pikermi clay, 23% calcite (CaCO_3) - corresponding to 9% calcium - was determined from the XRD diagram, using the intensity ratio method. This is in excellent agreement with the 10% calcium (14% CaO) found by EDX, considering that calcite might in fact not be the only phase in the Pikermi clay containing calcium, since certain feldspars and micas can contain this element as well.

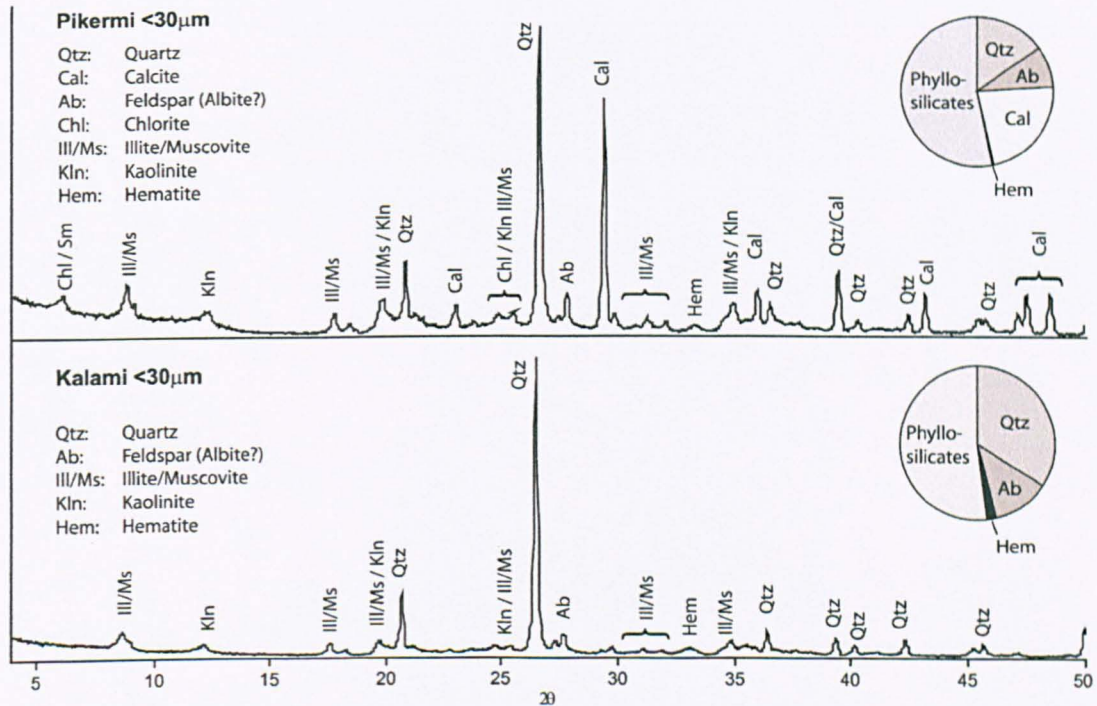


Figure 6.9 X-ray diffraction patterns of clay from Pikermi and Kalami. The measurements were performed on the $<30 \mu\text{m}$ fraction, on randomly orientated samples. The assignment of the reflections is indicated. Abbreviations of mineral names according to Kretz (1983). For the quantitative representation, provided by the pie diagrams, the clay minerals (phyllosilicates) have been summed up and are represented in a single slice.

The mineral phases in a ceramic are known to vary upon firing: some minerals decompose at elevated temperatures while others are formed, depending on the composition of the ceramic and on its thermal history. In archaeological science, this phenomenon is used frequently to assess the firing temperatures of pottery and structural ceramics by employing a 'mineralogical temperature scale' (Heimann 1982, 90), as has been discussed in detail in Chapter 5. It is primarily the fine clay matrix that is involved in these reactions, while the coarse temper particles usually remain relatively inert. In order to trace the changes that occur in the mineralogical composition of the experimental briquettes upon firing, XRD measurements were carried out on the untempered specimens which had been fired to different temperatures.

6.3.3 Compositional changes in the base clays upon firing

The thermal development of the mineral phases in the two base clays that were used in the manufacture of the experimental briquettes was monitored by XRD.

Calcareous clay (Pikermi)

Table 6.4 summarises the minerals that have been determined by XRD in the calcareous clay from Pikermi after firing to different temperatures.

PIKERMI				
	unfired	550°C	850°C	1050°C
Clay minerals				
Kaolinite	x			
Illite/Muscovite	x	x	traces	
Chlorite	x	traces		
Smectite	x			
Accessory minerals				
Quartz	x	x	x	x
Calcite	x	x		
Feldspar	traces	traces		
Hematite	traces	traces	x	x
Calcium aluminium silicates formed during firing				
Gehlenite			x	?
Wollastonite			x	
Diopside			?	x
Anorthite			traces	x

Table 6.4 Changes in mineralogical composition of the calcareous clay (Pikermi) upon firing.

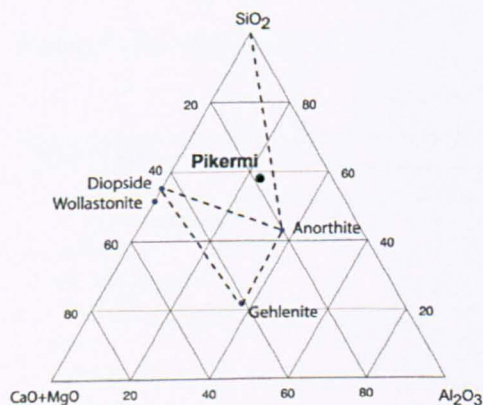


Figure 6.10 Ternary phase diagram for the Pikermi clay.

The clay from Pikermi follows the typical³⁷ behaviour of calcareous clay when thermally treated (Noll 1991, 95-104). The clay minerals decompose at relatively low temperatures: kaolinite has lost its structure at 550°C, while illite, the most stable clay mineral, can be detected up to 850°C (Table 6.4, Figure 6.11). As expected, cal-

³⁷ Other firing products, or formation sequences for the high temperature phases, have been observed in calcareous clays (e.g. Kacim and Hajjaji 2003). These are explained by other reaction mechanisms, based on differences in the composition of the raw clay.

cite has completely decomposed at 850°C. At this temperature, the metastable calcium-rich calcium (aluminium) silicates - gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) and wollastonite (CaSiO_3) - are formed. At 1050°C, diopside ($\text{CaMgSi}_2\text{O}_8$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), which contain less calcium, appear at their expense. The reason for this sequence is that at the start of the reaction, free lime CaO is available in excess and the calcium rich phases are formed preferably. The aluminium silicates which contain less calcium are formed only with increasing temperature and with increased availability of reactive silicate and alumina from the decomposition of the clay minerals. Additionally, gehlenite further reacts to anorthite, as is expected from the clay's composition: the ternary phase diagram for the Pikermi clay indicates anorthite and diopside as stable phases (Figure 6.10). The observed increase in the intensity of the hematite peaks with higher firing temperature suggests the formation of more crystalline Fe_2O_3 particles.

Non-calcareous clay (Kalami)

The Kalami clay follows the pattern of non-calcareous clays. As with the Pikermi clay, kaolinite has lost its structure after firing to 550°C, while the more stable clay mineral illite is detectable up to 850°C. Mullite is formed as a high temperature phase from illite/muscovite and kaolinite (Noll 1991) and can be identified in the diagrams of the high-fired clay. The hematite reflections become more intense and better resolved with increasing firing temperature also in the XRD diagrams of the Kalami clay (Figure 6.11).

KALAMI				
	unfired	550°C	850°C	1050°C
Clay minerals				
Kaolinite	x			
Illite/Muscovite	x	x	x	
Accessory minerals				
Quartz	x	x	x	x
Feldspar	traces	traces	traces	
Hematite	traces	traces	traces	x
High temperature phases				
Mullite				x

Table 6.5 Changes in mineralogical composition of the non-calcareous clay (Kalami) upon firing.

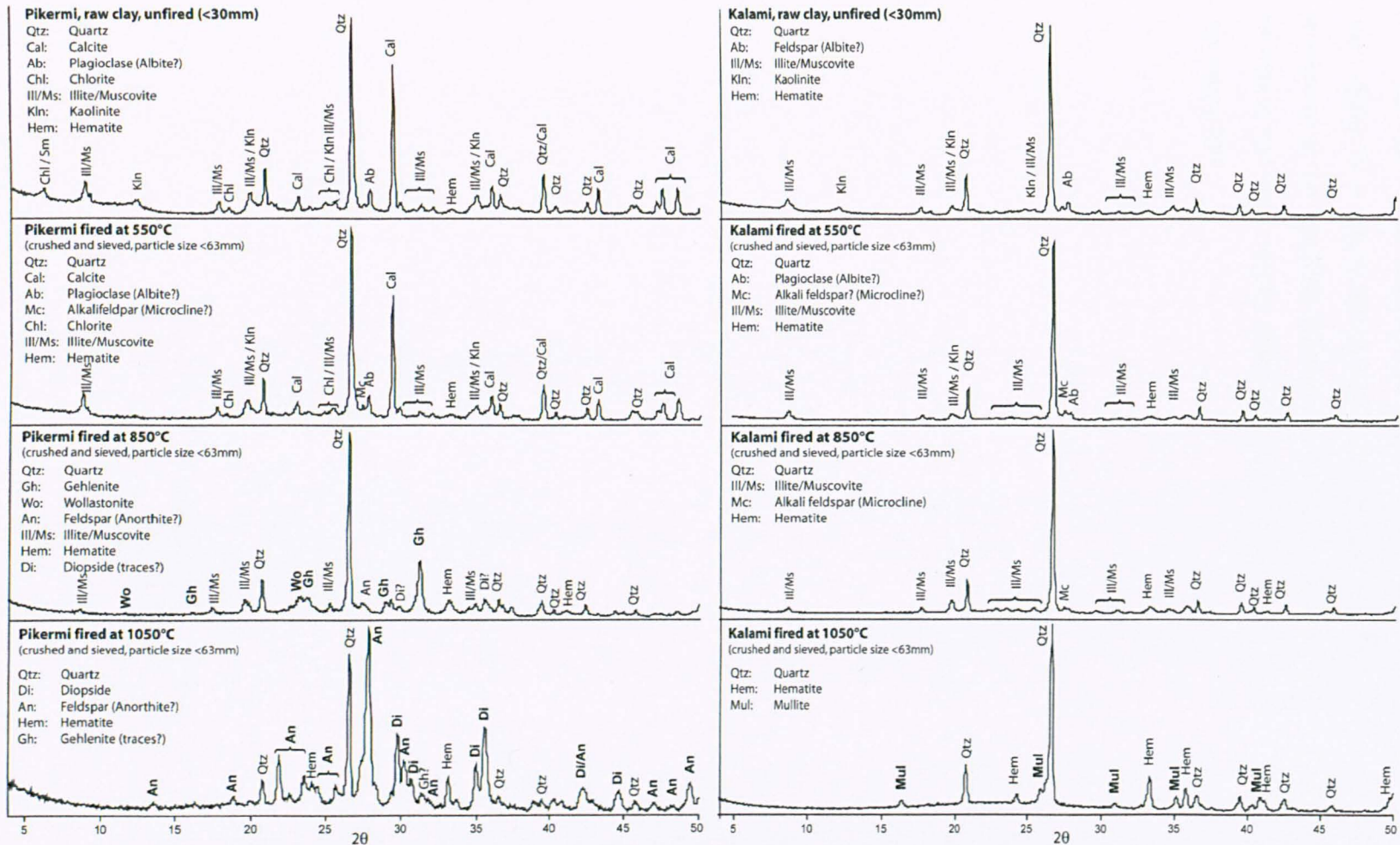


Figure 6.11 X-ray diffraction patterns of Pikermi and Kalami clay, unfired and fired to different temperatures (550°C, 850°C and 1050°C, increasing from top to bottom), showing the decomposition and neof ormation of mineral phases upon firing. High temperature phases are marked in bold.

These remarks conclude the present chapter. Following the description of raw materials employed in the manufacture of ceramic briquettes, and the presentation of the manufacturing protocol, the next two chapters deal with the mechanical and thermal properties of the resulting fabrics. The tests performed on the ceramic replicas are presented and their results discussed, based on changes observed in the ceramics' microstructure.

Chapter 7

Mechanical properties

Strength and toughness are important measures of the mechanical performance of archaeological ceramics. During manufacture and use-life, pottery is expected to withstand continuous exposure to various mechanical stresses, without experiencing structural damage or losing functionality. The nature and the extent of these external stresses depend to a large part on the function of the vessel: we might take amphorae as an example of vessels which need to survive stacking during transportation, while vessels used as containers should withstand the pressure exerted by their contents without bursting. The requirements put on cooking ware are of a somewhat different nature. As regards their response to mechanical stresses, cooking pots need to be able to retain their contents, especially when these are of fluid nature, but in addition they are exposed to continuous impacts by stirring, cleaning and by frequent handling, as they are used on a daily basis and manipulated repeatedly (Skibo 1992). For these reasons, both strength and toughness data provide criteria to evaluate a material's suitability for use in the production of cooking ware.

Fracture strength and toughness of traditional ceramics are known to be dependent on variables such as type of clay, temper and firing temperature. Most studies on this subject are, however, of a fragmentary nature in that they typically concentrate on the impact of only one factor on the mechanical properties. Additionally, a variety of factors, such as differing testing set-ups, makes it difficult to compare the results different studies, so that it is not always possible to draw general conclusions. The determination of mechanical properties of clay ceramics in view of archaeological material has been reviewed previously (Tite *et al.* 2001). The influence of firing temperature, amount, kind and size of temper, have all been assessed for fracture strength and toughness.

In most studies *fracture strength* has been determined as the modulus of rupture (MOR) in tensile bending tests³⁸, either on archaeological material (Stepionatis 1984) or on replicates (Feathers 1989; Hoard *et al.* 1995; Kilikoglou *et al.* 1995). It has been observed that an increase in firing temperature results in an increase in strength (Kilikoglou *et al.* 1998), that with higher amounts of temper the strength of a material decreases significantly (Stepionatis 1984; Kilikoglou *et al.* 1995), and that a smaller particle size reduces this decrease (Hoard *et al.* 1995; Kilikoglou *et al.* 1995). Comparing different temper material, Feathers (1989) found that tempering with shell resulted in stronger materials than the use of sand temper, an effect that is presumably linked to temper shape, while Hoard *et al.* (1995) report limestone fabrics to be stronger than granite or grog tempered ones. A few studies assessed what was termed *impact strength* (Bronitsky and Hamer 1986; Skibo *et al.* 1989). The results from those studies are difficult to assess, as impact testing is suitable to assess impact toughness in the case of brittle materials (Davidge 1986), when the initiation of a crack leads to fracture of a specimen and no additional energy is required to propagate a crack through the matrix. For the rather heavily tempered material that was tested, however, this requirement is not fulfilled; a stable fracture mode is expected and, indeed, observed (Bronitsky and Hamer 1986).

Toughness has been assessed on replicates, in loading experiments of different design. The use of different test set-ups makes a comparison difficult. Additionally, in the case of stable fracture, toughness is composed of an intrinsic part that accounts for crack initiation and of a part that accounts for the propagation of a crack. Non-standardised assessments of those parameters further complicate a comparison of the results. It has been observed that an increase in firing temperature results in a decrease of fracture toughness, while an increase in the amount of temper increases fracture toughness (Kilikoglou *et al.* 1995). Fracture toughness appears to be largely independent of temper size with perhaps a slight reduction for smaller temper sizes (Kilikoglou *et al.* 1995; Feathers and Scott 1989). Feathers and Scott (1989) found that the intrinsic fracture energy and, even more so, the energy that is required to propagate a crack through the ceramic, is higher in the case of shell tempered than of

³⁸ Since this testing method requires regularly shaped specimens and several measurements on different test bars cut from one sample, it can in many cases not be employed for archaeological specimens. There are, however, alternative tests better suited for archaeological ceramics (Neupert 1994; Vekinis and Kilikoglou 1998)

sand tempered fabrics. The tests of Hoard *et al.* (1995) were carried out on un-notched specimens, a fact that makes the numeric results difficult to interpret. However, from their graphs it becomes clear that grog and granite temper impart more to the stabilisation of crack growth than does limestone temper.

None of the studies based on archaeological material assessed the influence of different clay types. Carratero *et al.* (2002), however, compared a calcareous and a non-calcareous clay in respect of fracture strength with regard to building materials. A serious drawback of this specific study is the fact that the raw clays were not refined, therefore introducing an undefined 'tempering parameter' to the experiments. Tempering has a crucial influence on mechanical properties such as strength, toughness and porosity (Kilikoglou *et al.* 1998). In fact, the surprisingly low fracture strength found by Carratero *et al.* for the high-fired non-calcareous clay is most probably rather a result of its quite high amount of relatively large aplastic particles, than of the absence of calcite. Accordingly, Khaloufi *et al.* (2006) found significantly higher fracture strength for a non-calcareous clay fired to the same temperature.

This chapter provides a brief introduction to the basic principles of fracture mechanics before the influence of the investigated parameters on the mechanical properties of traditional ceramics is discussed. A variety of briquettes was manufactured as described in the previous chapter, to assess the influence of clay type, amount and type of temper - platy versus angular - on the mechanical properties over a range of firing temperatures. In the following pages, the results of measurements of strength, toughness and porosity on test bars cut from these replica briquettes are presented. Strength and toughness are interdependent variables; as an example, parameters increasing the toughness of a material in most cases simultaneously decrease its strength. Nevertheless, for reasons of clarity, the strength and toughness experiments are presented and discussed separately. Porosity is a material property that influences both strength and toughness, and is therefore presented first.

7.1 Porosity

Traditional ceramics commonly contain relatively high levels of porosity. In some cases organic temper is added to the clay pastes. The organic material burns out during firing and leaves additional pores and voids, thus increasing the overall porosity of the ceramic. This practice is frequently observed in the manufacture of ware types where a high porosity is beneficial in use, e.g., with water jars, to increase the cooling effectiveness (Skibo *et al.* 1989; Nicholson 1995) or with metallurgical ceramics, to increase heat resistance (Hein *et al.* 2007). The porosity of a material also has a substantial impact on mechanical properties such as fracture strength or Young's modulus (an increase in porosity for example leads to a decrease in strength as it introduces more flaws into a material). For this reason it was determined for all experimental fabrics.

7.1.1 Experimental procedure

Open and closed porosity were measured by water immersion according to standard methods (BSI 1999). Open or apparent porosity (π_{open}), the amount of pores connected to the sample surface, is defined as the ratio of the volume occupied by open pores to the total volume of the test piece, and is usually expressed in percentage terms. The open porosity can be determined by applying Archimedes' principle, as a function of dry (m_1), soaked (m_3) and immersed (m_2) mass of the test piece

$$\pi_{open} = \frac{m_3 - m_1}{m_3 - m_2} \times 100 \quad (7.1)$$

the closed porosity is given as

$$\pi_{closed} = \frac{\rho_{true} - \rho_{piece}}{\rho_{true}} \times 100 - \pi_{open} \quad (7.2)$$

where ρ_{true} is the true density of the material, and ρ_{piece} the actual density of the test piece. The density of the test piece, ρ_{piece} can be calculated from the weight measurements on the sample as

$$\rho_{piece} = \left(\frac{m_1}{m_3 - m_2} \right) \times \rho_{H_2O} \quad (7.3)$$

The true density (ρ_{true}) is expected to be in the range of 2750 kg·m⁻³ for all samples. The exact value of the true density of clay ceramics proves difficult to determine, however, as measurements have to be performed on finely ground powder, usually by immersion in water (BSI 2004b). On the one hand, the clay particles tend to aggregate and thus prevent a complete penetration of the liquid, on the other, some minerals incorporate the immersion liquid in their structure, thus changing their density (Grim 1968). An alternative way to determine the true density is to calculate it from the density of compressed powder pellets, assuming that the particles are densely packed. This, however, requires a powder with reasonable unimodal grain size distribution, a requirement unfortunately not usually met by clay ceramics.

	ρ_{true} [kg·m ⁻³]
Illite	2750 [†]
Muscovite	2820
Kaolinite	2600
Smectite (Montmorillonite)	2350
Chlorite	2420
Calcite	2710
Quartz	2620
Albite	2620
Hematite	5300
Kalami clay (non-calcareous)	2770
Pikermi clay (calcareous)	2680

Table 7.1 Densities of the constituent minerals* and calculated true densities of the base clays used in the experiments.

(*Source: Roberts et al. 1990 except [†]Zöller and Brockamp 1997, all cited in Barthelmy 2000).

density of 2780 kg·m⁻³ was assumed for the calculations. Since the density of clay minerals varies only slightly after heating to different temperatures (Rieke and

For the above reasons, the theoretical true density of the two base clays was determined as the sum of the values of the particular phases multiplied by their estimated volume fractions, calculated from the weight fractions as estimated by XRD (see Chapter 6). Table 7.1 lists the reference values used for the calculation of the theoretical true densities and the values obtained for the base clays. For illite and muscovite, which cannot be distinguished with roentgenographical means, a mean

Mauve 1942, cited in Grim 1968, 308), true density was considered independent of firing temperature.

In the same way, evaluating the X-ray diffractograms, the true density of the temper material was calculated as $2580 \text{ kg}\cdot\text{m}^{-3}$ for the Naxian granite and $2800 \text{ kg}\cdot\text{m}^{-3}$ for the phyllite procured from the Peloponnese. With these values, the true density of the tempered pastes could be calculated and, additionally, the effective volume fraction of temper material could be determined. The results confirmed that the volume percentage differs only negligibly from the weight percentage (Table 7.2).

clay	temper [weight%]	clay [volume%]	temper [volume%]	true density [$\text{kg}\cdot\text{m}^{-3}$]
Pikermi	10% granite	89.7	10.3	2670
	40% granite	59.1	40.9	2640
	10% phyllite	90.4	9.6	2690
	40% phyllite	61.0	39.0	2730
Kalami	10% granite	89.3	10.7	2750
	40% granite	58.3	41.7	2690
	10% phyllite	90.1	9.9	2770
	40% phyllite	60.3	39.7	2780

Table 7.2 Effective volume fraction (in percent) of clay and temper material, and calculated true densities for the different paste recipes.

Porosity was determined on pieces of approximately $25 \times 10 \times 10 \text{ mm}$. Prior to measuring the dry mass m_1 , the samples were dried at 115°C to constant mass. To achieve a complete saturation of the open pores the test pieces were boiled in water for about half an hour and then left to soak for a few days before the soaked mass m_3 was measured. The apparent mass (m_2) of the immersed test piece was determined by suspending the test bar from the scale pan suspension point of a hydrostatic balance while completely immersed in water.

7.1.2 Results and discussion

Besides the high-fired non-calcareous samples which will be discussed in detail, all clay mixtures resulted in fabrics with a total (open) porosity of $32 \pm 2\%$; closed po-

porosity has been determined as 0% (Table 7.3). Neither firing regime nor tempering influenced the porosity in these cases.

Paste recipe	bulk density [$\text{kg}\cdot\text{m}^{-3}$]			porosity [%]		
	550 °C	850 °C	1050 °C	550 °C	850 °C	1050 °C
Pikermi	1830	1830	1780	32	32	33
+ 10% granite	1880	1830	1820	30	31	32
+ 40% granite	1870	1830	1810	29	31	32
+ 10% phyllite	1880	1860	1810	30	31	33
+ 40% phyllite	1920	1840	1810	30	33	34
Kalami	1830	1850	2470	34	33	11 (10)
+ 10% granite	1870	1910	2400	32	31	13 (9)
+ 40% granite	1870	1880	2090	31	30	22 (3)
+ 10% phyllite	1850	1830	2450	33	34	12 (10)
+ 40% phyllite	1890	1900	2260	32	32	19 (4)

Table 7.3 Densities of the experimental briquettes and their overall porosity. Closed porosity is given in brackets if observed. When no closed porosity is indicated, it has been determined as 0%. In cases of fabrics with closed porosity, apparent porosity is the difference between overall porosity and closed porosity.

When comparing the untempered samples, the different behaviour of the high-fired, non-calcareous Kalami clay becomes immediately obvious. While the calcareous Pikermi clay displays a stable porosity that remains unchanged upon firing, the highest fired Kalami clay shows not only a considerable reduction in overall porosity but also the emergence of closed porosity. This process is accompanied by a significant increase in density (Table 7.3); accordingly, the briquettes made from Kalami clay, especially the untempered ones, are observed to shrink considerably after firing to 1050°C. This difference in the development of porosity is expected and has been observed elsewhere (Cultrone *et al.* 2004). The thermal decomposition of calcite provides the key for an explanation of the phenomenon. Before the vitrification process is initiated, both clays display a high (open) porosity, as the clay platelets are not connected or only loosely so. The different behaviour at higher temperatures can easily be explained by the absence or presence of gaseous carbon dioxide during firing. In calcareous clays, the decomposition of calcium carbonate at elevated temperatures results in the formation of an open cellular structure that is stable over a relatively wide temperature range. Up to a firing temperature of 1100°C, open porosity does not significantly change. In excess of this temperature, it reduces rapidly to nearly 0% (Maniatis and Tite 1975). In the absence of calcium carbonate, the platelets coalesce and the open pores and channels are closed with increasing vitrification,

leading to an overall decrease of open porosity and to the formation of closed pores from the onset of vitrification. In the case of non-calcareous clays, typically, open porosity decreases from 850°C in a roughly linear manner until 1000°C, where nearly no open pores are left (Khalfaoui *et al.* 2006), as the absence of CO₂ pressure allows the clay platelets to coalesce and increasingly close the open pores.

As stated above, tempering does not affect the porosity of the pastes based on Pikeremi clay within the firing temperatures chosen in this study. Also the porosity of mixtures with Kalami clay fired to 550°C and 850°C is not influenced by the addition of temper. Only the porosity of the high-fired Kalami pastes changes with the addition of temper. The untempered fabric shows a relatively low overall porosity of 11%, the addition of temper increases the porosity to up to 22%, so that the difference in porosity to the lower fired samples diminishes with increasing amount of temper (Figure 7.1). The type of temper seems not to play a significant role: adding angular, granitic temper appears to result in a slightly more pronounced increase in porosity than phyllitic temper. The introduction of temper also causes a change in the type of porosity; whereas the untempered sample is dominated by closed porosity, most porosity of the highly tempered specimen originates from open pores (Figure 7.1).

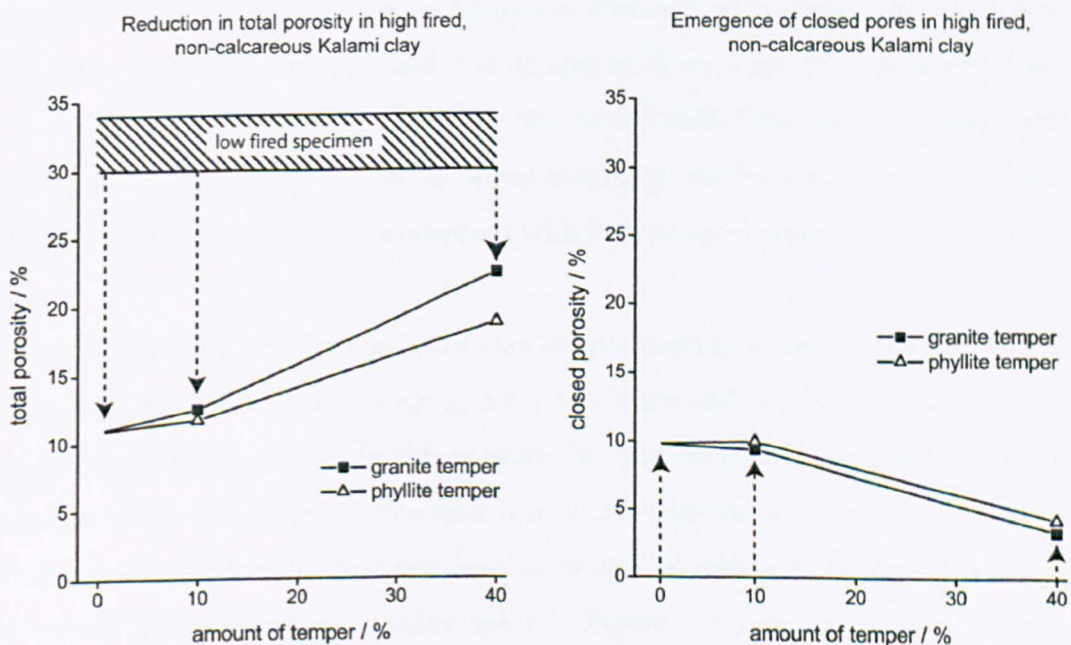


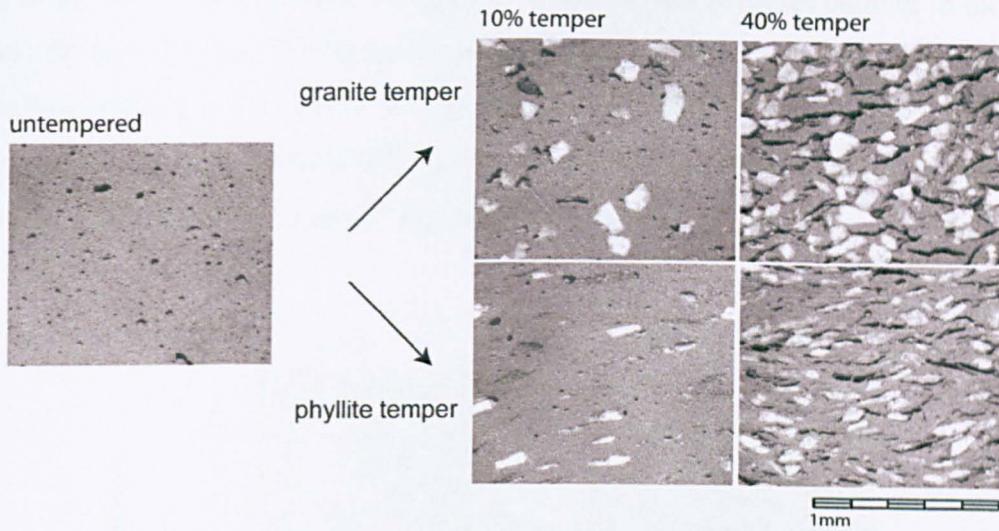
Figure 7.1 Total and closed porosity of the ceramic briquettes based on the non-calcareous Kalami clay and fired to 1050°C.

The fact that the addition of temper to high-fired, non-calcareous clay increases open porosity, might be explained by the formation of microcracks around the temper grains (Kilikoglou *et al.* 1995): the clay matrix contracts upon drying and thus experiences tensile stresses around the non contracting grains, these result in the formation of a damaged zone around the nonplastic inclusions. Adding more temper to a paste increases the chance that such damaged zones overlap and form an interconnecting network of open pores. The difference observed between pastes with phyllitic and granitic temper could accordingly be explained by differences in the extent of the damaged zones. These are caused by differences in the shape of the damaged zones around the temper particles, due to the different geometry of the inclusions (the effect of temper shape on damaged zones will be discussed in detail later on). Granite contains only a slightly larger amount of quartz (volume fraction 0.26 versus 0.19 in the case of phyllite), which undergoes a reversible volume expansion around 580°C, so that increased debonding of the inclusions is probably not the prevailing cause for the porosity differences observed between the two different types of temper.

The above might account for the changes observed at low temper grades. When looking at the cross sections of the high-fired specimens of both clays (Figure 7.2), however, we see that at 40% temper an altogether different effect comes into play. While the pores in the untempered and low tempered fabrics are predominantly below 1 mm size and of rather spherical shape, the fabrics with 40% temper are dominated by large elongated pores that are arranged parallel to the briquette's largest surfaces. The alignment of these voids is observed with both types of temper.

Upon firing to high temperatures, the clay matrix starts to shrink. In the case of 40% tempering, the rigid inclusions act as a solid skeleton and restrict the overall shrinkage of the briquette. Not being able to accommodate the resulting stresses, the matrix tears open and the observed structure with large voids results. These pores are not observed with the low-fired fabrics containing 40% phyllite and are significantly less prominent in the low-fired granitic fabrics (Figure 7.3), indicating that shrinkage during drying is not sufficient for the phyllitic fabrics, and that it is not until significant additional shrinkage occurs during firing, that the large voids emerge. As expected, the development of pores follows the vitrification pattern of the two different

Non-calcareous Kalami clay, fired at 1050°C



Calcareous Pikermi clay, fired at 1050°C

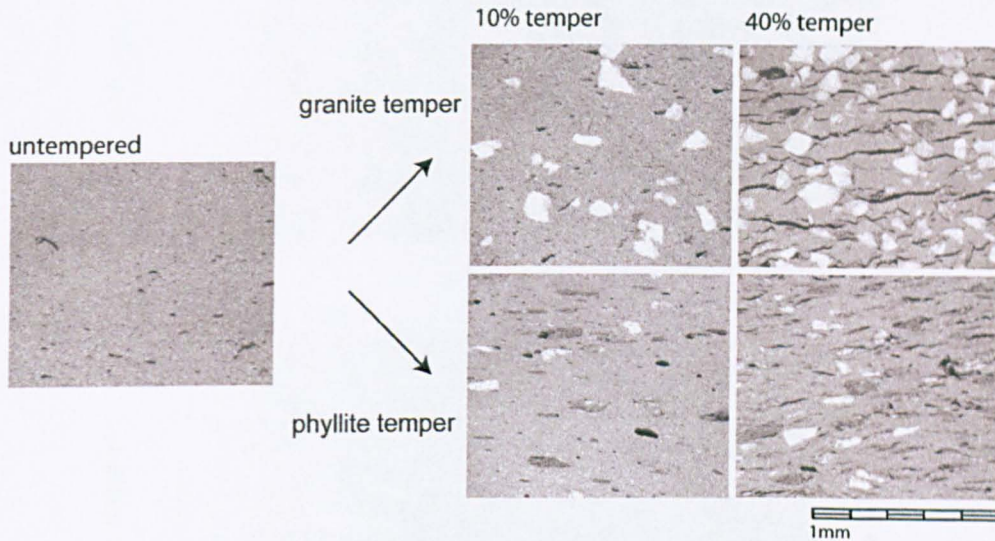


Figure 7.2 Structure of high-fired fabrics. The emergence of large elongated pores due to restricted shrinkage of the matrix can be observed in the highly tempered fabrics.

clays. (It is interesting to note here that the visual changes in porosity in the calcareous clay theoretically correspond to nothing more than a rearrangement of void volume elements, as is documented by the stability of the porosity values.) The vertical extent of the large pores seems more pronounced with the high-fired non-calcareous fabrics, in accordance with the higher shrinkage upon firing to 1050°C observed with the respective untempered briquettes. The orientation of the voids is related to manufacturing: clay particles are orientated when working the clay paste. In the case of the phyllite tempered fabrics, alignment is expected due to the repeated folding of the clay paste. However, the pores are orientated even in the granite tempered fabrics.

An alignment of clay particles is observed with mould formed briquettes, the pressing of the paste into a mould is enough to align the clay particles parallel to the surfaces (Rice 1987, 68). Shrinkage is greatest perpendicular to the clay platelets; the resulting stresses in the matrix are thus larger in this direction. Therefore, the opening of pores occurs preferentially perpendicular to the large surfaces of the briquettes, resulting in the observed horizontal alignment.

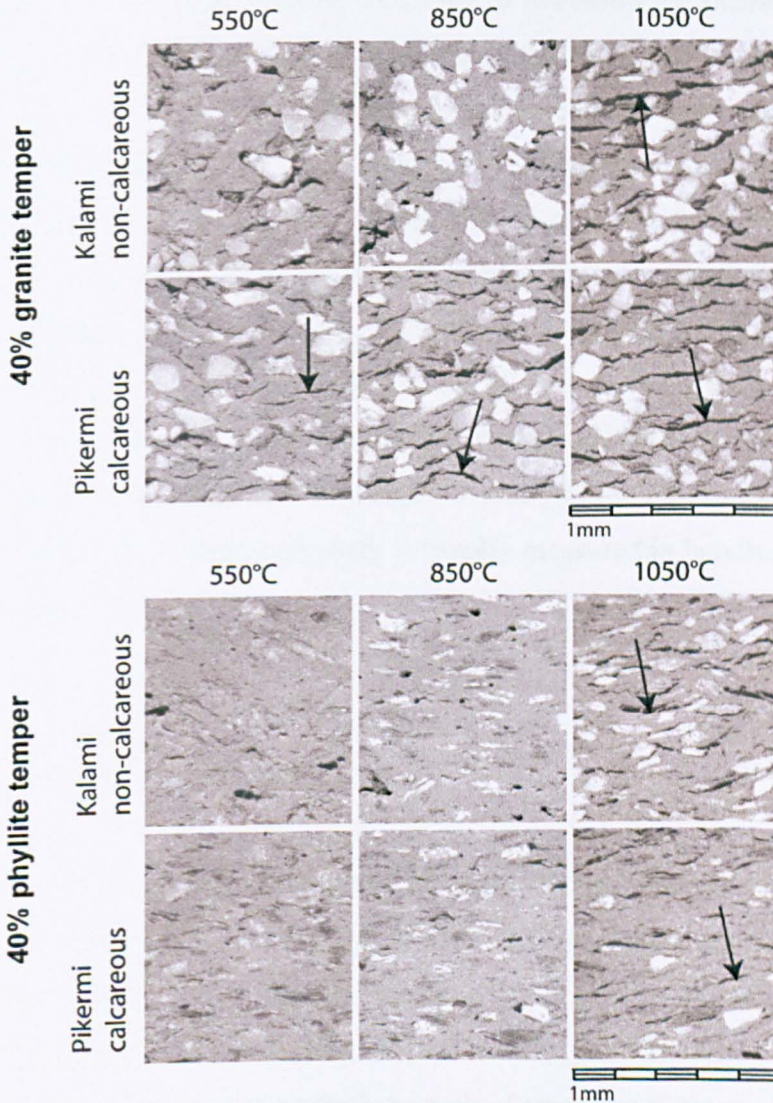


Figure 7.3 Development of shrinkage voids (examples indicated by arrows) in highly tempered fabrics. The scratches and surface irregularities in the low-fired specimens are due to abrasion by loose temper particles during cutting, as the inclusions adhere only very poorly to the low-fired matrix.

Accordingly, the observed differences between platy and angular temper, namely the fact that granitic temper introduces more porosity to the high-fired non-calcareous

fabrics, could be explained by different responses to shrinkage. Due to temper shape and the alignment of the inclusions, the phyllitic fabrics can better accommodate perpendicular shrinkage and less pores open up.

7.2 Strength

The strength of a material describes its ability to withstand the stresses it is subjected to without fracture. For pottery, compressive strength is of no importance; if it fractures, it usually does so in tension. Pottery is exposed to static stresses when stacked or used as a container, and to impact stress when dropped or hit. However, impact is mostly of such drastic nature that no conceivable practical strength increase would have prevented fracture (Dinsdale 1986). Impact strength can therefore not be regarded as a significant performance characteristic of pottery, as differences in it are neither meaningful nor behaviourally relevant when examining the performance of a vessel that is regularly used. For this reason, to study the influence of different material parameters on the perceivable strength of pottery, it makes most sense to look at *tensile strength*. This material property is usually measured in bending tests on rod or bar shaped specimens.

7.2.1 Theoretical considerations

The theoretical strength of a material can be calculated when assuming that an applied stress, in order to cause fracture, needs to deliver the energy that is required to break atomic bonds and create new surfaces. As a rule of thumb, the theoretical strength of a material is in the order of one tenth of its Young's modulus (Davidge 1979). The observation that the actual strength of ceramics is generally by a factor of 10 to 1000 lower than their theoretical strength, is commonly rationalised by the presence of flaws. Structural imperfections are present in every real material; composites are especially susceptible to high flaw concentrations. When examining the reaction of ceramic material to an applied external stress σ , the impact of such flaws can be quantified following the approach Griffith developed based on the work of

Inglis (Davidge 1986). Inglis showed that the maximal stress at the tip of an elliptical crack is

$$\sigma_{\max} = 2\sigma \sqrt{\frac{c}{\rho}} \quad (7.4)$$

where σ is the applied stress, ρ the radius at the crack tip, c the length of a crack at the surface and $2c$ the length of an internal crack. From equation 7.4, it follows that, the sharper the crack, i.e. the smaller the crack tip radius, the higher the maximal stress at the crack tip σ_{\max} which is created by an external applied stress σ . Flaws can therefore be considered as stress raising agents. (It is useful to keep in mind that the process of stress amplification also happens on a macroscopic scale, e.g. when an object has sharp corners, notches or similar). If the stress σ_{\max} at the crack tip exceeds the strength of the material, the crack starts to grow, as there is virtually no elastic deformation in ceramics, and, in the case of unstable fracture, leads to catastrophic failure without the need to apply further stress. Strength, determined as MOR, is defined by the maximum stress that can be applied to a specimen without cracks starting to grow. It can be calculated from the maximum load in the load-displacement curves that are obtained in bending tests. The strength of materials like ceramics with a multitude of microstructural imperfections that can act as fracture nuclei (e.g. inclusions, pores, debonded zones, microcracks) is not an intrinsic material property but strongly dependent on those pre-existent flaws, on their distribution and concentration. It is, therefore, difficult to compare strength measurements that have not been made under exactly the same conditions, and it is expected that the values for strength determined on different pieces of the same material will show some scattering, as the maximum stress that can be applied to a test bar is a function of the size and radius of its flaws.

7.2.2 Experimental procedure

Fracture strength, i.e transverse rupture strength (TRS) or modulus of rupture (MOR), was determined from three-point bending tests on bars of approximately 10 x 10 x 60 mm on an INSTRON 1195 universal testing machine, at a constant loading

rate of 109 $\mu\text{m}/\text{min}$. The load as a function of displacement was recorded for every specimen. For every ceramic type (corresponding to one set of parameters) fracture strength was measured on five bars. After breakage, the fracture area was examined visually. Data from bars with clearly identifiable macroscopic flaws in the fracture surface were not included in the determination of the mean. Fracture strength σ_f (in MPa) was then calculated using the following equation (BSI 2002):

$$\sigma_f = \frac{3P_{\max}s}{2bd^2} \quad (7.5)$$

where P_{\max} is the maximal load in N, s the span of the support rods, b the width and d the height of the specimen (all in mm), as denoted in Figure 7.4. (The fracture strength σ_f corresponds to the tensile strength of a material multiplied by a factor of about 1.5).

7.2.3 Results and discussion

Influence of clay type and firing temperature

The influence of clay type and firing temperature on TRS is illustrated in Figure 7.5 which shows the results of the strength measurements. At low firing temperatures, both clays exhibit similarly low strength, the calcareous samples being slightly stronger than the non-calcareous ones. With increasing firing temperature, fracture strength increases. In the case of the non-calcareous Kalami clay, a massive rise in strength is observed on firing to 1050°C, while with the Pikermi clay a significant strength increase is detected already at 850°C and upon further firing the fracture strength remains constant. The high-fired, non-calcareous clay is much stronger than its calcareous counterpart, the maximum strength of the Kalami clay being twice that of the Pikermi clay.

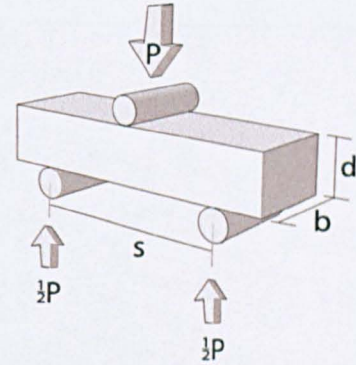


Figure 7.4 Set-up of the three-point bending test used for the determination of fracture strength. s was held at 40.8 mm for all experiments.

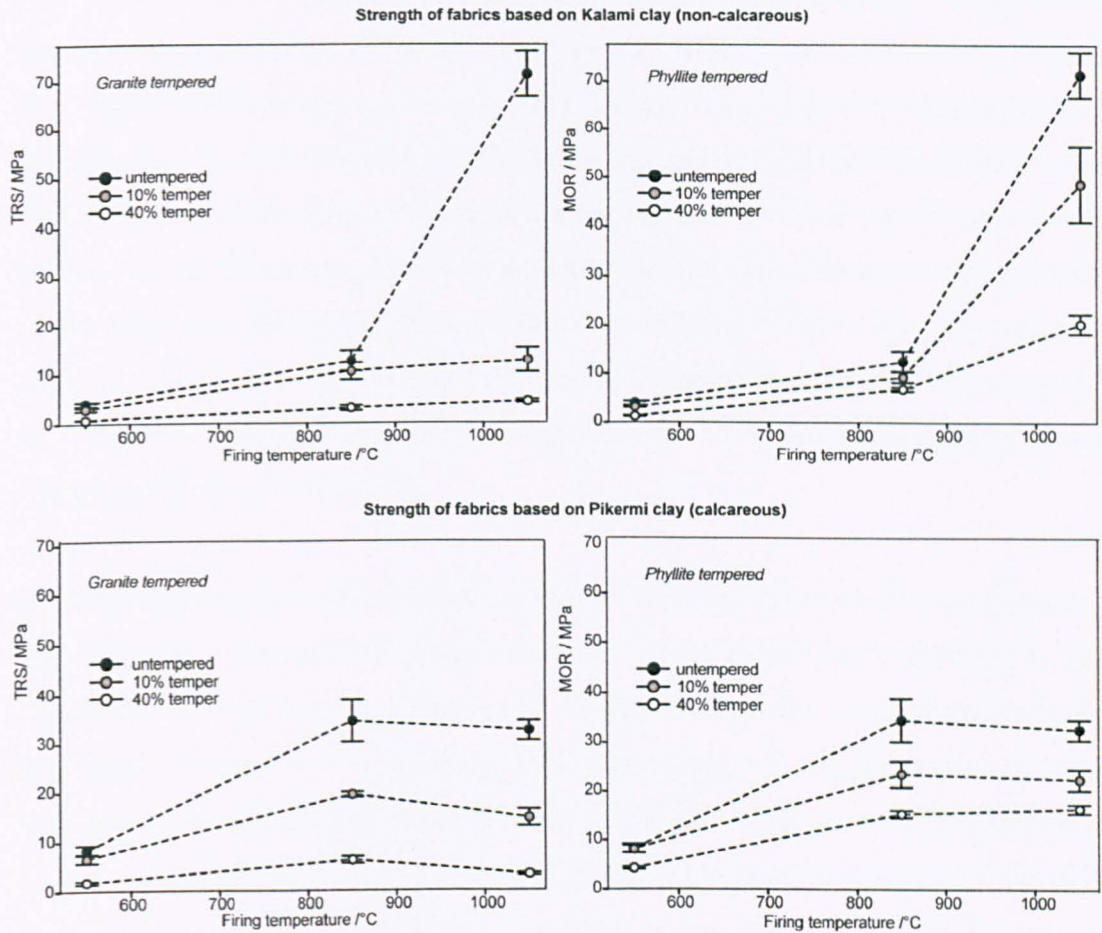


Figure 7.5 Fracture strength as determined on three point bending tests.

After firing at 550°C, the ceramics are virtually in their green state, a fact that is reflected by the fracture strength of the Pikermi clay that roughly corresponds to the green strength of the unfired material: Kilikoglou *et al.* (1995) determined the green strength of the Pikermi clay as 12.6 MPa. The subsequent vitrification of the clay matrix results in much stronger bonding than is the case with the only loosely connected clay particles in the low-fired specimen. It is therefore expected that changes in the degree of vitrification will be reflected in the measured strength values. In the case of the non-calcareous Kalami clay, the onset of vitrification occurs after 850°C, so briquettes fired to this temperature still exhibit relatively low strength. When the non-calcareous clay is fired to 1050°C, vitrification is complete (Figure 7.6), resulting in a massive increase in TRS: the strength of the high-fired Kalami clay is, at 71 MPa, comparable to that of mullite porcelain (Kingery *et al.* 1976, 791). Due to

the decomposition of calcium carbonate and the formation of calcium oxide which acts as a flux and reduces vitrification temperature, when fired to 850°C, the Pikermi clay, unlike the Kalami clay, already shows extensive vitrification. Accordingly, a significant increase in strength is observed in the specimen made from Pikermi clay. The strength level remains stable upon further increase in firing temperature, due to the fact that in calcareous ceramics the microstructure, including the extent of vitrification, does not change significantly between 850 and 1050°C (see discussion of porosity). The TRS of the Pikermi clay fired to temperatures of 850°C and above has been determined as 34 MPa, and is comparable to the 40 MPa found for the same clay by Kilikoglou *et al.* (1998).

It is striking that the high-fired Kalami clay is twice as strong as the corresponding Pikermi clay. This difference in maximum strength can be explained by the differences in microstructure: the area of vitrification is much more extensive in the non-calcareous than in the calcareous fabric (see Figure 7.6), an observation which is reflected in the significantly lower porosity and in the higher bulk density measured for the high-fired Kalami clay (Table 7.3). Pores act as flaws and as such reduce the strength of a material, so that any reduction in porosity leads to an increase in fracture strength.

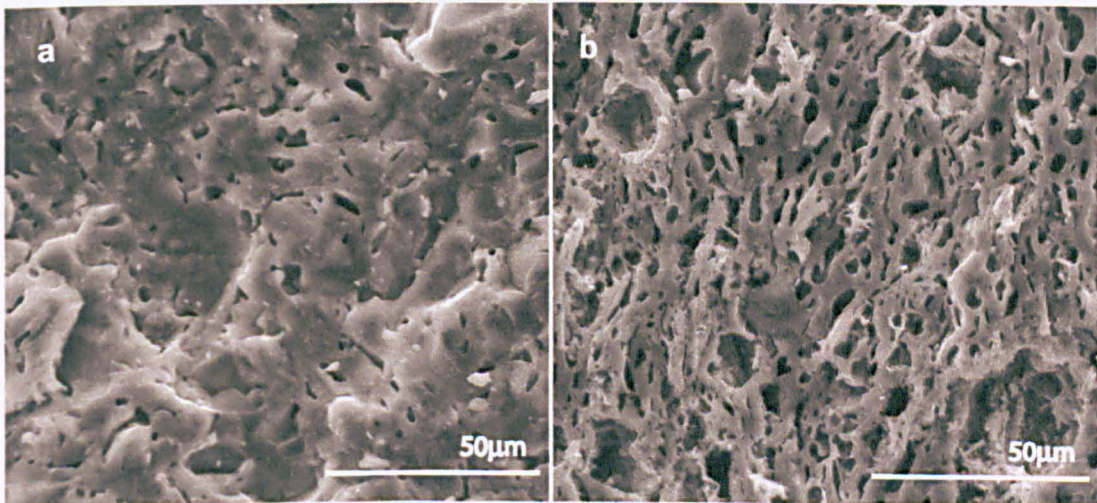


Figure 7.6 Scanning electron micrographs of fresh fractures of: *a*, Kalami clay fired to 1050°C; *b*, Pikermi clay fired to 1050°C.

At the other end of the spectrum, when examining the strength of the very low-fired specimen, it can be observed that the fracture strength of the Pikermi clay is nearly double the strength of the Kalami clay. At an effective firing temperature of 550°C, it can be assumed that the strength of the ceramics roughly corresponds to the green strength of the clay pastes. The higher strength of the low-fired calcareous clay can thus be explained by the cementing properties of calcite: the presence of calcite is known to increase the strength of a clay (Bell 2000, 98).

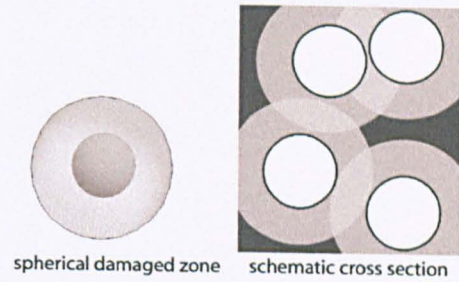
Influence of temper

From the graphs in Figure 7.5, two things become immediately apparent: first, any addition of temper reduces the strength of the material; secondly, this reduction becomes more pronounced when more temper is added. As discussed above, the strength of a material is dependent on the amount and size of the flaws it contains. These flaws range from pores to grain and phase boundaries. With the untempered specimen, the different levels of strength can be attributed satisfactorily to the relative porosities. The addition of temper particles, however, causes further matrix damage during firing and drying and introduces new types of flaws in the ceramic material. The observed decrease in fracture strength is a result of the consequential increase in overall flaw population.

A closer inspection of the graphs in Figure 7.5 reveals that the addition of phyllite has a less detrimental impact on fracture strength than the addition of granite. This effect becomes especially pronounced when adding high amounts of temper and at high firing temperatures. The reason that fabrics containing platy phillitic temper are stronger than their corresponding fabrics with the same amount of granite temper, is the relative amount of flaws in the two fabrics. These differences in flaw population introduced by different tempers are directly reflected in the relative porosity values of the high-fired Kalami clay (Figure 7.1). It might be argued that different thermal expansion of the temper material is responsible for this behaviour: quartz, which (at approximately 580°C) undergoes a reversible phase transition accompanied by a 7 percent volume change, is frequently cited in discussions of strength reduction (Tite *et al.* 2001).

As stated above, however, the volume fractions of quartz in both temper types, as determined by XRD methods, are quite similar (0.26 for granite and 0.19 for phyllite) and do not account on their own for the observed differences. Also, differences in the extent and amount of the large elongated pores, which are observed in some fabrics, cannot solely be responsible for the strength differences: this phenomenon occurs only in highly tempered fabrics whereas strength differences are also observed at lower levels of tempering. It is therefore necessary to look at the impact of temper shape on the integrity of the surrounding clay matrix. In the case of rather globular particles, the damage in the surrounding matrix that arises from drying can be described as a spherical damaged zone around the whole particle (Kilikoglou *et al.* 1995). In the case of platy particles, it can be argued the damaged zone corresponds roughly to a doughnut around the edges (Figure 7.7) and the overall volume fraction that is susceptible to developing microcracks during firing is thus much smaller, resulting in comparatively fewer flaws and higher fracture strength. These damaged zones influence not only fracture strength but also the toughness of a material and they are discussed in more detail in Appendix V.

A - Spherical inclusions



B - Disk shaped inclusions

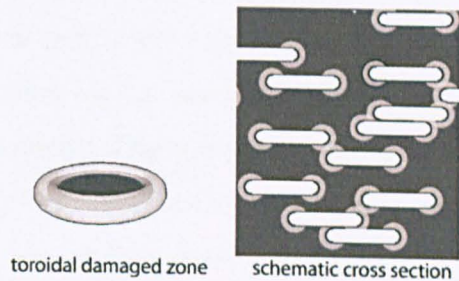


Figure 7.7 Different geometries of damaged zones due to different temper shape and resulting difference in amount of damaged matrix as illustrated by schematic cross sections (damaged area in grey).

7.3 Young's modulus

Young's modulus gives a measure of the stiffness of a material. As it is a basic material property and required, amongst others, for the determination of fracture toughness, its measurement will be discussed before proceeding to the determination of toughness. Young's modulus (E) is defined as the ratio, for small strains, of the rate of change of tensile stress σ with tensile strain ϵ (Davidge 1986). Materials with a

high tensile modulus of elasticity deform less for a given stress. For traditional ceramic materials, E commonly lies in the range of 50 up to 100 MPa (Dinsdale 1986).

7.3.1 Experimental procedure

To determine the Young's moduli of the different fabrics, the compliance corrected load-deflection curves from the strength measurements were graphically evaluated. E was obtained by determining the slope of the linear part of the curves and by subsequent application of a correction factor that accounts for the portion of shear stress that contributes to the overall stress due to test geometry. The compliance of the system was determined by measuring a comparatively huge steel specimen of assumedly infinite stiffness in the range of interest. $E_{bending}$ was then determined according to Kilikoglou *et al.* (1998) as:

$$E_{bending} = \frac{dP}{dx} \frac{s^3}{4bd^3} \quad (7.6)$$

where b and d are width and height of the test bar and s the distance between the notches (see Figure 7.4). When measuring the modulus of elasticity in bending, it is expected to find a lower value than when determining it in compression, because, due to the geometry of the set-up, shear stresses also start to play a role, whereas Young's modulus is associated with tensile stress only. In order to determine a correction factor that accounts for this, the Young's modulus of a material with well known elastic moduli, aluminium, was measured on a bar with the same dimensions as the ceramic test bars. The correction factor was found to be 1.2, so that the Young's modulus could be determined from the elastic modulus found in bending as:

$$E = 1.2 \times E_{bending} \quad (7.7)$$

7.3.2 Results and discussion

Influence of clay type and firing temperature

The Young's moduli vary considerably depending on base clay and firing temperature. For all paste recipes examined, an increase of Young's modulus with increasing firing temperature was observed. This increase is most pronounced in the case of the untempered Kalami clay between 850°C and 1050°C. In the case of the Pikermi clay, the Young's modulus increases earlier, but then remains stable upon further firing. The Young's modulus of ceramic material is known to increase significantly with increasing firing temperature (e.g. Kanygina *et al.* 1999), an observation linked to the increasing vitrification of ceramic material at higher firing temperatures (Wang *et al.* 2004). The different behaviour of the two clays can readily be explained by the development of different microstructures in calcareous and non-calcareous clays (see discussion of porosity). The measured Young's moduli correlate with the development of an open cellular structure that remains virtually unchanged between 850°C and 1050°C for calcareous clays, versus a later onset of vitrification that leads at 1050°C to a glassy phase with isolated pores for the Kalami clay (see Figure 7.6).

The Young's modulus is highly dependent on the porosity of a ceramic. When considering a pore as an inclusion, albeit with zero stiffness, it shows that the addition of pores results in a decrease in Young's modulus (Davidge 1986). A multitude of equations relate Young's modulus to porosity (Pabst *et al.* 2006). As a rule of thumb, it can be assumed that introducing 15%-20% porosity reduces the Young's modulus by half and 30-40% porosity by three quarters (Asmani *et al.* 2001; Latella *et al.* 2005; Pabst *et al.* 2006). This relationship is reflected in the different values for the untempered high-fired specimen. In accordance with the increased porosities that are measured when tempering high-fired Kalami pastes, decreased Young's moduli have been observed. However, the corresponding decreases are too high to be explained by an increase in porosity alone, as will be discussed below.

Influence of temper

In all cases, a high volume fraction of inclusions resulted in a pronounced decrease of the elasticity modulus, as compared to the untempered ceramic. Theoretically, the addition of material with a higher Young's modulus than the matrix should result in an increase of the ceramic's elasticity modulus. The Young's modulus of granite is in the range of 40-60 GPa, while the stiffness of metamorphic rocks, such as schist, phyllite and slate, is usually lower, in the range of 30 GPa (Bell 2000). An increase in Young's modulus would thus be expected in all tempered fabrics, with the sole exception of the high-fired Kalami clay (where, additionally, differences in porosity should play an important role). In reality, the opposite is observed, namely a decrease for all paste mixtures. This can be explained by the damage in the matrix that is caused by the temper particles.

The Young's moduli of granite tempered fabrics experience a higher reduction than those of the corresponding phyllitic fabrics. The influence of particle shape on the modulus of elasticity has been discussed for low temper concentrations (Rossi *et al.* 1972): it has been observed that a higher sphericity coincides with a more pronounced reduction in the elasticity modulus. This can be rationalised by the different extent of damaged zones that are caused by angular and platy temper as discussed in detail in Appendix V (influence of shape on fracture strength). The influence of microcracking on the modulus of elasticity is well established (Zimmermann 1985): an increase in microcracks is directly reflected in a reduction of stiffness.

KALAMI CLAY

Firing temperature	Untempered	10% granite	40% granite	10% phyllite	40% phyllite
550°C	2.3 (±0.3)	2.6 (±0.5)	0.28 (±0.02)	2.1 (±0.2)	0.7 (±0.1)
850°C	5.5 (±0.8)	6.2 (±1.0)	1.1 (±0.2)	5.0 (±0.6)	2.7 (±0.5)
1050°C	68.4 (±7.5)	13.4 (±1.4)	2.3 (±0.2)	47.1 (±9.4)	12.0 (±1.6)

PIKERMI CLAY

Firing temperature	Untempered	10% granite	40% granite	10% phyllite	40% phyllite
550°C	3.8 (±0.4)	4.2 (±0.4)	0.7 (±0.1)	4.4 (±0.4)	1.9 (±0.4)
850°C	21.4 (±2.0)	12.1 (±2.0)	3.1 (±0.7)	18.4 (±2.6)	4.8 (±0.3)
1050°C	24.2 (±3.2)	18.6 (±2.6)	1.3 (±0.2)	25.5 (±3.4)	8.7 (±0.6)

Table 7.4 Experimental Young's modulus values (in GPa) for the different paste recipes and firing temperatures. The values given are the mean of the determinations made on five independent load-displacement curves; standard deviations are given in brackets.

7.4 Toughness

Toughness describes the ability of a material containing a crack to withstand fracture by resisting crack propagation when exposed to external stresses. For pottery, especially for vessels such as amphorae or cooking pots that endure frequent handling, fracture toughness is a very important characteristic, as it is linked to maintaining structural integrity after crack initiation. Pre-existing flaws, ubiquitous in a material such as pottery, are potential origins of crack propagation. It is thus important that a crack, once initiated, is stopped effectively before leading to fatal fracture. As discussed above, cooking vessels are continuously exposed to a multitude of stresses; it is therefore a prerequisite for this kind of ware to be able to deal with incidental impact without failing.

7.4.1 Theoretical background

Fracture energy, the energy needed to fracture a specimen with a defined cross section area, consists of an intrinsic and a dissipation part. The intrinsic part describes the energy that is needed for the onset of fracture, i.e. for the crack to start growing, while the dissipation part describes the material's ability to stabilize crack propagation through processes such as deflection and arrest. For brittle materials, where only the first part plays a role, fracture toughness K_{Ic} is defined as the critical value of the stress intensity factor at a crack tip that is necessary to produce catastrophic failure under simple uniaxial loading. It can be shown that

$$K_{Ic} = Y\sigma_f\sqrt{\pi c} \quad (7.8)$$

This equation is commonly referred to as the Griffith criterion for fracture; c is the length of a crack at the surface and $2c$ is the length of an internal crack, σ_f the stress at which fracture occurs, and Y a dimensionless geometry factor. Fracture toughness K_{Ic} is usually measured in four point bending tests on a bar shaped specimen in which a standard fault (notch) has been introduced for comparability reasons. Toughness is linked to fracture energy by

$$K_{Ic} = \sqrt{EG_{Ic}} \quad (7.9)$$

In the case of brittle materials, the fracture energy is only determined by the intrinsic part G_{Ic} and can be determined by measuring fracture toughness K_{Ic} and Young's modulus E independently. However, various materials dispose of different mechanisms to dissipate energy during crack propagation and accordingly show stable fracture. Some examples of such dissipation mechanisms include crack deflection, bifurcation or arrest by introducing microcracks to the matrix or by tempering. Additionally, energy may be absorbed by the fracture of temper particles or by pull-out mechanisms (fiber reinforced materials), elastic deformation of the material or by phase-transitions (zirconia) (Davidge 1986; Shackleford 1996). This dissipation part, that contributes to fracture energy in stable fracture, can best be determined by integration of the load displacement curve after onset of fracture.

7.4.2 Experimental procedure

To assess toughness, the fracture energy was determined from four-point bending tests on notched bars of approximately 10 x 10 x 60 mm, with a notch depth of 1mm. The loading rate was held constant at 54 $\mu\text{m}/\text{min}$, load - displacement curves were recorded for every specimen. For every ceramic type (corresponding to one set of parameters) three bars were tested. The results of the few test bars where breakage would not originate from the notch but from pre-existing macroscopic flaws in the fabric were not included in the determination of the mean values. Fracture energy was calculated as described by Kilikoglou *et al.* (1998) as the sum of intrinsic G_{Ic} and dissipation energy G_t , with the dissipation energy being zero in the case of unstable fracture. To

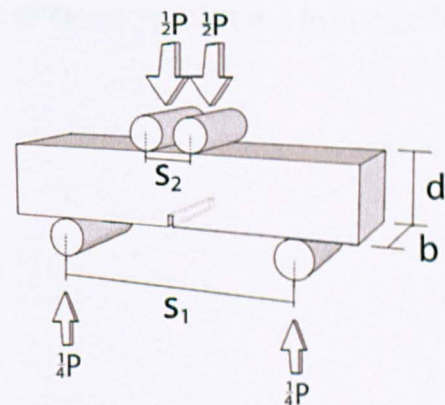


Figure 7.8 Set-up of the four-point bending test used for the determination of the fracture energy. s_1 was held at 40.8 mm, s_2 at 6.0 mm for all experiments.

determine the intrinsic energy, in a first step the critical stress intensity factor K_{Ic} was calculated as

$$K_{Ic} = \frac{3P_{max}(s_1 - s_2)}{2bd^2} \sqrt{\pi} F(\alpha) \quad (7.10)$$

where P_{max} is the maximal load in N, t the depth of the notch, (s_1-s_2) the difference in the span support rods, b the width and d the height of the specimen (all in mm), as shown in Figure 7.8. $F(\alpha) = 1.122 - 1.121\alpha + 3.74\alpha^2 + 3.873\alpha^3 - 19.05\alpha^4 + 22.55\alpha^5$ and $\alpha = t/d$. All K_{Ic} values were divided by a factor of 1.25, accounting for finite notch width. The intrinsic fracture energy can then be determined by applying equation (7.9) as

$$G_{Ic} = \frac{K_{Ic}^2}{E} \quad (7.11)$$

The energy dissipated during stable fracture G_s (the so called toughening component that corresponds to the tail contribution of the load-displacement curve) was determined by dividing the area under the stable part of the curve, obtained by integration, by the fracture area $(d-t) \cdot b$.

7.4.3 Results and discussion

Influence of clay type and firing temperature

No significant influence of clay type on fracture toughness is discernible. The K_{Ic} values of the higher fired specimen that show brittle fracture are compared to some common materials in Table 7.5. The slightly higher value for the Kalami clay is due to the increased matrix strength in the high-fired briquettes. In the case of untempered specimens, firing

Material	K_{Ic} [MPam ^{-1/2}]
Cement/Concrete (unreinforced)	0.2
Pikermi , fired (850/1050°C)	0.5
Electrical Porcelain	1
Kalami , fired (1050°C)	1.2
Alumina (Al ₂ O ₃)	3-5
Mild steel	140

Table 7.5 Comparison of the toughness values K_{Ic} of the fired raw clays with some common materials (source: Shackelford 1996).

temperature does not considerably influence fracture energy. However, the impact of firing conditions cannot be generalised as the toughness of a material is also dependent on the amount and kind of temper added (Figure 7.9). In the case of phyllitic temper, the highest toughness is observed at intermediate temperatures, decreasing with further firing, whereas high firing of granitic tempered ceramics is not accompanied by a decrease in toughness. Generalising, one could say that maximal toughness is observed at intermediate firing temperatures. This can be explained by the fact that G_{Ic} , the intrinsic part of fracture energy which is related to the energy that is necessary to start crack propagation, is linked to fracture strength and increases with firing temperature due to increasing strength of the matrix. The part that accounts for the energy that is absorbed during crack propagation (G_f), decreases accordingly, as a crack initiated at high loads normally results in brittle fracture, not allowing the fabric to absorb energy during crack propagation. As a consequence, an optimum in toughness is usually found at intermediate temperatures.

Influence of temper

Generally, the addition of temper increases the fracture energy of a material. The higher the volume fraction of inclusions, the higher is the toughness of the corresponding material. This behaviour is expected, as the rigid inclusions provide the ceramics with additional means of energy dissipation through crack deflection, bifurcation and arrest. With platy particles, pull-out processes are also expected. At low and intermediate firing temperatures, the nature of the temper material does not have a discernible influence on the toughness of the ceramics, both types of temper result in fabrics with similar fracture energies. Only when fired to 1050°C, do the fabrics containing phyllitic temper behave distinctively differently from their granitic counterparts: their toughness decreases in comparison to the lower fired pastes, while the toughness of the granitic tempered ceramics remains stable at a high level. Thus, for high firing temperatures, the addition of phyllitic temper results in significantly less tough material than granitic temper.

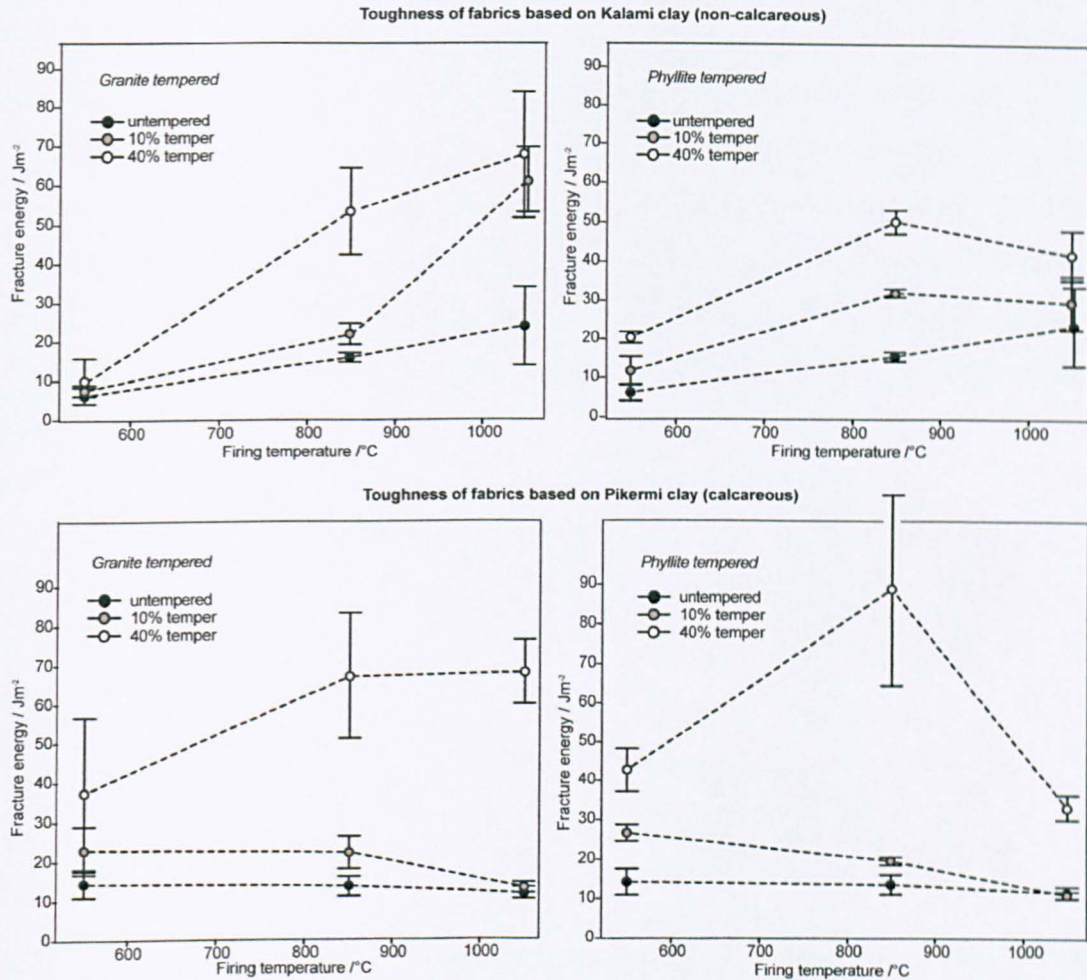


Figure 7.9 Fracture energy as determined in four-point bending tests.

The reason that fabrics containing platy phyllite are less tough than the corresponding fabrics with the same amount of granite temper is their different fracture mode. As illustrated in Figure 7.10 for the example of the high-fired non-calcareous fabric containing 40% temper, the intrinsic toughness G_{IC} is actually greater in the case of phyllitic temper. The decisive factor is the toughening component G_t that accounts for the energy that is absorbed during crack propagation. In the case of granitic temper, a significant amount of energy is needed to propagate the crack through the ceramic. In the case of phyllitic temper in a high-fired matrix, when fracture starts, the stored energy is so high that the crack propagates in an unstable way and the contribution of the toughening component G_t to the overall toughness G_{tot} becomes negligible. This behaviour can be explained by the different fracture mechanisms that occur in granite and phyllite tempered fabrics that are fired to 850°C and 1050°C respectively. In the ceramics that are fired to 850°C, both

temper types exhibit toughening properties. Crack propagation initiates at lower fracture loads, the stored energy is lower and it can be absorbed by crack deflection and through pull-out mechanisms of the particles. At higher firing temperatures, due to increasing strength of the matrix, crack propagation starts at higher loads. The stored energy is great enough for the crack to propagate *through* the particles, breaking the thin plates in half. As a result a trend to brittle fracture is observed in the phyllitic fabrics. The energy required to break through an angular granitic grain is much higher, so that the inclusions still act as barriers to crack propagation (see Figure 7.11).

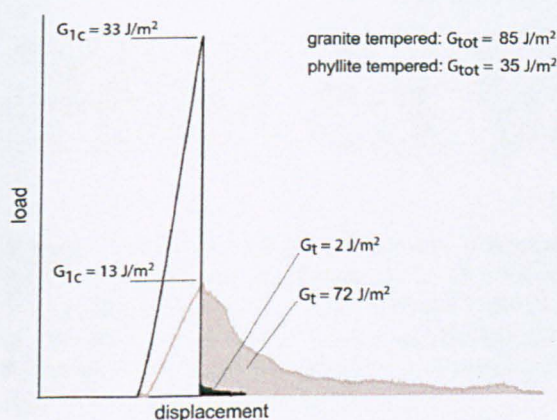


Figure 7.10 Load-displacement curves for two specimens made from Kalamy clay with 40% temper each.

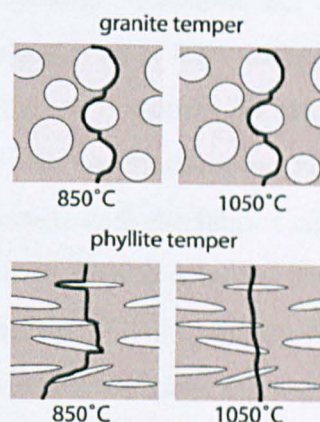


Figure 7.11 Schematic crack paths for phyllite and granite tempered fabrics fired to 850°C and 1050°C respectively.

For very low-fired ceramics, higher toughness has been found for platy temper material as compared to more equant inclusions (Feathers and Scott 1989), a phenomenon which has been explained by higher energy dissipation during crack propagation through pull-out mechanisms. The means of the toughness values of the lower fired samples in this study show a similar trend: before the onset of vitrification (i.e. for the non-calcareous clay in samples fired to 550°C and 850°C, for calcareous clay in samples fired to 550°C), phyllitic temper seems to result in slightly higher values for fracture toughness than granitic temper. Fracture initiates at very low loads in these cases, and all energy is absorbed by crack propagation. Due to the different geometry of the particles, more energy can be absorbed in the case of the phyllitic temper. When looking at the complete picture (Figure 7.9), however, these differences do not seem to be significant: first, because of the rather broad scattering

of the single measurements and the resulting high standard deviations; and secondly, because the values are very similar compared to the huge differences observed at higher firing temperatures.

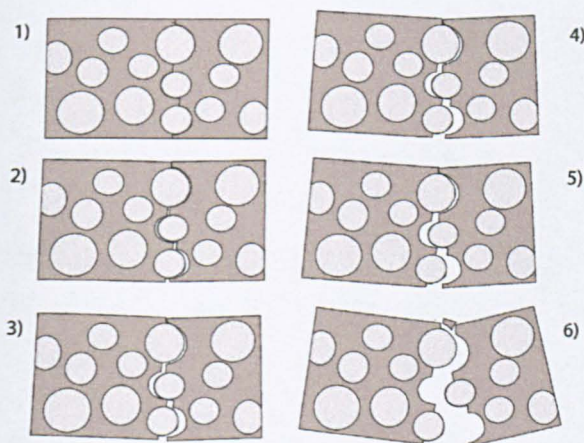


Figure 7.12 Indentation mechanism observed in highly tempered granitic ceramics. Even after complete fracture (1) the two pieces still hold together due to interlocking. Complete separation (6), usually by breakage of the 'weakest link' part of the matrix occurs only after significant bending (2-5).

As discussed above, high-fired ceramics with granitic temper showed significantly higher toughness than the corresponding phyllitic fabrics, due to the fact that the granite inclusions act as crack barriers even at high strength levels of the clay matrix. In addition to this, an indentation mechanism is observed with the fabrics containing 40% of granite temper. Even after complete division of the test bars into separate pieces, the two fracture surfaces still hold together, due to interlocking that is comparable to

Lego™ bricks. The protruding granitic grains act as studs while their impressions provide the sockets. As a result, the bars are able to undergo significant bending without losing structural integrity (Figure 7.12). This effect seems especially effective with the relatively large size of temper used here.

Finally, with the fabrics tempered with 10% granite, there is a clear difference in the behaviour of non-calcareous and calcareous fabrics. While in the samples made of Pikermi clay no energy dissipation is observed, the corresponding Kalami samples break in a stable manner. The impact of this different behaviour becomes especially pronounced with the high-fired samples. Figure 7.13 identifies the contribution of intrinsic toughness G_{Ic} and toughening component G_t to overall toughness for fabrics containing granite temper. The addition of 10% temper results in the case of the non-calcareous fabric fired at 1050°C in a substantial toughening component G_t , whereas in the corresponding calcareous fabric the contribution of G_t is negligible and overall toughness is determined by intrinsic toughness alone.

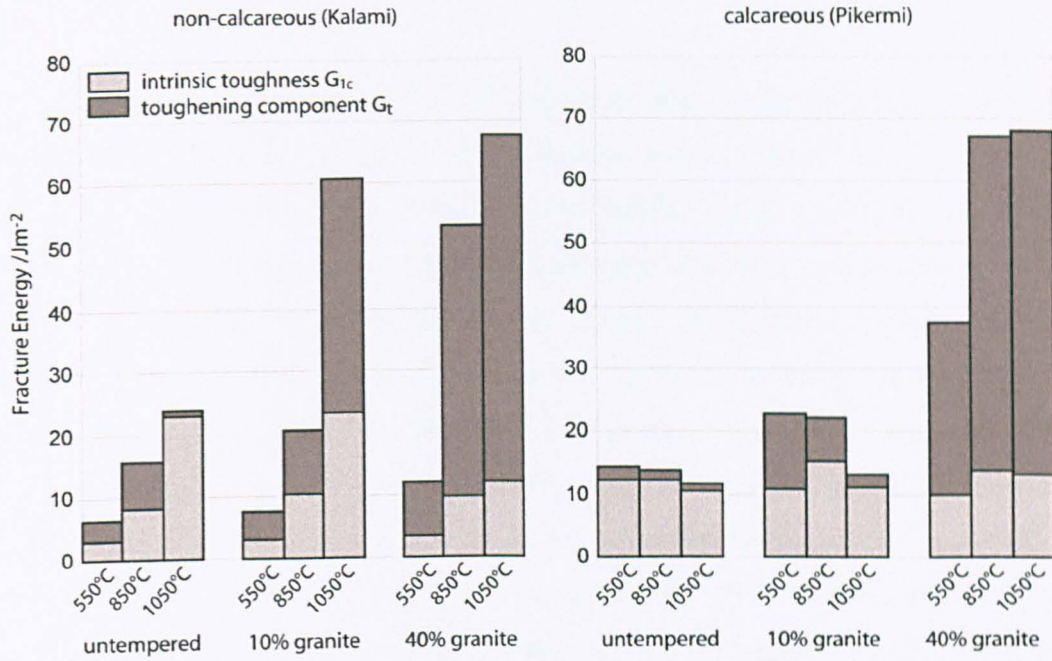


Figure 7.13 Contribution of intrinsic toughness G_{1c} and energy dissipation part G_t to total fracture toughness of granite tempered fabrics.

It has been observed for quartz tempered ceramics made of Pikermi clay that a change in the mode of fracture from brittle to stable occurs at around 20 volume% of temper material (Kilikoglou *et al.* 1995). The granite tempered Pikermi samples seem to follow this pattern; fabrics with 10% temper exhibit brittle fracture, while the ones containing 40% break in a stable manner. In the case of non-calcareous fabrics - at least when high-fired - this transition in fracture mode takes place at lower volume fractions of inclusions, as the ceramics containing 10% temper already show considerable energy dissipation during crack propagation. An explanation for this difference is provided by the larger shrinkage of the Kalami clay when fired to 1050°C. The pressure that the contracting matrix exerts on the rigid inclusions is higher in the case of the non-calcareous clay; accordingly the stresses experienced in the surrounding matrix are higher. The zones of microdamage and residual stresses that remain in the matrix after cooling down are therefore larger in the non-calcareous fabric. Microcracks and residual stress fields are both candidates for increasing the fracture toughness of a material (Green *et al.* 1999; Shackleford 1996, 322).

7.5 Summary and conclusions

It could be demonstrated that the - expected - increase in strength levels upon firing are linked directly to the degree of vitrification and to porosity development in the clay matrix. It follows that, within the temperature range examined, significantly higher fracture strength can be obtained with non-calcareous in comparison with calcareous base clays. In agreement with earlier experiments (Steponaitis 1989; Kilikoglou *et al.* 1995) a reduction of fracture strength was observed with increasing amounts of temper material. The observed differences in strength reduction with different temper shape could be qualitatively assessed by adapting the damaged zone model developed by Kilikoglou *et al.* (1995) to disk-shaped particles and confirmed measurements on low-fired specimens by Feathers (1989). The present study illustrates that an increase in firing temperature does not generally cause a decrease in toughness; at least in the case of coarse granitic temper, high firing temperatures can be reached without losing toughness. However, it has been substantiated that the single most important parameter for obtaining high fracture toughness is the presence of relatively high amounts of temper material. When comparing the impact of temper shape, differences seem to become relevant only at high firing temperatures, where platy temper results in significantly lower fracture toughness of the corresponding material, due to the high stresses reached at fracture initiation and the relative ease of breakage of the flat temper plates.

Table 7.6 summarizes the influence of the parameters that were varied in manufacture, i.e. firing temperature, amount of temper and temper material/shape on the strength, toughness and porosity of calcareous and non-calcareous fabrics. For the mechanical properties of clay cooking vessels, fracture toughness might be considered more important than strength. High fracture toughness can be obtained by adding a substantial amount of temper and firing the ceramics to intermediate firing temperatures. While the toughness of granitic fabrics remains stable at higher firing temperatures, care has to be taken with phyllitic fabrics not to fire the pottery too high, as otherwise fracture toughness decreases again. Only with granitic temper in a high-fired non-calcareous matrix can high fracture toughness be achieved with a relatively smaller amount of added temper. When comparing the strength of those fabrics with high fracture toughness, it shows that the highest values were obtained in the

case of a calcareous base clay when adding 40% phyllite and firing to 850°C. For a non-calcareous clay, a relatively high fracture strength, without losing toughness, was observed with a high-fired fabric containing 10% of granite.

A - Increasing firing temperature (550°C to 1050°C)

	non-calcareous clay	calcareous clay
strength	↑	
toughness - <i>untempered</i> - <i>phyllite temper</i> - <i>granite temper</i>	depending on temper <i>slight increase</i> <i>no influence</i> <i>max at 850°C</i> <i>max at 850-1050°C</i>	
porosity	↓	<i>no influence</i>

B - Increasing amount of temper (0 to 40%)

	non-calcareous clay	calcareous clay
strength	↓	
toughness	↑	
porosity - <i>low to intermediate firing temp.</i> - <i>high firing temperatures</i>	depending on firing temperature <i>no influence</i> <i>no influence</i>	
	↓	

C - Replacing granite with phyllite temper

	non-calcareous clay	calcareous clay
strength	↑	
toughness - <i>low to intermediate firing temp.</i> - <i>high firing temperatures</i>	depending on firing temperature <i>no influence</i>	
	↓	
porosity	↓	<i>no influence</i>

Table 7.6 The influence of different actions, which are under the potter's control during manufacture, on the mechanical properties of the resulting clay ceramics.

A rough classification of the main fabrics of the Akrotiri cooking ware assemblage according to their theoretical mechanical performance characteristics, as estimated based on the results from the replica study, concludes this chapter, for a more detailed discussion, the reader is referred to Chapter 10. The main *non-local fabric* is a

granitic fabric presumably of Naxian origin. This non-calcareous fabric that is generally fired to rather low temperatures and contains generous amounts of angular inclusions of granitic to granodioritic composition, is found in large quantities at the site, especially in the earlier periods. Considering its mechanical properties, it is expected to be rather tough, but of low fracture strength. For the discussion of the *local fabrics*, it is useful to have a look at the sequence of fabrics. The volcanic rock fabric of the Final Neolithic and the Early Cycladic period is characterised by high amounts of angular volcanic rock fragments in a low calcareous matrix, while the local fabric of the earlier Middle Cycladic periods is calcareous and the pumice content appears increased compared to the earlier material. Both fabrics are generally fired to a rather low temperature; for both a low fracture strength but a rather high fracture toughness is therefore expected. In the latest material, dated to the Middle Cycladic Phase C and an early Late Cycladic period, the addition of phyllite is observed; this change in paste preparation is in many cases accompanied by a significant increase in firing temperature, so higher fracture strength but less toughness than in the earlier fabrics is expected.

If we consider solely the influence of the characteristics assessed so far, and assume that fracture toughness is more central to the performance of cooking vessels than strength, we can state the following. First, it appears that the imported Naxian fabric is roughly equivalent to the local fabrics in its mechanical properties. Secondly, the addition of phyllite in conjunction with higher firing temperatures, observed in much of the later local ware, would appear to result in cooking ware of inferior quality. When assessing cooking ware ceramics, however, it is important not to forget that they are used to heat foodstuffs, and, in doing so, are put in contact with a source of heat, usually a fire. Therefore thermal performance properties, such as thermal conductivity and thermal shock resistance are of paramount importance when assessing the relative aptness of different fabrics for the manufacture of cooking vessels; the determination of those thermal performance properties is the subject of the next chapter.

Chapter 8

Thermal properties

Thermal properties such as thermal shock resistance and thermal conductivity are important in cooking vessels, which are exposed to heat in fulfilling their function. To be of use, cooking ware is expected to survive frequent, more or less sudden changes in temperature: a measure of this ability is provided by thermal shock resistance. Thermal shock resistance is a rather complex parameter, depending not only on the conditions of shocking, but, amongst other factors, also on the strength and toughness of a material and on its thermal conductivity. A high thermal conductivity allows a more even temperature distribution through a ceramic body, lessening the thermal stresses that arise in the material. Furthermore, through its impact on thermal diffusivity, thermal conductivity plays an important role in heating rate, and, simultaneously but conversely, governs the ability of a vessel to keep its contents warm once it is removed from a heat source. While there is an obvious positive dependence between the parameter and performance for thermal shock resistance - the greater the better - the establishment of a causal relationship between its thermal conductivity and the suitability of a vessel to be used for cooking purposes is unfortunately not as straightforward.

While the impact of thermal shock resistance on the suitability of a vessel to be used for cooking is more easily established than the impact of its thermal conductivity, exactly the opposite can be said for the definition of the two parameters: thermal conductivity is a physical quantity and as such clearly defined. Thermal shock resistance on the other hand is a complex parameter, dependent not only on different material properties such as thermal expansion coefficient, strength or toughness but, importantly, also on the conditions of thermal shock. As thermal conductivity is one of the many factors that influence the thermal shock behaviour of a material, it will be discussed before proceeding to thermal shock.

8.1 Thermal conductivity

Thermal conductivity is a measure of the heat transfer in a material under a particular temperature gradient; it indicates the ability of a material to transfer heat, a property that is significant for cooking ware. It is important to note that although it influences it, thermal conductivity is not a direct indicator of the *rate* a vessel heats its contents - heating rate is linked to thermal diffusivity which is not a material constant in itself, but a combination of thermal conductivity, heat capacity and density (Kingery *et al.* 1976). Thermal conductivity is a measure of the heat flux through a vessel wall at *steady state*. Steady state is reached for example when water in a pot is boiling, thus ensuring a constant temperature of the inner surface of 100°C. A material with a higher thermal conductivity distributes the heat within a vessel more evenly. However, thermal conductivity through thermal diffusivity also influences the retention of heat. Accordingly, ceramic vessels keep their contents warm for a longer time period than metal ones, due to their relatively lower thermal diffusivity (Tada 2002). Thermal diffusivity and conductivity direct the choice of different materials for specific cooking methods at least in contemporary kitchens: ceramic ware is usually selected to allow slow, prolonged simmering of foods whereas metal vessels such as stainless steel or aluminium pans are of advantage where rapid heating and relatively low duration at peak temperature are desired, e.g. for boiling or frying. Thermal diffusivity and conductivity are very different in these materials, which, however, are all used in the preparation of cooked foods. Higher thermal conductivity or diffusivity is thus *per se* not necessarily tantamount to better performance; cooking practices have to be taken into account when evaluating the suitability of a material.

8.1.1 Theoretical background

Heat transfer can occur through three different mechanisms according to the diffusion medium: convection, conduction and radiation. When considering cooking processes, heat transfer by radiation can normally be neglected; at the relatively low temperatures, the contribution of heat radiation is still small compared to the other heat transfer processes. Heat convection, the heat transfer between a solid surface and a moving fluid, such as water (or air) in a cooking pot, has to be considered only

at the ceramic surfaces (Hein and Kilikoglou 2007). Heat conduction, finally, describes the heat transfer in solid materials. Under steady state conditions, the heat flux is proportional to the temperature gradient in a body. The proportionality factor k is a material constant and is called *thermal conductivity* (Kingery *et al.* 1976)

$$\frac{dQ}{dt} = -kA \frac{dT}{dx} \quad (8.1)$$

dQ is the amount of heat flowing perpendicular to the area A in a time dt and $-dT/dx$ the temperature gradient. In the case of clay based ceramics, thermal conductivity typically lies in the range from 0.1 up to 1.7 W·m⁻¹·K⁻¹, normally with increasing values at higher temperatures (Dinsdale 1986; Shakleford 1996). These values are very low compared to the thermal conductivity of metals, ceramics are therefore usually considered to be an insulating material. Heat transfer under non steady state conditions is described with the heat conduction equation (Kingery *et al.* 1976),

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T \quad (8.2)$$

where α is the thermal diffusivity and defined as the quotient between the thermal conductivity k and the heat capacity per unit volume ρc_p . A material with a high thermal diffusivity is able to rapidly adjust its temperature to that of its surroundings.

Heat transfer in ceramics takes place by transfer of phonons (quanta of energy) through vibration of atoms in the crystal lattice; anything that hinders the flow of energy, such as defects, pores, and grain boundaries thus lowers the thermal conductivity. The thermal conductivity of a multiphase material such as clay based ceramics depends not only on the amount and the individual conductivities of the constituents, but also on their size, shape and orientation (Kingery *et al.* 1976). It is important to note here that porosity has a significant effect on thermal conductivity, as the pores act as heat barriers.

Up to now, discussions concerning the adaptation of pottery to fulfil different use requirements with regard to material properties and specialisation, have usually fo-

cused on strength, toughness and their relationship to thermal shock resistance (Tite *et al.* 2001). Surprisingly little emphasis has been put on *thermal conductivity*, although this material property arguably plays an important role in ceramics used in connection with heat, such as cooking ware. Nonetheless, much of the discussion on thermal properties is restricted to thermal shock resistance. Thermal conductivity is, if at all, referred to in passing as being controllable through wall thickness (Tite and Kilikoglou 2002; Broeksman *et al.* 2004); Braun (1983) linked the development of thinner walls, and therefore higher thermal conductivity, to changes in nutrition patterns.

In an approach to quantify heat transfer in cooking vessels, the parameter *heating effectiveness* was defined (Skibo *et al.* 1989; Schiffer 1990), a factor that describes the rate with which the temperature of a vessels' content is raised when applying an external heat source, determined as the time that is needed to bring water contained in a vessel to boiling. Sand temper was reported to increase heating effectiveness (Skibo *et al.* 1989) relative to other types of temper and non tempered pottery. Also slips or linings appeared to increase this parameter, assumedly by reducing permeability (Schiffer 1990; Longacre *et al.* 2000; Pierce 2005). However, heating effectiveness is not a physical quantity but a complex product of thermal conductivity, heat flux, heat capacity, permeability and shape of the vessels. Thus, while such experiments might give some answers on behavioural aspects of pottery, they do not provide enough evidence to understand the exact principles that control these properties.

To determine the thermal conductivity of different clay ceramics, a set-up has been developed that is based on the so-called Lees' disk, a classical schoolbook experiment to assess the thermal conductivity of insulating materials (Hein *et al.* 2008b). Its design and the underlying principles are described in detail below.

8.1.2 Experimental procedure

The thermal conductivity of the ceramic samples was determined with a modified Lees' disk set-up (Figures 8.1 and 8.2), a simple steady state method for the determination of the thermal conductivity of insulating materials. The sample *S* is sandwiched between a heat source *P* and a heat conductor *B*. The temperature of the heat

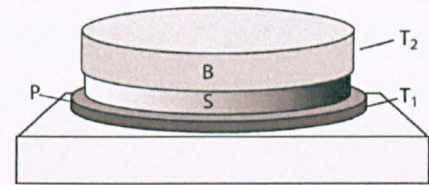


Figure 8.1 Schematic representation of the modified Lees' disk method employed in the present study. *P*: heating plate, *S*: sample, *B*: brass disk.

source is controlled and stabilized. In the standard form of the experiment, the heat source consists of a hollow cylinder through which water vapour from a steam heater is passed. In order to be able to reach temperatures higher than 100°C, a heating plate was employed in this set-up which allowed choosing measurement temperatures of up to 400°C. The temperature T_1 of the heating plate was controlled electronically and monitored with a thermocouple attached to the heating plate. The temperature of the brass disk T_2 was monitored with a second thermocouple. Both thermocouples were connected to a data logger, so that the temperature development during the measurement could be recorded.

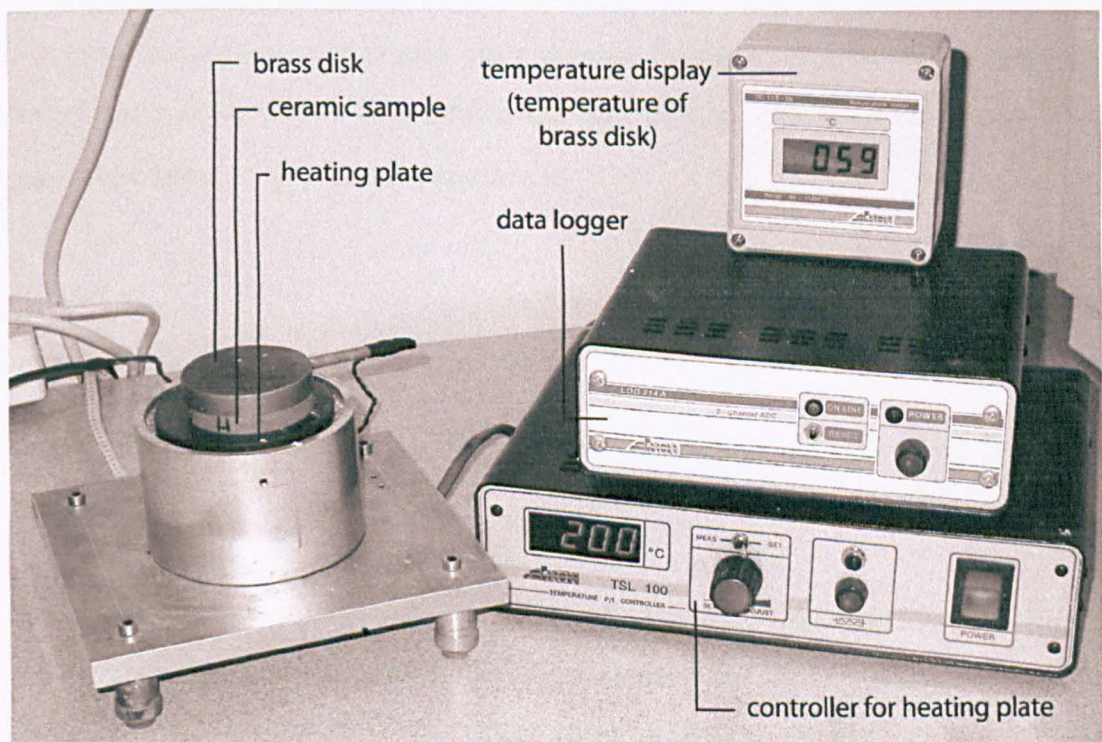


Figure 8.2 Experimental set-up for the determination of the thermal conductivity of disk-shaped ceramic samples.

It is assumed that the ceramic surface that is in contact with the heating plate adopts its temperature T_1 , while the temperature of the brass disk T_2 indicates the temperature of the samples' opposite surface. For steady state conditions (T_1 and T_2 constant) equation (8.1) can be integrated for the sample geometry (Kingery *et al.* 1976) resulting in:

$$k(T) = \dot{q}_{loss}(T_2) \cdot \frac{d}{A \cdot (T_2 - T_1)} \quad (8.3)$$

At steady state, therefore, the temperature difference between heat source and the ceramic surface in contact with the heat conductor $T_1 - T_2$ provides the thermal conductivity of the ceramic sample, taking into account its area A and its thickness d . Heat loss from the rim of the sample disk can be neglected provided that its height is small compared to its diameter; ceramics are insulators and as such the lagging at the sides will not significantly reduce the energy losses. However, an independent measurement is needed to determine the heat loss of the heat conductor into the environment in relation to a particular temperature $\dot{q}_{loss}(T)$. This can be achieved by heating the brass disk up and subsequently let it to cool down while recording its temperature development. During cooling, the surface which is in contact with the sample during a normal measurement is placed on a thermal insulator. Therefore, the measured temperature decay allows determining the heat flux $\dot{q}_{loss}(T)$ from the brass disk to the environment at specific temperatures as

$$\dot{q}_{loss}(T) = m \cdot c_p \cdot \frac{dT}{dt} \quad (8.4)$$

where dT/dt is the slope of the cooling curve, c_p the heat capacity of the brass disk and m its mass.

Disk shaped samples were prepared using a PVC mould (diameter: 58 mm, height: c. 8 mm), in the same way as described in Chapter 6 for the briquettes. The ceramic disks were measured at different temperatures as thermal conductivity is a temperature dependent property. The samples' surfaces were ground flat and, in the case of flaws, conductive paste was applied in order to ensure good contact between the

samples and the hot plate as well as between the samples and the brass disk. Sufficient time was allowed for the experiment to reach steady state: the measurement was not stopped until the temperature T_2 of the sample surface remained stable for at least 15 minutes. The measurement period depended on the measurement temperature T_1 and the type of sample. The slope of the heating curve, i.e. the time required to reach steady state, depends on the thermal diffusivity of the ceramics, and could range from 40 minutes up to 2 hours per experiment. The experimental set-up has been shown to provide reproducible results, however, all measurements were repeated at least twice, in order to detect possible contact problems between thermocouple and brass disk that would lead to too large temperature differences (Hein *et al.* 2008b). This, together with the fact that the thermal conductivity of all samples was determined at different temperatures, explains the rather time-consuming nature of the experiment. During the measurements the ambient temperature was monitored and possible draughts were restrained in order to provide consistent experimental conditions. The cooling curve of the brass disk was plotted once, letting the disk cool down from 300°C while recording its temperature. Its heat capacity was determined as $366 \pm 10 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$, its mass as $225.5 \pm 0.1 \text{ g}$. For the purposes of this experiment, it was assumed that the heat capacity of the brass disk is constant over the temperature range examined.

8.1.3 Results and discussion

Temperature dependence of thermal conductivity

In all cases thermal conductivity was observed to increase slightly with increasing measurement temperature. The relative order of conductivity, however, seems unchanged within the temperature range examined. The following discussion that is based on the results of the measurements performed at 164°C therefore is also valid for higher and lower temperatures.

Influence of clay type and firing temperature

For the untempered samples, an increase in firing temperature resulted in an increase in thermal conductivity for calcareous as well as non-calcareous specimens (Figure 8.3). The non-calcareous high-fired ceramic has a clearly higher thermal conductivity than the corresponding calcareous one.

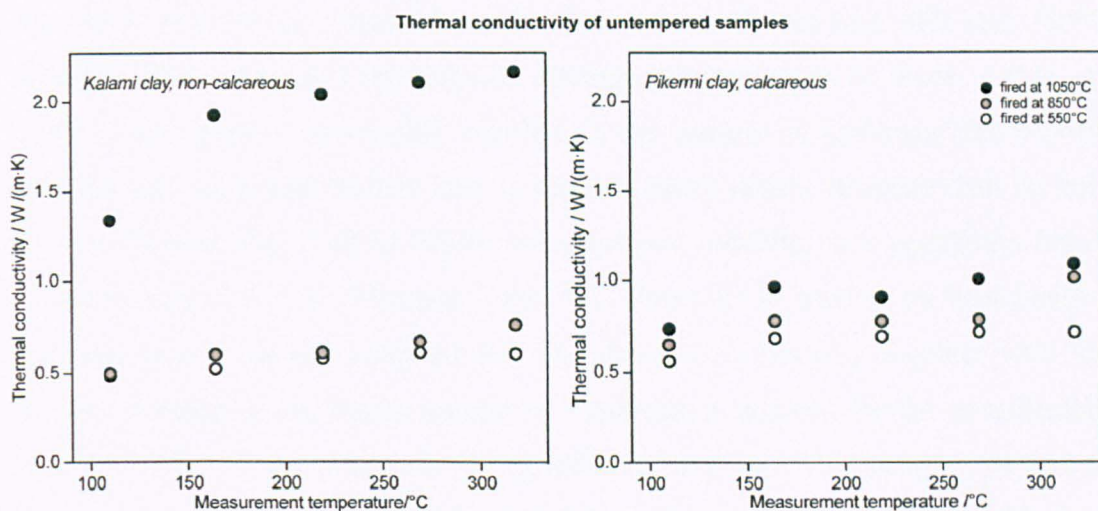


Figure 8.3 Thermal conductivity of untempered clays fired to different temperatures, determined at various temperatures of the heating plate. The different dots represent different firing temperatures: black - fired at 1050°C, grey - fired at 850°C, white - fired at 550°C). Thermal conductivity is plotted against the measurement temperature.

The observed increase in thermal conductivity with increasing firing temperature can be correlated with the changes that occur in the microstructure of the ceramics. In the case of the calcareous Pikermi clay, there are consistent although relatively small differences in thermal conductivity between the three firing temperatures. As has been discussed in the previous chapter, porosity is stable at around 32% in the case of the untempered Pikermi clay. The variations in thermal conductivity must thus be caused by changes in microstructure and/or in mineralogical phases. Although the formation of new phases has been observed upon firing the Pikermi clay to 850°C and 1050°C respectively (see Chapter 6) it seems much more probable that the differences in thermal conductivity are caused by increasing bonding within the matrix as reflected by the microstructural changes that are observed under the electron microscope (*cf.* Figure 8.8). After firing to 550°C, the calcareous clay shows no signs of vitrification, at 850°C incomplete vitrification with coalescing clay particles is ob-

served, and at 1050°C the ceramic is completely vitrified but still has a cellular structure. For the non-calcareous Kalami clay, vitrification sets in later: the electron micrographs of samples fired at 850°C do not show any signs of vitrification yet, accordingly, their thermal conductivity is not much higher than the one of the lower fired samples. The slight increase observed is most probably due to solid state sintering that starts well before 850°C, but does not result in structural changes which could be observed under a SEM. Neck growth and sintering between clay particles that occur prior to the onset of vitrification, commonly between 500 and 700°C (Kingery 1992), require a transmission electron microscope to be made visible. At 1050°C, the matrix is thoroughly vitrified: in the absence of carbonate decomposition, the non-calcareous Kalami clay develops a much denser structure than the calcareous Pikermi clay fired to similar temperatures, resulting in a significant lower overall porosity of 11 vs. 32% (see Table 7.3). Pores act as barriers for heat transfer and thus reduce thermal conductivity. The decrease in porosity together with the stronger bonding in the matrix caused by vitrification, account for the considerable increase in the thermal conductivity respective to the lower fired samples, as well as respective to the calcareous counterpart that is observed with the high-fired, non-calcareous Kalami clay.

Influence of temper

In most cases, the addition of temper decreases thermal conductivity. Only the samples containing 10% granite temper that were fired to moderate firing temperatures show an increase in thermal conductivity compared to the untempered specimen.

The addition of phyllite leads to a decrease in thermal conductivity with both base clays and at all firing temperatures. A higher amount of temper material results in a more pronounced reduction of thermal conductivity. Figure 8.4 shows the thermal conductivities, determined at 164°C, for the calcareous Pikermi clay. Porosity cannot account for the differences in thermal conductivity in this case, as it remains constant at 32±2% (see Chapter 7). The conductivity of phyllite is anisotropic due to its sheet-like structure. When heat is transferred perpendicular to the sheet silicates, its thermal conductivity is expected to be significantly lower than the one of the clay matrix

(Clauser and Huenges 1995). The briquettes were produced to achieve preferred orientation of the temper particles and the measurements were performed perpendicular to their arrangement axis, the overall decrease in conductivity is therefore expected.

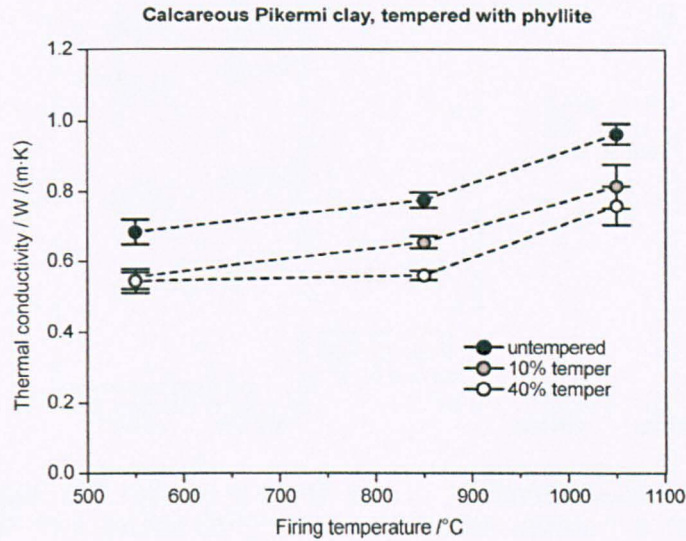


Figure 8.4 Effect of phyllite tempering on the thermal conductivity of fabrics based on the calcareous Pikermi clay. (All thermal conductivities measured at 164°C).

The case of granite tempering is slightly more complex: any addition of granite to a high-fired specimen results in a decrease in thermal conductivity for both base clays. At lower firing temperatures an increase of thermal conductivity is observed when adding 10% of temper; adding a high amount of temper to ceramics that are fired to temperatures below the onset of vitrification can lead to some decrease of the thermal conductivity of the resulting sample. Only for the case of the non-tempered Kalami clay fired at 550°C the addition of 40% of granite temper resulted in a further increase of thermal conductivity. In the samples fired at 1050°C, any addition of granite gives rise to a reduction in the thermal conductivity. With the non-calcareous base clay, this reduction is slightly more pronounced when adding granitic temper than with phyllite, for the calcareous clay the opposite seems to be the case (Figure 8.5).

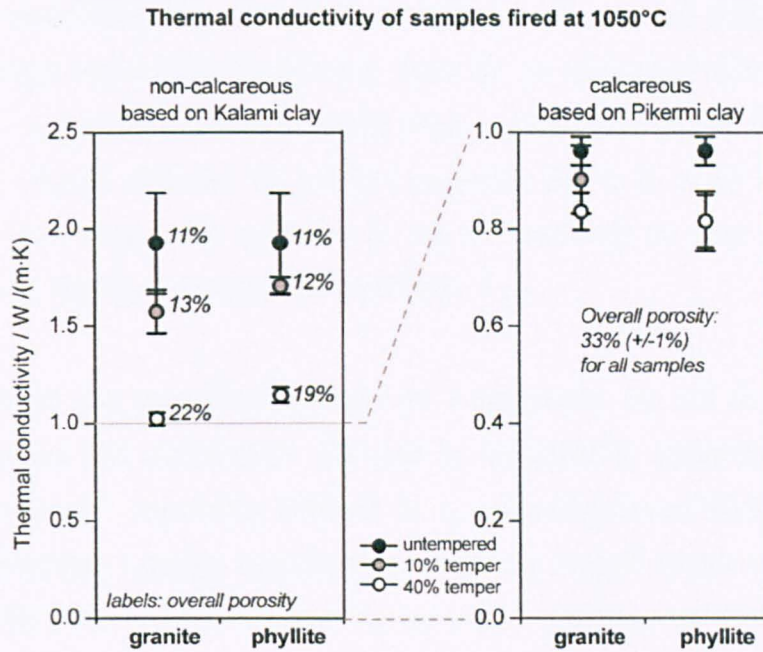


Figure 8.5 Influence of temper type on the thermal conductivity of high-fired samples. (All thermal conductivities measured at 164°C). Note the difference in scale for the two different clay types.

The thermal conductivity of granite is expected to be in the same range or slightly higher than the untempered high-fired Kalami clay, i.e. roughly in between 1.5 to 3.5 $\text{Wm}^{-1}\text{K}^{-1}$, according to feldspar content and porosity (Clauser and Huenges 1995). The decrease observed in overall conductivity when adding granite to *high-fired ceramics*, therefore, cannot be explained with a lower thermal conductivity of the temper material. We need to assume that, rather than being part of the matrix, the temper particles induce cracks and pores to the samples, thus lowering the overall conductivity. As discussed in the previous chapter, the different geometries of the temper particles lead to a different extent of damaged zones around the rigid inclusions, and, in the highly tempered fabrics, additionally to a different extent of manufacture induced porosity. This is even more pronounced in the high-fired specimens where due to shrinkage of the body the damaged zones develop to macrocracks. Both variables, damaged zones and amount of manufacture-induced porosity, are greater in granite tempered fabrics than in the phyllitic ones, resulting in the higher porosity values for this type of temper in the case of the non-calcareous clay which accounts for the relatively smaller conductivities of the related samples. In the calcareous samples, where porosity is stable for all tempering grades, we observe a much smaller variation in

thermal conductivities upon tempering. In this case, the thermal conductivity of the temper material seems to be the decisive factor for the amount of reduction observed: the thermal conductivity of granite is one order of magnitude greater than the thermal conductivity that is expected for phyllite perpendicular to its sheet layers. Accordingly, in these samples, the reduction in thermal conductivity seems to be slightly greater for the phyllite tempered fabrics (Figure 8.5).

For the samples that were fired to moderate temperatures, the addition of 10% granite increased thermal conductivity. This can be explained by assuming that the inclusions are adherent to the matrix at lower firing temperatures and the thermal conductivity of the temper particles contributes towards the overall conductivity. However, when looking at the conductivities of the samples tempered with 40% granite we do not observe a further increase, as we would expect. Instead, in most cases a decrease relative to the untempered reference samples can be discerned. This is due to the fact that a high amount of temper particles induces additional porosity, as has been discussed previously. The preferred orientation of manufacture-induced pores parallel to the larger surfaces of the briquettes and consequently perpendicular to the heat flow in the samples additionally enhances their effect as heat barriers. The extra porosity over-compensates the theoretical increase of the samples' thermal conductivity due to the addition of granite and results in an actual reduction in conductivity compared to the untempered samples. The exceptional case of increased thermal conductivity found for the non-calcareous briquette containing 40% of granite temper fired at 550°C, is most probably due to the very low shrinkage of this clay when fired to so low temperatures. This low shrinkage manifests in much less pronounced shrinkage pores compared to the higher fired specimens, but also compared to the corresponding low-fired calcareous paste (*cf.* Figure 7.3).

It should be mentioned that the thermal conductivities that were determined in this study apply for the dry state of the ceramics. Unless the pottery is glazed or made impermeable by other means (e.g. application of resins, sealing of pores through cooking, by deposition of organic residues) the open pores will be saturated with the fluid content of a cooking pot. A water saturated vessel is expected to have a higher thermal conductivity than a non saturated pot, as the conductivity of water is signifi-

cantly greater than the one of air (room temperature conductivities: water $0.6 \text{ Wm}^{-1}\text{K}^{-1}$ as opposed to air $0.025 \text{ Wm}^{-1}\text{K}^{-1}$, data from Stöcker 1994).

8.2 Thermal shock resistance

Thermal shock resistance gives a measure of the ability of a material to withstand sudden changes in temperature; the response is usually considered in terms of fracture initiation and crack propagation. In the case of traditional ceramics, this performance characteristic is relevant only for pottery that typically comes in contact with heat during use. The types of thermal shock experienced by different ware types can vary significantly. A common requirement is to retain hot contents and survive the resulting temperature gradient to the colder outside: this is the case with teacups that are filled with boiling water, oil lamps and portable hearths with their much hotter fluid or solid contents, and crucibles that have to deal with temperatures well in excess of 1000°C . The thermal shock conditions are somewhat different for pots that are placed on a hot surface to keep their contents warm and for cooking ware that is put in contact with a heat source or into an oven in order to cook the food it contains. For cooking vessels that are used for boiling, it seems essential at first sight to avoid fracture initiation, so a pot is able to retain its contents. With baking trays, on the other hand, the control of crack propagation to ensure that the plates keep structural integrity appears more important. While there is no doubt that cooking ware frequently experiences thermal shock, it is important to keep in mind the actual conditions a pot is exposed to in use: the relative suitability of ceramic materials with regard to thermal shock resistance is not absolute but depends on the conditions of the shock (Davidge 1986), making a general rating of different materials impossible. Furthermore, as with mechanical properties, the influence of shape should not be underestimated, not only wall thickness, but also curvature play a very central role in thermal shock resistance; generally speaking, sudden changes in both parameters are undesirable (Dinsdale 1986). However, as in the previous chapter with mechanical properties, the following discussion is restricted to materials; the shape factor will be discussed separately in the next chapter.

8.2.1 Theoretical background

Thermal stresses arise in a material due to changes in temperature. Commonly two different situations are considered where thermal stresses in ceramics occur. The first is the uniform thermal expansion or contraction of an object that is constrained in its flexibility (e.g. a tube that is fixed on both ends by rigid supports), and the second is the presence of a temperature gradient within an object that results in internal stresses due to non uniform expansion or contraction (Davidge 1986; Shackelford 1996). Additionally, in multiphase ceramics, stresses arise from different thermal expansion coefficients of the different phases that are restrained in the same body.

For cooking ware the first case is not an issue, as the whole pots are not constricted. Usually, therefore, the discussion focuses on stresses arising from a temperature gradient through the vessel wall and on those arising from the different thermal expansion coefficients of matrix and inclusions. The latter, however, already occur during the firing of a ceramic object and introduce microdamage into the body, as has been discussed previously. It can be assumed that because these damaged zones are established during firing, they enable the ceramic to accommodate for the stresses when they reoccur upon heating a fired pot. Accordingly, it can be argued that the effect of differing thermal expansion coefficients on thermal shock resistance in a *fired* ceramic is not that significant. Nonetheless, much of the archaeological literature assesses thermal shock resistance on the basis of the thermal expansion coefficients of the pottery's constituents as discussed previously, and explains tempering choices on these grounds. However, more relevant seem the stresses that arise from non uniform expansion or contraction due to temperature *gradients*. Exposure to a sudden change in temperature leads to temperature gradients within an object, when, due to finite heat conductivity of the material, the exterior that is in contact with the cooling or heating medium adopts its temperature, while the core has still the previous temperature. Here, the stresses are caused by the fact that the single volume elements cannot freely expand or contract as they are constraint in the same body.

At low enough rates of temperature change, heat conductivity is efficient, resulting in a uniform expansion of the object which does not give rise to internal stresses. The response of a material to temperature changes is therefore usually studied under con-

ditions of rapid quenching (worst case scenario). In doing so, two things can be assessed, namely the condition for fracture initiation and the degree of damage. In analogy with what has been discussed in the previous chapter on strength and toughness, theoretical approaches to thermal shock involve the consideration of the nucleation of cracks and/or the investigation of their propagation (Kingery *et al.* 1976).

Fracture will *initiate* when the thermal stresses reach the strength of a material. Hasselman (1969) developed thermal stress resistance parameters to assess the suitability of ceramics to resist thermal shocking under different conditions. For brittle materials, in the case of a very sudden change in ambient temperature, the thermal stress resistance parameter R is given as

$$R = \frac{\sigma(1-\nu)}{E\alpha} \quad (8.5)$$

The second thermal stress resistance-parameter R' gives a useful indication of the performance of a particular material in the case of relatively slow heat transfer:

$$R' = \frac{k\sigma(1-\nu)}{E\alpha} \quad (8.6)$$

In the above equations, σ is the tensile strength, k the thermal conductivity, E the Young's modulus, ν Poisson's ratio and α the thermal expansion coefficient of the material. According to equations 8.5 and 8.6, a high strength and high thermal conductivity but low Young's modulus and low thermal expansion coefficient are desirable to avoid fracture initiation through thermal shock.

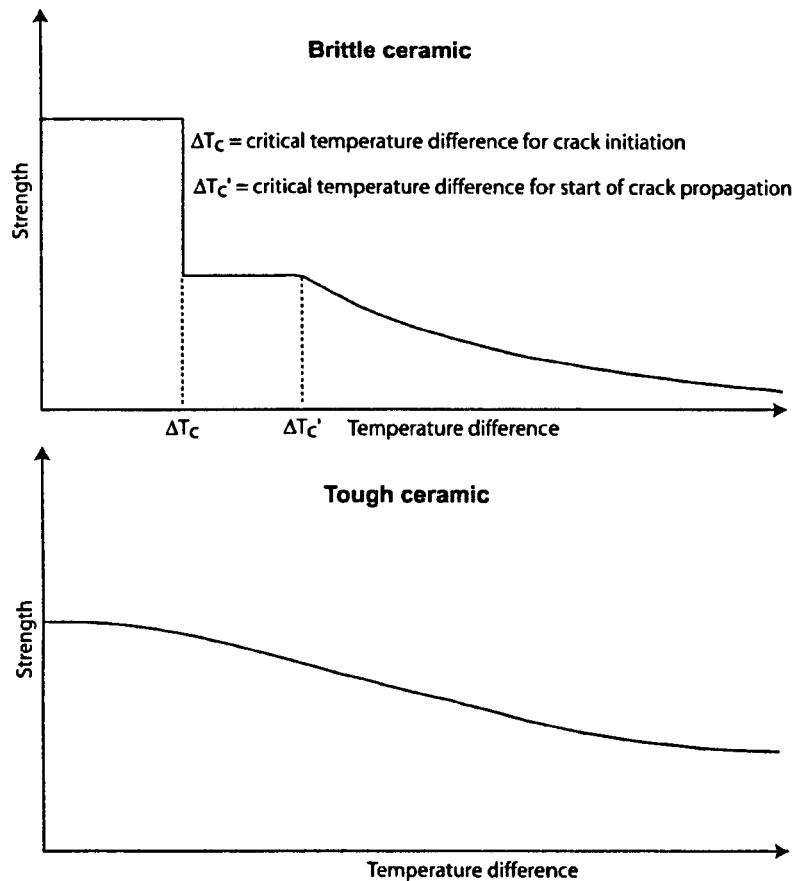


Figure 8.6 Different behaviour of relatively strong (brittle) and weaker (but tougher) ceramics upon thermal shocking. While brittle ceramics experience an abrupt strength loss at a critical temperature difference ΔT_c due to initiation of fracture (Hasselman 1969), the loss in fracture strength in tough ceramics is gradual due to more controlled crack propagation (*cf.* unstable and stable fracture).

When considering the *propagation of cracks*, a distinctively different behaviour can be observed for different ceramic materials, according to their initial toughness. Figure 8.6 compares the reduction in fracture strength after thermal shock for a typical brittle material, with the one observed in a tough material. In strong but brittle materials, due to the large amount of stored energy at the point of fracture, cracks experience a sudden large expansion when initiation occurs, in a weaker material with a higher initial toughness cracks propagate in a more controlled way. Consequently, the strategy for optimising thermal shock resistance in a material which fractures in a stable way is fundamentally different than the one for a brittle material in that it involves avoiding crack propagation rather than crack initiation. The relevant thermal stress resistance parameters in this case are:

$$R''' = \frac{E}{\sigma^2(1-\nu)} \quad (8.7)$$

and

$$R'''' = \frac{\gamma_{eff} E}{\sigma^2(1-\nu)} \quad (8.8)$$

which represent the minimum in elastic energy at fracture that is available for crack propagation (R''') and the minimum in the extent of crack propagation on initiation of thermal stress fracture (R'''') (Hasselmann 1970). To avoid crack propagation therefore, low strength, high Young's modulus and fracture surface work are beneficial. Looking at equations 8.7 and 8.8 it becomes apparent that with increasing resistance to crack initiation, the damage that occurs when a crack starts, becomes more and more catastrophic. While for refractory ceramics an optimisation of the fourth and the fifth thermal stress resistance parameter is usually considered favourable, R and R' are relevant for porcelain and electrical ceramics (Kingery *et al.* 1976). It has been argued that for cooking pot ceramics, by analogy to refractories, only the propagation of cracks must be considered (West 1992). This presumes that only ceramics that exhibit a stable fracture mode are used in the production of cooking ware. However, a huge variety of fabrics has been - and still is - used successfully for cooking purposes (e.g. Woods 1986) so that an *a priori* exclusion of the consideration of crack initiation might be overly rash. In this context it should also be mentioned that cooking ware and refractories are typically exposed to changes in temperature that are of a fairly different range (cooking pottery is expected to experience far smaller changes in temperature, especially when taking into account the cooling effect of evaporating water). Furthermore, opposite requirements are put on those two types of ware in terms of thermal conductivity. Also the thermal shock *conditions* are thus quite different for the two types.

In his seminal work on thermal shock resistance, Hasselman (1969) advocated caution in predicting thermal shock resistance in one environment based on thermal shock data obtained in another. Due to the complexity of the responses of a material that is exposed to thermal shocking and due to the difficulties in assessing heat trans-

fer parameters in specific applications, thermal shock resistance is usually measured, rather pragmatically, by assessing the material's performance under simulated service conditions (BSI 2004a). The thermal shock resistance of ceramic materials is commonly assessed by measuring their performance after exposure to a series of sudden changes in temperature. According to the stipulated use of the material, the temperature differences as well as the quenching medium chosen for the tests show considerable variations: whereas refractory materials are usually exposed to changes in the range of 1000°C in air (BSI 2006; ASTM 2003), tiles are subjected to changes of not more than 150°C and quenched in water (BSI 1998).

8.2.2 Previous work on thermal shock resistance of archaeological ceramics

With regard to archaeological ceramics, *thermal shock resistance* is a performance characteristic that is frequently referred to in connection with cooking pottery. However, only rarely is this property experimentally determined; in most cases the discussions are based on theoretical considerations. Thermal shock resistance seems a more easily accessible concept than strength and toughness at first sight. However, owing to the complexity of the underlying mechanisms this is unfortunately not the case. Most studies did not approach the subject in an integrated way but rather isolated one mechanism on which argumentation would be based. It is, therefore, difficult to summarize and compare the results of the existing literature, and virtually impossible to distil generally valid conclusions regarding the influence of manufacturing parameters on thermal shock resistance. In the following discussion, therefore, greater emphasis is put on the different ways in which thermal shock resistance has been approached, rather than on the actual results of the studies.

When looking at the *origin* of thermal stresses, two different sources are usually discussed. For one, thermal stresses can arise because of the different thermal expansion factors of clay and temper. It has been argued frequently that a change in temper material is connected to the respective thermal expansion factors, insofar as the stresses upon exposure to heat are reduced with increasing similarity of the factors (Braun 1983; Stepionatis 1984). In fact, the similarity of the thermal expansion coefficients of calcite and clay remains a popular explanation for the observation of calcite tem-

per in cooking ware, a temper that is assumedly beneficial for the pottery's thermal shock resistance (e.g. Rye 1976; Hoard *et al.* 1995; Killebrew 1999; Broekmans *et al.* 2004).³⁹ Furthermore, thermal stresses can originate from differing thermal expansion within an object due to a temperature gradient: Braun (1983), for instance, argues for an increased thermal shock resistance as a result of increased thermal conductivity, caused by a decrease in wall thickness and therefore smaller temperature gradients. When considering the *response* of a ceramic to thermal stresses, crack initiation and crack propagation play a role. While Hoard *et al.* (1995) argue for an increased thermal shock resistance based on a higher threshold for crack initiation, Feathers (1989) and Feathers and Scott (1989) set out that an increased resistance for crack propagation, as assessed by toughness measurements, results in an increased thermal shock resistance of the respective fabrics. The latter approach has been taken up by West (1992). On a different stage, Steponaitis (1984) aimed at a calculation of the thermal stress resistance parameters as developed by Hasselman (1969; 1970) through measuring or estimating the constituent parameters.

In the archaeological literature, as summarised above, thermal shock resistance has been discussed on different levels: on the one hand the reduction of thermal stresses, arising either from differing thermal expansion coefficients of clay and temper or from thermal gradients within a material, has been considered; on the other the ability of a ceramic to respond to such stresses with regard to crack initiation and propagation was examined. It seems a matter of course that, when discussing the impact of a manufacturing parameter on thermal shock resistance, an integrated approach, taking all these points into account, would be much preferable. Unfortunately, even a more complete discussion is of restricted use, as too many factors influence both the emergence of thermal stresses in a ceramic and its response to such stresses, sometimes in opposing ways. It is therefore common practice in engineering to measure thermal shock resistance in simulated service test rather than to infer it solely from material characteristics (BSI 2004a). Nevertheless, actual measurements on replicas to assess the influence of single parameters on thermal shock resistance in traditional

³⁹ The concept is problematic: one could argue that crack propagation rather than crack initiation is decisive when assessing the thermal shock resistance of coarse ceramics: a differing thermal expansion coefficient results in damaged zones around the temper particles and effectively *increases* a materials potential to resist crack propagation, as has been shown for the example of quartz temper (Kilikoglou *et al.* 1995).

ceramics are rare. An exception is the work of West (1992) who assessed the influence of different temper materials on the thermal shock resistance of replicates. Apart from measuring the toughness of the different paste mixtures, he also determined the residual strength of thermally shocked test rods, in a bid to assess the thermal shock behaviour of ceramics tempered with a variety of materials. With the exception of untempered and grog tempered material that were reported to lose significantly more strength, however, all temper types resulted in fabrics with similar thermal shock resistance. This fact led West (1992, 138) to the conclusion that the 'most effective means of improving thermal shock resistance is the addition of tempering material, regardless of its morphology or thermal expansion'. In another attempt to study the influence of differing temper materials, Bronitsky and Hamer (1986) and Skibo and Schiffer (1989) both determined thermal shock resistance as strength degradation upon quenching, through cycling experimental briquettes in boiling and ice water. Unfortunately, due to problems arising from the use of an impact tester in assessing strength levels (see previous chapter), their results are difficult to assess. Furthermore, Schiffer *et al.* (1994) assessed the influence of surface treatments - and ultimately permeability - on the thermal shock resistance of a ceramic vessel. This study also is hampered by methodological problems: their experimental procedure (few cycles with only small changes in temperature and testing on uncracked areas) rather unsurprisingly did not lead to conclusive results concerning strength degradation. Moreover, the data they resort to in order to support their hypothesis, namely the total length of visible thermal cracks, is difficult to rationalise. Similarly, also Pierce (2005) struggled with difficulties to interpret strength degradation measurements on plain and corrugated cooking vessels that had been subjected to prolonged cooking.

8.2.3 Experimental procedure of the present study

Temperature differences of up to 400°C can be expected when placing a cooking vessel on a fire. The severity of this upward shock is reduced when the pot contains boiling water and has permeable walls, as the continuous evaporation of water through the vessel walls cools the outer surface and reduces the effective temperature gradient. When removing a vessel from the heat source, downward shock occurs.

The magnitude of the downward shock is dependent on the quenching conditions: minimal shock is expected when the pot is left to cool down slowly, i.e. placed on an insulating surface such as soil, while higher stresses occur if the same vessel is placed on e.g. a metal plate which is a good thermal conductor and therefore leads to a higher thermal gradient within the vessel. The thermal stresses a ceramic cooking vessel in Bronze Age Akrotiri is expected to have had to deal with during normal use-life are therefore the same or less (due to evaporation of potential fluid contents) than the stresses arising from exposure to temperature changes in the range of 400°C. For this reason, in a first pre-test, the influence of those assumed normal service conditions was assessed on a selection of test bars. The test bars were subjected to ten cycles of changes in temperature of 400°C, by alternately placing them in an oven maintained at 430°C and letting them cool down in ambient air (*c.* 30°C). However, none of the paste mixtures examined showed a reduction in fracture strength, suggesting that thermal shock is not a critical parameter for the performance of the selected fabrics under normal use conditions. Based on this observation, thermal shock resistance was assessed by quenching the test bars in water, a procedure that resulted in a reduction in fracture strength and allowed a relative comparison of the different fabrics thus offering the opportunity to study the effect. With water quenching, the downward shock is expected to be more severe: heat transfer is more efficient between sample and water than sample and air, consequently, less time is available for heat transfer to occur within the body, resulting in a greater temperature gradient through the sample. However, one should keep in mind that the chosen test procedure simulates an actual abuse scenario, as it corresponds to either placing an empty vessel on a heat source and filling it with water when hot, or immersing a hot vessel in water, practices that can easily be avoided by careful handling.

Thermal shock resistance was determined as the reduction in TRS (*cf.* Chapter 7, 143-144) after exposure to a series of sudden changes in temperature. Of each kind of briquette three test bars of approximately 10 x 10 x 60 mm were cut and measured. After placing these test bars for 20 minutes in a furnace whose temperature was

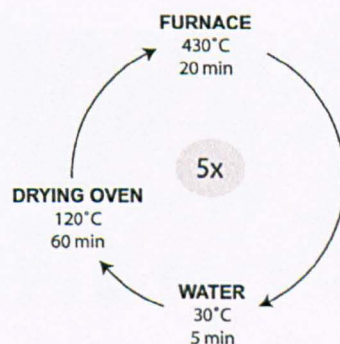


Figure 8.7 Test procedure for thermal shocking of the ceramic test bars.

maintained at 430°C, they were quenched in a water bath (27-30°C) and left to cool down for 5 minutes. After drying the pieces for 1 hour at 120°C, they were transferred to the furnace again. This procedure was repeated five times before the residual strength of the shocked test bars was measured as described in Chapter 7.

8.2.4 Results and discussion

Influence of clay type and firing temperature

The reduction in TRS was clearly dependent on the temperature the tested fabrics were fired to. Calcareous and non-calcareous clays did behave differently, but this seems to be connected to the differing development of vitrification in the samples rather than to their different compositions directly. For the fabrics made of untempered clays that were fired to temperatures below the onset of vitrification, the reduction of strength was univocally 50%; fabrics where vitrification can be observed under the SEM showed a remarkably constant strength reduction of roughly 80% (Figure 8.8).

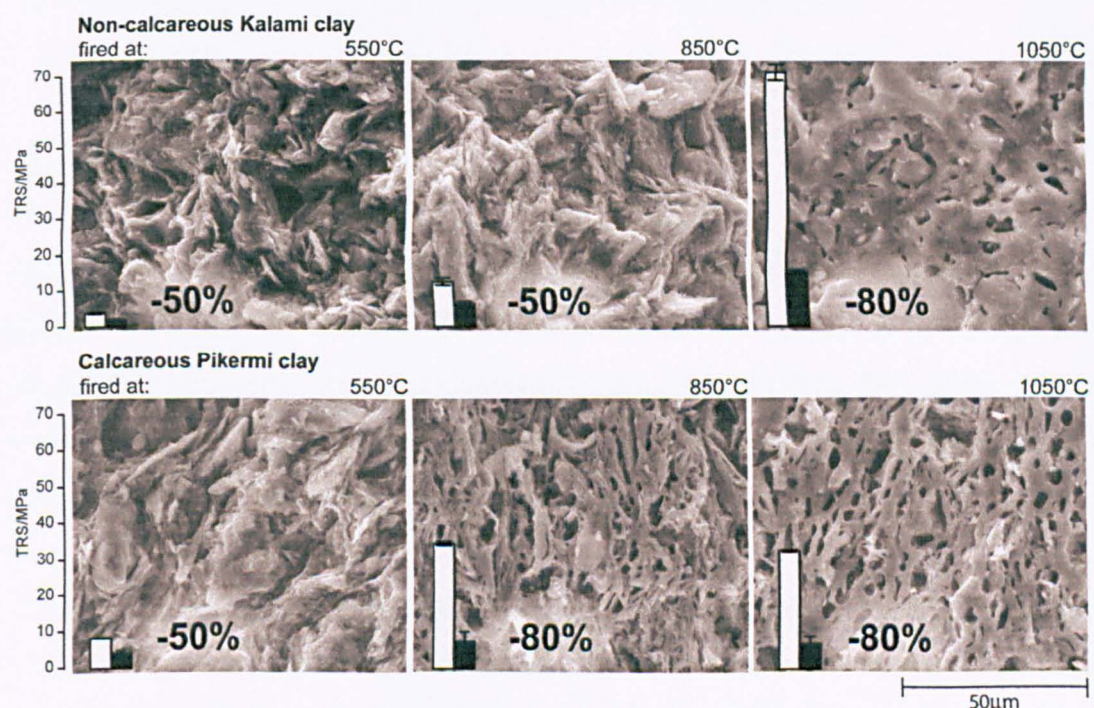


Figure 8.8 Reduction in strength of untempered specimen after thermal shocking. (Light grey: TRS before thermal shocking, dark grey: TRS after thermal shocking). The relative loss of strength (in %) is linked to the vitrification of the clay matrix as observed under the electron microscope.

If the stresses that build due to thermal shocking exceed the strength of a material, microcracking occurs, in order for the material to accommodate the tensions that arise from differing thermal expansion. A structure with a high amount of flaws and cracks can better deal with such different expansions and fewer new cracks form, resulting in a smaller reduction in fracture strength. Nevertheless, under the thermal shock conditions assessed here, porosity seems not to play a role in thermal shock resistance. Even though the high-fired untempered Kalami briquettes are significantly less porous than the corresponding calcareous Pikermi ones, both fabrics react in the same way to exposure to thermal shock. This suggests that the main factor influencing thermal shock resistance in the untempered ceramics studied here is the relative bonding strength of the matrix, as reflected in its degree of vitrification. An examination of the thermal stress resistance parameter R (equation 8.5) that is an indication of the thermal shock resistance of brittle ceramics under conditions of rapid quenching, while keeping in mind that porosity influences strength and Young's modulus in a similar way and is thus cancelled out of the equation, provides an explanation for this observation. Also, a material with a high thermal conductivity is expected to respond better to thermal shock; as, in reality, ideally fast quenching as required by equation 8.5 cannot be achieved and thermal conductivity will start playing a role (equation 8.6) even when shocking by water quenching.

Influence of temper

The addition of temper material generally results in an increase in thermal shock resistance; the more temper added, the lower is the measured reduction in strength levels. Phyllite tempered fabrics lose relatively more strength than their granitic counterparts (Figure 8.9), indicating that this temper type is less efficient in increasing the thermal shock resistance of a ceramic.

As discussed with strength and toughness, the addition of temper material introduces zones of microdamage within the material. These damaged zones enable the material to better accommodate tensions arising from differing thermal expansion and therefore increase its thermal shock resistance. According to the different extent of those

damaged zones, the thermal shock resistance of the granitic tempered fabric is higher than that of the corresponding phyllitic tempered ones.

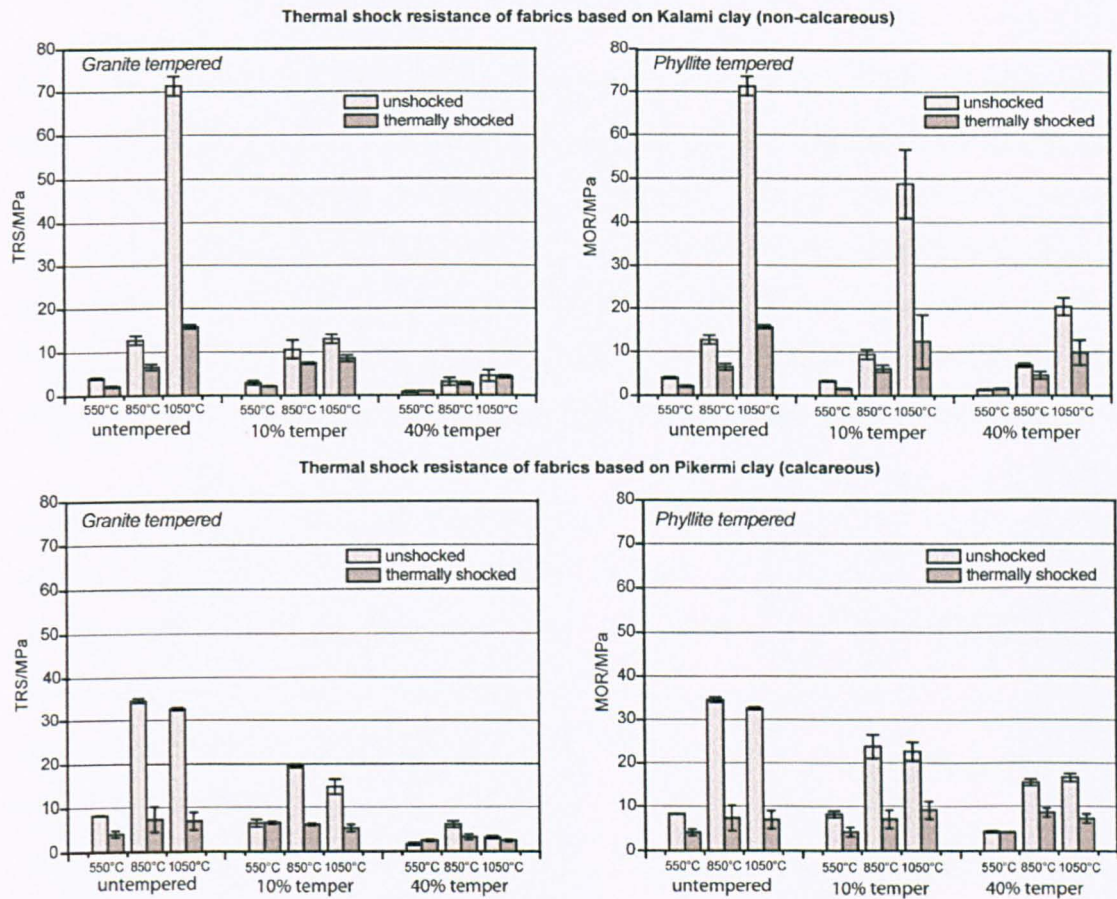


Figure 8.9 Comparison of TRS of experimental briquettes before and after thermal shocking.

For the same temperature differences, the strength reduction through thermal shocking associated with tough ceramics is less severe than with brittle ceramics due to the different response of the material as illustrated in Figure 8.6. It has been observed that the addition of temper induces a change in fracture mode from brittle to stable fracture (see previous chapter). It is therefore expected that the reduction in strength level diminishes with increasing amount of temper due to this shift in fracture mode. Accordingly, the observed differences in calcareous and noncalcareous fabrics tempered with 10% granite can be explained with the different fracture modes of the unshocked fabrics: as discussed earlier, the addition of 10% granite suffices to cause

a change in fracture mode in the Kalami based fabrics but not with the Pikermi fabrics. As a result, the thermal shock resistance of the high-fired, noncalcareous Kalami samples containing 10% granite is significantly greater than that of the corresponding calcareous fabrics.

Under the conditions studied, a lower firing temperature, a higher amount of temper and a change from platy to angular temper, all increase the thermal shock resistance of the corresponding fabrics with regard to the *stability of the strength level*. However, when examining absolute values, i.e. the *residual strength* after thermal shocking, a rather different picture emerges (Figure 8.9). Also after thermal shocking, the high-fired low tempered fabrics generally exhibit the highest strength, while the addition of angular granitic temper results in weaker fabrics than platy phyllitic one.

Another point that is worth considering is that a decrease in strength upon thermal shocking can be accompanied by an increase in fracture toughness. Occasionally, also a change in fracture mode has been observed. Table 8.1 lists the fracture modes observed before and after thermal shocking; a general trend towards a more stable fracture after thermal shocking is evident. This is further illustrated for the example of a calcareous fabric containing 10 % of granite temper (Figure 8.10). The

load-displacement curves of the same fabric before and after thermal shocking show a change from semi-stable to stable fracture after exposure to thermal shock. Considerably more energy is expended to propagate a crack through a thermally shocked sample as is indicated by the respective tails of the curves. Unlike strength, the toughness of the ceramics experiences *an increase* upon thermal shock. This can be explained by a microcrack toughening mechanism.

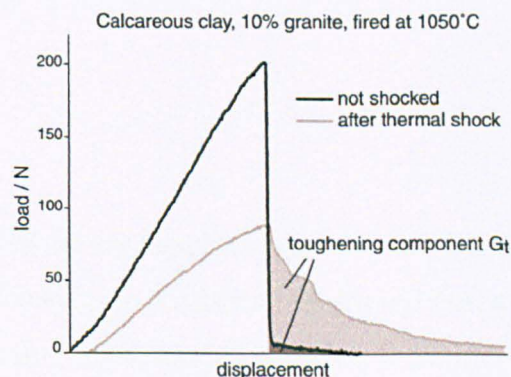


Figure 8.10 Load displacement curves of two samples of the same fabric before and after thermal shocking. The areas under the tails of the curves correspond to the respective toughening components G_t due to energy dissipation during crack propagation.

fired to:		Non-calcareous Kalami clay						Calcareous Pikermi clay						
		before thermal shock			after thermal shock			before thermal shock			after thermal shock			
		B	SS	S	B	SS	S	B	SS	S	B	SS	S	
untempered	550°C	5				1	2	5			1	2		
	850°C	5				3		5			3			
	1050°C	5			2	1		5		1	2			
10% granite	550°C		5			2	1	5	5			3		
	850°C		5			3		5			2	1		
	1050°C		3	2		1	2	3	2		1	2		
40% granite	550°C			5			3			5			3	
	850°C			5			3		1	4			3	
	1050°C			5			3			5			3	
10% phyllite	550°C		5				3			5			3	
	850°C		5			3		5				1	2	
	1050°C	5			1		2	5			1	1	1	
40% phyllite	550°C			3			3			2	3		1	2
	850°C		3	2			3			5			2	1
	1050°C	3	2			3		2	3				2	1

Table 8.1 Changes in fracture mode observed upon thermal shocking. B: brittle, SS: semi-stable, S: stable fracture.

8.3 Summary and conclusions

The results obtained for the thermal conductivity of the samples reveal that this property depends a great deal on the level of vitrification in a ceramic, its overall porosity, and, to a somewhat lesser extent, on the nature of the temper particles. It could be demonstrated that firing to sufficiently high temperatures results in a considerable increase in thermal conductivity due to the related emergence of an extensive glassy phase, while the addition of temper decreases the thermal conductivity of a material in almost all cases. The one exception that has been observed in this case study is the addition of limited amounts of granite, a material with higher thermal conductivity than the matrix, to ceramics that have been fired to moderate temperatures. Thermal shock resistance expressed as strength retention under quenching conditions has been determined as being greatest for high tempered and low-fired ceramics, with granite temper being more efficient than phyllite.

Unlike strength and toughness, the thermal properties of a ceramic unfortunately do not allow classification of the different fabrics according to inferred suitability for cooking purposes in a straightforward way, due to a variety of reasons that are described in more detail below.

Although *thermal conductivity* is not directly linked to the heating rate of a vessel, computer modeling using finite difference methods revealed that this material property seems to be the single most important parameter directing the heating rate of a vessel (Appendix VI). Furthermore, it can be linked to fuel efficiency and to an even distribution of heat within a vessel. As thermal conductivity is also related to the loss of heat a pot experiences once it is removed from the fire, a careful consideration of the context a cooking vessel is used in, especially taking into account requirements and restraints of different cooking methods (e.g. used on open fire or in oven, employed for boiling or simmering) is a prerequisite to determine whether a higher or rather a somewhat lower thermal conductivity enhances the suitability of a vessel. In general it can be argued that for boiling and for the use of vessels on an open fire, a high thermal conductivity seems beneficial, while a lower thermal conductivity is of advantage when using a pot for simmering or in an oven.

Caution must be exercised when using the results of *thermal shock resistance* measurements to judge the suitability of a vessel to be used in applications connected to exposure to temperature changes, for a series of reasons. First, the results apply only to conditions of sudden quenching, indeed, pre-tests performed under conditions comparable with actual use, i.e. cooling down in ambient air did not show any deterioration of strength levels. Second, none of the test bars actually failed during the experiments and their residual strength is still reasonable, especially when taking into account that, thirdly, thermal shocking results in a shift towards more stable fracture. In-line with the argument in the previous chapter that, for cooking ware, toughness seems to be the more relevant parameter than strength, we could argue that quenching the ceramics actually *improves* the suitability of a fabric to be used for cooking purposes, due to *thermal shock toughening*. For these reasons, the testing of thermal shock resistance to assess the suitability of a material for cooking purposes seems somewhat problematic. Having in mind that the shape of an object critically influences its thermal shock resistance, it seems therefore inevitable to resort to computer modelling using finite element methods, when aiming to obtain meaningful conclusions considering the performance of a cooking vessel in terms of its response to thermal shock.

It seems doubtful from the results of this study that the differences in resistance to thermal shock are of importance for the suitability of a fabric for cooking purposes. However, simulations using finite element methods must be performed to confirm this hypothesis. Differences in thermal conductivity on the other hand, do not provide a means of judging a vessel's suitability for cooking as such but allow us to gauge its aptness for different cooking methods. It can be hypothesised that a high-fired fabric with a relatively low amount of temper is better suited when it comes to boiling the contents of a vessel, whereas slow simmering would preferably be achieved using a lower fired ceramic containing a higher amount of temper.

Assessing the main fabrics that are observed in the Akrotiri cooking ware assemblage on the base of their thermal properties, we can state the following: all fabrics seem fit to resist crack propagation through thermal shocking, as considerable tempering is observed in all samples without exception. While the earlier local fabrics could be argued to be of relatively low thermal conductivity (*cf.* Chapter 10), for the main imported group, characterised by a granitic fabric, we might expect an increased thermal conductivity due to the type of non-plastic inclusions. Also, at least some of the later local material is expected to be of higher conductivity due to the significant higher firing temperatures that over-compensate for the adverse effect of the added phyllite. This has implications for the cooking procedures performed at Akrotiri and will be discussed in more detail in Chapter 10. First, however, it is necessary to assess the influence of vessel shape on the performance characteristics of a cooking vessel.

Chapter 9

Finite element analyses

This chapter presents the results of computer simulations using the finite element method (FEM) which were conducted on digitised models of typical cooking vessels of the later Bronze Age periods at Akrotiri. Finite element analyses were carried out to examine the response of cooking vessels to mechanical and thermal stresses. Structural analyses were performed to highlight the influence of shape and material parameters on the magnitude of stresses that are likely to emerge during the handling of cooking vessels, while thermal finite element analyses aimed at calculating the magnitude and illustrating the development of stresses that arise when cooking ware is exposed to heat.

The finite element method is used mainly in engineering sciences and for industrial applications. Finite element analyses are employed for a broad array of engineering problems, spanning from mechanical through magnetic to fluid analyses. A major application of FEM is to evaluate product design on virtual models in the early stages of development, thus substantially reducing development time and cost. Calculations by FEM allow, for example, the visualisation of the distribution of stresses in an object which has been digitised and to which specified loads and constraints have been applied, and thus can detect structural weaknesses.

Apart from its widespread use in the study and development of modern materials, FEM has recently also been employed to assist the performance assessment of ancient objects and materials. Case studies dealt with structural problems (Kilikoglou and Vekinis 2002; Hein *et al.* 2008a) but also with the examination of thermal properties (e.g. Hein and Kilikoglou 2007). Structural analyses allow the study of a vessel's response to different loads by examination of the resulting strains. Kilikoglou and Vekinis (2002), for example, examined the stresses a particular type of jar is exposed to during handling and storage, in order to assess its lifting mode, while Hein *et al.* (2008) studied the stresses which arise from the piling of amphorae during transportation, and compared the suitability of different shapes to be used as trans-

port vessels. Previous thermal analyses by FEM focused on the examination of metallurgical ceramics, more specifically on smelting furnaces (Hein *et al.* 2007). Calculations using FEM allowed for an estimation of the temperature development in the furnace walls and - by comparison with analytically established temperature profiles on actual sherds - provided information on the operation conditions of the furnaces. Furthermore, the influence of porosity and especially the influence of pore shape and pore orientation on the thermal conductivity of the ceramic materials have been studied by FEM.

The structural analyses which were performed in the course of the present study do not differ greatly from the approaches followed in the cited literature: it is the influence of shape and fabric on the magnitude of stresses which arise in cooking vessels during their handling that are examined. The focus of the thermal analyses, on the other hand, is somewhat different from the one maintained in previous studies. Rather than calculating the temperature profiles in the objects of interest as end in themselves, the profiles were employed to assess the magnitude and the development of the thermal stresses which arise in cooking vessels during use.

Finite element analyses on archaeological material require knowledge of the shape of the object under examination, as well as of the mechanical and thermal properties of the constituent material. While for the former the survival of whole objects or at least reconstructable profiles are needed, the latter requires material tests, either on archaeological sherds or on relevant replicates. The determination of the specific material characteristics is usually rather labour-intensive, but for the present case, where these material properties have been established on model materials (Chapter 7 and 8), computer modelling using FEM can readily build upon these previous results.

9.1 The finite element method

The finite element method is a numerical analysis technique which is employed in order to obtain approximate solutions to the differential equations that describe a wide variety of engineering problems (Hughes 2000). The need for such numerical methods arises since, with increasing complexity, physical problems become analyti-

cally intractable. Difficulties are introduced, for example, by complex geometry, such as is the case for irregularly shaped ancient artefacts. The underlying principle of FEM is that a complex domain can be subdivided into a series of smaller regions so that the particular problem can be solved approximately. A model of the object of interest is divided up into a large number of virtual sub-regions, the so-called finite elements. These elements are connected with each other at specific points, called nodes. For the elements approximate functions are employed to describe the particular problem, which, in this way, is reduced to interactions between the elements. The parametric solution of the resulting equation system provides the solution of the problem. Since the method uses large numbers of equations it requires the aid of computers. The inputs which are needed for a computational analysis depend on the type of analysis, but commonly include geometric characteristics, loading mode and constraints, and material properties, such as Young's modulus and Poisson's ratio.

When investigating the performance of ancient ceramic vessels by FEM, first the shape and material parameters must be defined and an appropriate element size must be chosen. Subsequent meshing then defines the elements and nodes. After applying loads and possible constraints, the vessel and its response to different types of loading can be examined by calculating the structural deformation and the resulting strains in the body. By comparing the calculated strains on the finite elements with the fracture strain of the material, it is possible to assess the response of the examined vessel under the specific loading: if the calculated strain exceeds the fracture strain of the material, this means that fracture will initiate and - at least in the case of brittle materials - that the vessel will fail. The fracture strain can either be determined experimentally on test specimens cut from the particular object, or, alternatively, it can be inferred from tests on model materials.

9.1.1 Digital models

The first step in any finite element analysis is to describe the geometry of the object which is to be investigated. For the purposes of the present study, two and three-dimensional models have been created from archaeological drawings of typical cooking vessel shapes of the Middle and Late Cycladic periods at Akrotiri. The simula-

tion experiments were restricted to these phases partly because the evidence is much richer for the later periods, which produced most of the complete and reconstructable cooking vessels in the assemblage. The analysed shapes include a cooking jug with pedestal, a funnel-mouthed jar, and three different tripod-cooking pots (Figure 9.1). Various simplifications have been made for ease of modelling. So has rotational symmetry been assumed for the creation of the vessels' bodies in case of the three-dimensional models, legs and handles feature sharp angles, and surfaces are smooth.

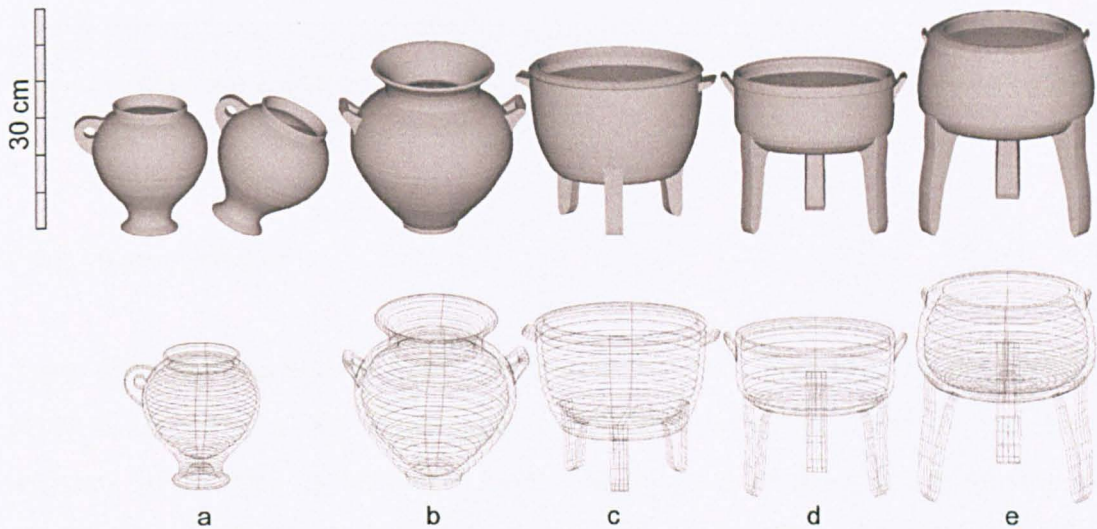


Figure 9.1 Digital models of cooking vessel shapes of the Middle and Late Cycladic periods at Akrotiri. Rendered (top) and wire-frame models (bottom): *a*, cooking jug with pedestal, upright and tilted; *b*, funnel-mouthed jar; *c-e*, tripod cooking pots. The fill level used for content calculations is indicated in the rendered models (darker grey).

Two-dimensional models usually provide results which are amply sufficient for estimating a vessel's response to loading, especially when these are axially symmetric. Three-dimensional models, although allowing for more realistic simulations, generate an increased number of elements. This results in simulations which require considerably more computer resources and are therefore substantially more time-consuming, while the level of detail - determined by model geometry as well as element size - is limited by the available computing power. Consequently, while structural analyses have been calculated on three-dimensional models, the thermal simulations are based on two-dimensional models.

The maximum capacity as well as the mass of the various cooking vessels which are illustrated in Figure 9.1, have been calculated from the digital models (Table 9.1). For the calculations of the vessels' mass, an average apparent density of $1900 \text{ kg}\cdot\text{m}^{-3}$ (*cf.* Chapter 8) has been assumed. The empty mass relates to the amount of raw mate-

rial required for the manufacture of a vessel, while the content data provide an indication of food capacity.⁴⁰

Vessel	Mass empty [kg]	Content [l]	Mass filled [kg]	Height [cm]
a) Cooking jug with pedestal, upright	1.0	1.5	2.5	17.9
Cooking jug with pedestal, tilted	1.0	1.3	2.2	-
b) Funnel-mouthed jar	2.3	3.1	5.4	22.2
c) Tripod flat	2.2	3.1	5.4	21.2
d) Tripod low	1.3	1.9	3.3	20.3
e) Tripod rounded	2.8	3.2	6.0	26.5

Table 9.1 Mass and content of the cooking vessels analysed by finite element analyses (*cf.* Figure 9.1).

9.1.2 Material models

Apart from the geometrical input, an analysis by FEM also requires the relevant physical properties of the constituting materials to be defined. For the structural analyses, which were carried out to assess the influence of shape and tempering on the stresses arising due to different loads, material parameters which had been determined on relevant experimental briquettes were employed. For the thermal analyses, whose aim was to investigate the magnitude of stresses that emerged in Late Bronze Age cooking vessels from Akrotiri when they were exposed to heat, the values of the physical properties were estimated, based on the analyses performed on the archaeological material. The specific material data employed for the particular calculations is stated in the relevant sections.

9.1.3 Critical fracture strain

Once the shape, material parameters and possible constraints have been defined, an object and its response to different types of loading can be examined by calculating its structural deformation and the resulting strains. To assess whether an object will survive the stresses it is exposed to, the limits of the material it is composed of, the

⁴⁰ The listed values relate to the specific vessels on whose drawings the models are based, and are not generally valid for the particular vessel types since, especially for the tripod cooking pots, considerable variation in size is observed. The data do, however, provide an indication of the order of magnitude for the various cooking ware types' capacities.

so-called *critical fracture strain*, must be known. By comparing the calculated strains on the finite elements with the critical fracture strain of the material, it is possible to assess the response of the examined object under the specific loading. If the calculated strain exceeds the fracture strain of the material, cracks will initiate and, at least in the case of a brittle material, the vessel will fail.⁴¹ The critical fracture strain can either be determined experimentally, by testing specimens cut from the material of interest, or established indirectly, by inference from model materials. For the purposes of the present study, the critical fracture strains of both the model materials assessed in the structural analyses, and of the ceramic recipe used in the manufacture of the local Late Bronze Age cooking vessels of Akrotiri (investigated in the thermal analyses) were estimated from the literature (Kilikoglou and Vekinis 2002). The values listed in Table 9.2 were estimated from the failure prediction diagram established for calcareous ceramics fired to 950°C. Since the microstructure of calcareous clays stays virtually unchanged between 850°C and 1050°C (Tite and Maniatis 1975), the literature values are applicable more generally for intermediate to high-fired calcareous ceramics. For the same reason, also the relevant material properties such as thermal conductivity, Young's modulus or strength do not differ greatly in this temperature range (Chapters 7 and 8), so that it can be argued that the results of the following simulations - although essentially based on the physical properties determined on ceramic mixtures fired to 850°C - are more generally applicable for intermediate to high-fired ceramics.

Material	Young's modulus (<i>cf.</i> Chapter 8)	Estimated critical fracture strain
calcareous base clay fired at 850°C with:		
- no temper	21.4 GPa	0.12%
- 10 % phyllite temper	18.4 GPa	0.11%
- 40 % phyllite temper	4.8 GPa	0.06%
- 10% granite temper	12.1 GPa	0.09%
- 40% granite temper	3.1 GPa	0.06%
Local fabric in the late Bronze Age at Akrotiri	5 GPa (estimated min. value)	0.06%

Table 9.2 Critical fracture strain of the model materials employed in the subsequent analyses, as estimated from Kilikoglou and Vekinis (2002).

⁴¹ It is important to note, however, that the critical fracture strain provides the *maximum* strain that a (brittle) material can withstand in bending. Strain values that are lower than the critical strain of a material do not guarantee that a vessel remains intact under the examined loads, since the model assumes a perfect material and does not take into account stress-concentrating flaws that always exist in ceramic materials. Kilikoglou and Vekinis (2002) found, for example, when assessing the method for its applicability to archaeological material, that two replica vessels fractured after loads had reached 85 and 95% of the theoretical maximum given by the fracture strain of the material they were made of.

Since the critical strain values derive from tensile tests, strictly speaking, they are applicable only for the simulation of conditions that can be considered as loading under static flexure, such as gravitational loads or compression on the outer periphery of a vessel (Kilikoglou and Vekinis 2002), the two types of loading which will be examined in the following structural analyses. The situation is slightly more complicated with thermal loads, since thermal gradients in an otherwise unconstrained specimen give rise to tensile as well as compressive stresses (Davidge 1986). However, since ceramic materials are much stronger in compression than in tension, the critical strain as obtained by measurements of transverse rupture strength can still be employed to provide a lower limit for failure.

9.2 Structural analyses

In a first part, structural finite element analyses were carried out to examine the handling of cooking vessels. The influence of shape and material parameters on the strains that emerge under two types of loading was investigated. Gravitational loading was used to simulate lifting a filled vessel by its handles. In addition, the response to point loading on a vessel's outer surface has been assessed.

9.2.1 Gravitational loads

The stresses and strains which develop when lifting a filled cooking vessel by its handles were calculated for different shapes and materials. As material input, data of a calcareous base clay tempered with various amounts of phyllite and granite temper and fired to 850°C (see Chapter 7 for Young's moduli and apparent densities) was employed. The Poisson ratio was estimated as 0.27 (Kilikoglou and Vekinis 2002). The density of the vessel content was approximated with the density of water at room temperature ($997 \text{ kg}\cdot\text{m}^{-3}$), the fill level is indicated in Figure 9.1. All calculations were carried out on three-dimensional models, using the SOLID45 element and an element size of 7.5 mm, by fixing the handles and applying gravitational force.

Different shapes

In order to compare different shapes, the material parameters were held constant and the data of the calcareous Pikermi clay, fired at 850°C and containing 40% phyllite temper were employed for all calculations. Table 9.3 compares the strains which arise in different vessel types upon lifting a filled cooking pot.

Vessel type	Handle		Body		Elements
	Stress [MPa]	Strain [%]	Stress [MPa]	Strain [%]	
a) Cooking jug with pedestal, upright	2.34	0.055	0.33	0.009	53791
Cooking jug with pedestal, tilted 30°	1.72	0.042	0.20	0.005	38132
b) Funnel-mouthed jar	0.56	0.013	0.01	<0.001	84407
c) Tripod flat	0.54	0.013	0.10	0.003	102237
d) Tripod low	0.22	0.006	0.03	0.001	53834
e) Tripod rounded	0.83	0.022	0.07	0.002	93474

Table 9.3 Maximum stresses and strains arising in the handles and body of filled vessels when lifting various cooking pots by their handles. All calculations have been carried out for the same model material, the calcareous Pikermi clay tempered with 40% phyllite and fired at 850°C. The critical fracture strain of this material has been estimated as 0.06% (see above). The last column indicates the total number of elements for each model.

Generally, the different vessel shapes are comparable in terms of resulting strains, the observed variations seem to stem mainly from differences in the filled vessels' mass (*cf.* Table 9.1). Increased values are found only for the cooking jug with pedestal. This can readily be explained by the fact that in this case only one handle, which must bear the whole weight, is available for lifting the vessel. For the same vessel, it is observed that less strain develops when lifting the vessel in a tilted than in an upright position (as illustrated in Figure 9.1). This is partly due to a reduced maximum fill level and accordingly reduced total mass. Mass differences alone, however, cannot account for the total differences in strains, since the strains which develop in the tilted vessel are roughly a quarter less than what is expected when only considering mass. Additional reduction is due to a more even distribution of the strains over the parts of the vessel body which is attached to the handle, since in a tilted vessel, the gravitational force acts normal to the attached vessel body.

The highest strains emerge at the handles, where they are connected with the vessel's body. In the case of the cooking jug with pedestal, these approach the value of the critical fracture strain of 0.06% for the model material investigated. It can be argued that the stresses calculated in the handles are likely to be overestimated. As mentioned above, the handles were simplified in modelling, so that the digital models feature a sharp angle at the joint of handle with vessel body. In reality, the transition from handle to body is smoother and the handles are reinforced at the joints so that the actual stresses are expected to be reduced. The strains in the adjacent body (Table 9.3), therefore, provide perhaps a better indication for the magnitude of strains that can be expected. It should be noted here that joints - such as where handles are connected to a ceramic body - are potential weak points in a ceramic object, since at places where two parts are joined during manufacture, flaws are likely to be introduced during drying and subsequent firing of the vessel. It would appear, however, that potters were well aware of the consequences of the potentially catastrophic (from a vessel's point of view) combination of an increased possibility for flaws and the high demands placed on this particular part of a vessel. Testimony to this bears not only the smoothing and reinforcement which is observed at such joints, and which reduces the magnitude of the stresses that arise at these critical points, but also the observation of the use of different ceramic recipes for handles and body of the same vessel (Day *et al.* 2006, 46): handles were found to be higher tempered than the body, resulting in a reduced shrinkage during drying and, accordingly, in a reduced probability for the introduction of critical flaws.

The influence of tempering

Further to the examination of the influence of shape, several model materials - chosen in order to highlight the influence of tempering - were compared for a fixed shape, a rounded tripod cooking pot (*cf.* Figure 9.1, vessel e).

Material				Handle			Body		
Clay	Fired to	Temper type	% Temper	Stress [MPa]	Strain [%]	S/CFS	Stress [MPa]	Strain [%]	S/CFS
Pikermi (calcareous)	850°C	-	-	0.83	0.005	0.04	0.07	<0.001	<0.01
	850°C	Phyllite	10%	0.84	0.006	0.05	0.07	<0.001	<0.01
	850°C	Granite	10%	0.77	0.008	0.09	0.07	<0.001	<0.01
	850°C	Phyllite	40%	0.83	0.022	0.36	0.07	0.002	0.03
	850°C	Granite	40%	0.83	0.033	0.55	0.07	0.003	0.05

Table 9.4 Maximum stresses and strains emerging in the rounded tripod cooking pot, when lifting the filled vessel by its handles, calculated for different ceramic materials. The strain/critical fracture strain (S/CFS) ratio is an indication for the material's response: in cases where this ratio is >1 fracture initiation is expected, since the strain exceeds the threshold for the fracture strain of the corresponding material. For critical strain values of the relevant materials, see Table 9.2.

The outcome of these analyses (Table 9.4) illustrates the influence of tempering on the strains that emerge when lifting a filled vessel. High amounts of temper result in strains which are significantly higher than the ones in corresponding low or untempered materials. Similarly, higher strains are observed for granite tempered materials than with phyllite tempered ones. These differences can be explained with the decrease of the Young's modulus upon tempering, which is more pronounced with granitic than with phyllitic temper, and with the accordingly higher elasticity of those materials (*cf.* discussion Young's modulus, Chapter 7) which gives rise to greater deformation.

The listed strain/critical fracture strain (S/CFS) ratio provides a measure for the response of a material: fracture initiation is expected if the S/CFS ratio is greater than one. Since lower Young's moduli result in lower critical fracture strains, the differences between the various materials are further enhanced when examining the S/CFS ratios. When comparing the reaction of various materials to loading, however, it is also important to take into account the differences in toughness, as this property critically influences the reaction of a material. This will be discussed in detail in the next section.

Again, it can be argued that the strains in the handles are overestimated and that the strains calculated in the adjacent body provide somewhat more realistic estimates. Therefore, it seems - not really surprisingly - that lifting the filled cooking vessels by their handles does not appear to have posed a threat to their integrity (it can be as-

sumed that the material parameters of the archaeological vessels fall within the range of the parameters investigated). The analyses highlight, however, the substantial impact of tempering on the magnitude of strains that develop in the material, and the reduced loads which are required for fracture initiation in highly tempered materials, expressed through differences in the respective S/CFS values.

9.2.2 Point loads

Further to the examination of gravitational loads, response to point loading has been investigated. Calculations have been performed for different magnitudes of loads and

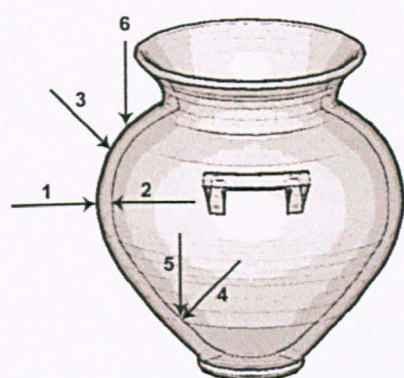


Figure 9.2 Point loads applied to 3D-model of a funnel-mouthed jar.

for two different model materials. The material parameters of two ceramic pastes which differ in temper grades (40 and 10% phyllite temper) but are both based on the calcareous Pikermi clay and fired at 850°C, were selected for the analyses. As above, the Poisson ratio was estimated as 0.27. The loads applied range from 100 to 1000 N, corresponding to 10 to 100 kg of weight load. Calculations were performed on a three-dimensional model of a funnel-mouthed jar using

the SOLID45 element and an element size of 5 mm, resulting in a total of 82182 elements. In all analyses, the foot of the vessel was fixed and loads were applied symmetrically, on each side evenly distributed on two neighbouring key points (Hein *et al.* 2008a). Figure 9.2 locates the point loads which have been applied to the model of a funnel-mouthed jar, the resulting maximum strains at the opposite sides in the vessel wall are listed in Table 9.5.

Pik85010P

E =18.4 GPa / Critical fracture strain (CFS) =0.11%

Pointload	100N		200N		500N		1000N		Stress [MPa]
	Strain (s) [%]	S/CFS	Strain (S) [%]	S/CFS	Strain (S) [%]	S/CFS	Strain (S) [%]	S/CFS	
1	0.006	0.05	0.011	0.10	0.028	0.25	0.056	0.51	7.77
2	0.007	0.06	0.014	0.13	0.036	0.33	0.072	0.61	10.44
3	0.006	0.05	0.012	0.11	0.029	0.26	0.058	0.53	8.63
4	0.007	0.06	0.015	0.14	0.037	0.34	0.073	0.66	10.61
Average 1-4	0.007(1)	0.06(1)	0.13(2)	0.12(2)	0.033(5)	0.30(4)	0.065(9)	0.59(8)	9(2)
5	0.005	0.05	0.010	0.09	0.025	0.23	0.051	0.46	7.37
6	0.005	0.05	0.010	0.09	0.026	0.24	0.053	0.58	7.61

Pik85040P

E=4.8 GPa / Critical fracture strain (CFS) =0.06%

Pointload	100N		200N		500N		1000N		Stress [MPa]
	Strain (S) [%]	S/CFS	Strain (S) [%]	S/CFS	Strain (S) [%]	S/CFS	Strain (S) [%]	S/CFS	
1	0.021	0.35	0.041	0.68	0.103	1.72	0.206	3.43	7.77
2	0.028	0.47	0.055	0.92	0.138	2.30	0.276	4.60	10.44
3	0.022	0.37	0.044	0.73	0.111	1.85	0.221	3.68	8.36
4	0.028	0.47	0.056	0.93	0.140	2.33	0.281	4.68	10.61
Average 1-4	0.025(4)	0.41(6)	0.050(8)	0.8(1)	0.13(2)	2.1(3)	0.25(4)	4.1(6)	9(2)
5	0.019	0.32	0.039	0.65	0.096	1.6	0.195	3.3	7.37
6	0.020	0.33	0.040	0.67	0.101	1.7	0.201	3.4	7.61

Table 9.5 Results of FEM simulations for point loads applied to a funnel-mouthed jar (see Figure 9.2 for location of loads). The maximum strain in the vessel walls opposite the point of contact are indicated for two different materials: a calcareous clay fired at 850°C, tempered with 10% phyllite (Pik85010P) and 40% phyllite (Pik85040P) respectively. For a load of 1000 N not only the strains but also the corresponding stresses are indicated. The strain/critical fracture strain ratio (S/CFS) provides an indication for the response of the material, and if it exceeds one, fracture initiation is expected.

When first looking at the same magnitude of loads applied to the same model material, it is found that the resulting strains vary for the different point loads. Loads 1 to 4 are all applied normal to the vessel surface. In this case, variations in the resulting strains are mainly caused by differences in the distance of key points. The practice of distributing the load over two neighbouring key points introduces a dependence of the strain from the key points' distance: closer key points result in increased strain, since the force is in fact applied to a smaller area. Therefore, if loads are distributed over key points when comparing different vessel shapes (Hein *et al.* 2008a), modelling must ensure a uniform distribution of these key points both within and across the vessels. Only then can one be sure that the resulting differences in strain reflect real differences caused by shape variations, rather than being introduced during modelling.

For loads 5 and 6, where the force does not act normal to the vessel walls, slightly smaller strains are observed than when the force acts normal to the vessel wall (loads 1 to 4). The effect of the incident angle becomes especially clear when comparing the values obtained for point loads 4 and 5, where the same load is applied on the same key points. If the incident angle is smaller than 90° , as is the case for load 5, only the part of the load which acts perpendicular to the vessel surface results in tensile stresses, the horizontal component causes shear stresses parallel to the vessel surface. Since the vessel walls are not equidimensional, having a much greater lateral than vertical extension, in a first approximation it can be assumed that shear strains do not significantly contribute to the total strain.

Further to the above, also slight differences in wall thickness lead to variations in strain. Since wall thickness critically influences a vessel's response to loading (Kilikoglou and Vekinis 2002), the dependence of the strains on wall thickness has been calculated on a simplified model. The analyses were carried out for a load of 500 N and the calcareous Pikermi clay fired to 850°C and tempered with 10% phyllite, using the same modelling parameters as in the complex model of a funnel-mouthed jar above. Figure 9.3 illustrates how the resulting strains decrease with increasing wall thickness.

The resulting graphs (Figure 9.3) illustrate that in order to maintain the same level of resistance to static loading, the strength of the material needs to be improved (e.g. by firing to higher temperatures) when reducing the wall thickness of a vessel. Similarly, the shortcomings of using a relatively weak material may be compensated by increasing wall thickness. It should be kept in mind, however, that with increasing wall thickness also the probability of a catastrophic flaw becomes greater.

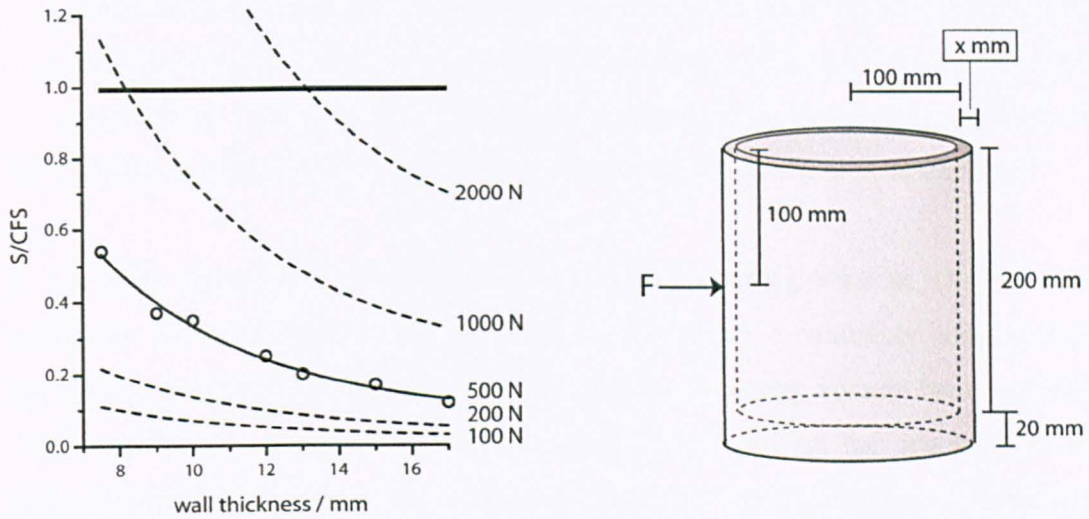


Figure 9.3 The influence of wall thickness on the response of a vessel to point loads. A simplified model of a vessel (right) has been used for the calculations, employing the SOLID45 element and a mesh size of 5 mm. The foot of the vessel was fixed for the calculations. The response in terms of S/CFS at the inner side of the wall has been calculated for the model material Pik85010P (see Table 9.5) and a load of 500 N. Graphs for different magnitude of loads are inferred from 500 N results. Loading is expected to lead to fracture initiation if the S/CFS ratio exceeds one.

Returning to the results of the complex model (Table 9.5) and comparing the response of the two materials investigated, it can be seen that, as discussed above, decreasing Young's moduli (caused in the present example by higher amounts of temper material), result in vessels which are more sensitive to point loads. The strain values obtained in this study for the material containing less temper fall within the range of values calculated for comparable materials and loads on other three-dimensional vessel models (Hein *et al.* 2008a). The increased fragility of vessels made of higher tempered materials is illustrated when comparing the loads which are required to initiate fracture in a hypothetical funnel-mouthed jar for the two model materials investigated. From Table 9.5, it can be inferred that for a jar made of the model material tempered with 40% phyllite, the criteria for fracture initiation ($S/CFS > 1$) is met for loads exceeding *c.* 250 N (25 kg), while in the case of 10% temper, in theory, only a point load of *c.* 1500 N (150 kg) becomes critical. It must be considered, though, that especially highly tempered materials usually exhibit considerable toughness⁴² (*cf.* Chapter 7), enabling the system to dissipate at least some

⁴² The assessment by FEM does not take into account toughness, since the critical strain values have been obtained from the TRS tests, and therefore indicate the critical strain for fracture initiation, which is not necessarily coincident with failure.

of the energy acquired during loading. If the strains exceed the critical strain values in a tough material, therefore, this does not necessarily lead to failure of the vessel. Care is therefore required when interpreting the calculated failure criteria, especially when comparing a brittle with a more tough material, since the model employed for the calculation of the S/CFS ratios does not allow for the dissipation of energy.⁴³

In summary, although in the production of ceramic cooking ware at Akrotiri comparatively coarse, heavily tempered fabrics - for which a relatively low Young's modulus is expected - dominate, it appears that the resulting vessels have not been overly sensitive with respect to static loading. This is due on the one hand to the magnitude of static loads: when comparing the results for highly tempered material with literature data calculated for fabrics used in the production of transport jars, one should not forget that cooking ware is not normally expected to be exposed to the same magnitude of loads during handling as are transport vessels. On the other hand, the fragility caused by a material with a low Young's modulus cannot only be counteracted by increasing the wall thickness of a vessel⁴⁴, but, since highly tempered materials show significant toughness levels, it can be assumed that the adverse effect of a low Young's modulus is at least partly compensated by increased ability to dissipate energy.

9.3 Thermal analyses

The second part of this chapter focuses on the strains that emerge in cooking vessels due to their exposure to heat. The following thermal analyses examine two vessel types in use at Akrotiri in the Late Bronze Age, the tripod cooking pot and the funnel-mouthed jar. Thermal analyses were carried out in order to examine the stresses which arise in these cooking vessels during simulated boiling activities (steady-state analyses) and when placed on a fire (transient analyses). The underlying principle employed for both of these types of analysis is to pin-point the areas of maximal

⁴³ The same is obviously also valid for the previous example, where the handling of filled vessels has been considered. Since toughness, however, results in an increased resistance to stress, the obtained values can be taken as upper limits.

⁴⁴ Increasing wall thickness appears, however, not to be the most ideal solution to overcome problems posed by high fragility, not only because of increased material demands for production, but also because this strategy will result in vessels which are much heavier, making their handling less convenient.

stress in a vessel by using the output of a thermal analysis, i.e. the temperature gradients in an object, as load for a subsequent structural analysis. This procedure is referred to as 'a coupled structural-thermal analysis'.

9.3.1 Influence of mesh size on thermal strains

In contrast to the preceding analyses, the thermal simulations were performed on two-dimensional models. As thermal stresses are particularly sensitive to the influence of shape, with sharp corners acting as stress concentrators, care had to be taken not to induce stresses artificially during modelling. For this reason, curved lines rather than polygons were used for the design of the two-dimensional models. In this way, straight lines are introduced in the contours of a model only during meshing.⁴⁵ With decreasing element size, the angles between adjacent elements are reduced and the actual stresses can be approximated. In order to ensure an adequate choice of mesh size for the thermal analyses, the influence of element edge length on thermal stresses was assessed before comparing different shapes.

The influence of the mesh size on thermal stresses was assessed for the example of a tripod cooking pot during cooking activities. Here, the maximum strains arise at the outer surface of the vessel and they are therefore particularly susceptible to changes in element edge length. Calculations were performed using the same loads, constraints and procedure as in the subsequent steady-state thermal analysis (see below). The data of the calcareous Pikermi clay tempered with 40% granite and fired at 850°C were employed to study the effect of mesh size and not the material parameters estimated for the archaeological fabric that had been used in the subsequent calculations. This explains the slight differences in actual strain values for the 0.5 mm mesh size that can be noticed when comparing the respective simulation results (Figure 9.4 and 9.5).⁴⁶

⁴⁵ This method, however, results in models with only very few key points, so that loads and constraints must be applied on the exterior nodes of a model.

⁴⁶ The differences in material parameter input were as follows: the Young's modulus of the model material is 4.8 GPa compared to 5 GPa estimated for the archaeological material, the apparent density of the model material is 1840 kg·m⁻³, compared to the 1900 kg·m⁻³ estimated for the archaeological material used in the following calculations.

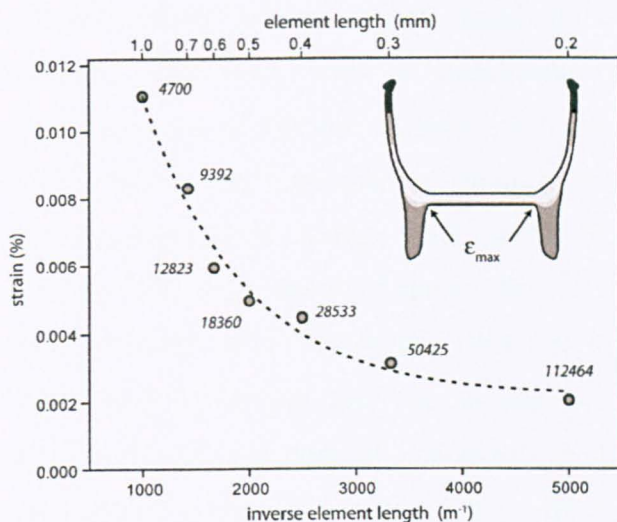


Figure 9.4 Dependence of the maximal thermal strain (ϵ_{max}) from element size. Italic labels indicate the number of elements in the model. The areas of maximal strain are indicated with arrows, different shades of grey within the vessel walls indicate the temperature profile (cf. Figure 9.5 below).

Several calculations with gradually decreasing element size were performed, so as to illustrate the effect of meshing on the thermal strain. The maximal strains appear at the bottom side of the vessel, where the vessel wall is joined to the feet (Figure 9.4). The maximum strain decreases with decreasing element size and with increasing smoothness the solution for a rounded edge is approximated. A mesh size of 0.2 mm, corresponding to 112464 elements,

proved to be the smallest element size for which the present problem could be solved; smaller element edge lengths resulted in equation systems whose solution exceeded the available computing capacity.

When trying to establish the actual strains in a vessel, one should consider that a ceramic vessel never has perfectly rounded and smooth corners, but will always have a certain surface roughness. This results in an actual strain that is higher than in the theoretical, ideally smoothed case. For the following thermal simulations therefore, an element length of half a millimetre was employed to simulate actual surface roughness. Given the fact that vessels are frequently wiped or burnished, sometimes even slipped, all surface finishes which increase smoothness and therefore aid to reduce thermal strains, this is admittedly a fairly conservative assumption. It provides, however, not only a worst case scenario, but also allowed calculations to be run smoothly.

9.3.2 Material parameters

The Late Bronze Age cooking pots, which are examined with the thermal finite element analyses, were manufactured from calcareous clays with substantial amounts of

relatively coarse temper material. Based on the analyses performed on the sherds (*cf.* Chapters 5 and 6 and relevant appendices), the physical properties of the material were estimated as follows: Young's modulus: 5 GPa, Poisson ratio: 0.27, apparent density $1900 \text{ kg}\cdot\text{m}^{-3}$, and thermal conductivity $0.8 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (Chapters 8 and 9). For the heat capacity an average value of $900 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ was assumed (Kilikoglou and Vekinis 2002; Hein and Kilikoglou 2007) and the thermal expansion coefficient was taken to be $3.5\cdot 10^{-6} \text{ K}^{-1}$ (Dinsdale 1986). The critical fracture strain was estimated as 0.06% from Kilikoglou and Vekinis (2002). No structural changes are expected to occur in the ceramic body of a cooking vessel after firing, even though cooking pots are exposed to heat on a regular basis. This is because the actual temperatures they are exposed to during use are not sufficient to induce such changes.⁴⁷ It can be safely assumed, therefore, that physical parameters such as thermal conductivity and Young's modulus, which are critically dependent on firing temperature, do not only remain unchanged during any one heating cycle but also stay essentially unaffected throughout the life-time of a ceramic cooking vessel.

9.3.3 Steady-state analyses: thermal stresses in a cooking vessel during cooking activities

In a first instance, the thermal stresses which emerge in a vessel when different parts of it are exposed to different temperatures that remain essentially unchanged were examined. This is typically the case for example during boiling activities, when the exterior of a cooking vessel is in contact with the heating medium, while its inside is restricted to a maximum of 100°C , determined by the boiling temperature of water.

In order to examine the thermal stresses under such conditions, steady-state analyses were performed on two-dimensional models of a tripod cooking pot and a funnel-mouthed jar. For all analyses, the temperature of the heat source was taken as 450°C , while the inside of the vessel was held at 100°C , simulating it containing boiling water. Heat convection was considered for the upper part of the vessel, assuming a film

⁴⁷ Cooking ware is exposed to far lower temperatures than are metallurgical ceramics, which were the subject of previous analyses (Hein and Kilikoglou 2007). It is for this reason that, unlike for metallurgical ceramics, it is not possible to obtain information on the operating conditions of cooking ware.

coefficient of $10 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ (Stöcker 1994), and an ambient temperature of 30°C , while at the inside of the vessel above the water level, where the walls are expected to be exposed to steam from the boiling water, a film coefficient of $1000 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ and a temperature of 100°C was applied. Finally, on the outer sides of the vessels a temperature gradient simulated the transition from the heat source to ambient air, reducing the 450°C over roughly 4-5 cm to 100°C . The thermal part of the analyses was performed using the thermal PLANE55 element; the chosen mesh size of 0.5 mm resulted in 25251 and 31275 elements for the funnel-mouthed jar and the tripod cooking pot respectively. For the ensuing structural analyses, the element was switched to the corresponding structural PLANE182 element. The parts of the vessel which are in contact with the ground were fixed in the vertical direction and the temperature profile obtained in the thermal analysis was applied as load.

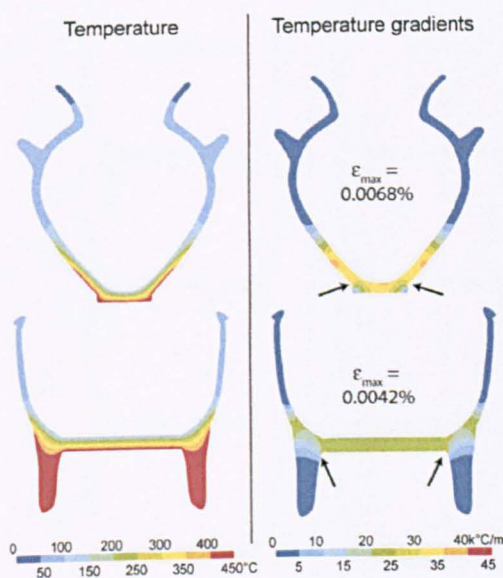


Figure 9.5 Temperature profiles and corresponding temperature gradients in a tripod cooking pot and a funnel-mouthed jar during simulated boiling activities. The areas of maximal strain are indicated with arrows.

The temperature profiles and the corresponding thermal gradients which are expected to arise in the tripod cooking pot and in the funnel-mouthed jar during boiling activities are compared in Figure 9.5. While lower thermal gradients arise in the tripod cooking pot, the maximum strains are comparable, 0.004% for the tripod cooking pot and 0.007% for the funnel-mouthed jar. The highest strains appear in both cases at the outer vessel surface which is in contact with the heat source, in the area which exhibits the highest curvature (indicated with arrows in Figure 9.5). The maximum strain is clearly

below the critical value of 0.06% for both vessel types. It should be noted that the calculated maximum strains arise in the surface elements; the strains emerging inside the vessel walls are substantially lower (see also transient analysis below). Furthermore, the mesh size chosen, as discussed above, probably leads to an overestimation of the resulting strains. Together with the observation that the thermal stains at the points of maximum strain are the product of compressive rather than tensile stresses,

this indicates not only that the maximum strain values calculated here can in all likelihood be considered as worst-case values, but also that the thermal stresses which arose in those vessels during cooking activities were clearly not critical.

9.3.4 Transient analyses: thermal stresses developing in a cooking vessel due to sudden changes in temperature

Thermal stresses are not only caused by differences in temperatures but they also arise due to changes in ambient temperature. If these changes occur with a very fast rate, temporarily extreme temperature gradients emerge, and we speak of thermal shock. For cooking ware, this condition is met for example when a cold vessel is placed on a heat source. Transient analyses allow the simulation of such conditions

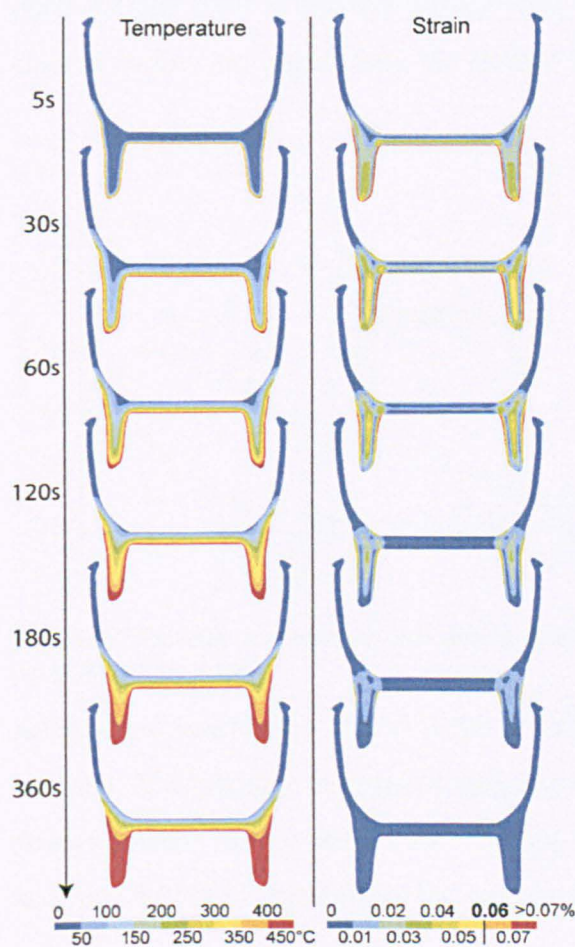


Figure 9.6 Development of temperature and strain in a tripod cooking pot over time. The critical strain, 0.06%, is indicated in bold on the strain scale. The time after $t=0$ (application of temperature loads) is indicated in seconds.

when the temperature gradients are not constant but change over time.

In order to simulate the stresses which arise due to a sudden change in ambient temperature, and to monitor their development in the vessel over time, a transient analysis was performed for the tripod cooking pot. The calculations were performed on the same digital model and with the same parameters, constraints and loads as used for the steady state analysis above. The only difference to the static analysis is that the inner surface of the vessel was held at 30°C, assuming that it is filled with cold water when first placed on a heat source. Since only the first few minutes after placing the vessel in contact with a heat source were calculated, the heat trans-

fer from the vessel to the water and the resulting temperature increase of the contents was neglected. Transient analyses also require definition of initial conditions; here the initial temperature of the vessel was taken as 30°C.

Figure 9.6 illustrates the development of the temperature and strains in the tripod cooking pot over time. The temperature loads are applied at $t=0$, corresponding to the time when the vessel is put in contact with the heat source. The left column shows how the temperature profile inside the vessel changes over time. After six minutes, steady state conditions appear to be almost reached for the constraints applied.⁴⁸ In the right column of Figure 9.6, the corresponding strains are mapped. The maximum strain, as in the steady-state case, is found at the inner connection of the feet with the vessel body. This maximum strain is clearly highest immediately after placing the vessel in contact with a heat source and decreases over time. Furthermore, there is an outer surface layer of perhaps a millimetre, mainly around the feet, in which the calculated strains are higher than the critical fracture strain in the first minute (orange and red colours).

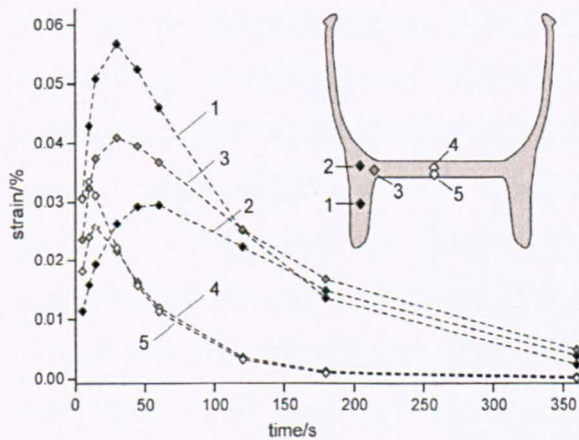


Figure 9.7 Development of strain over time at different points in the vessel.

parts of the vessel vary, but also the point in time when these maximum strains are attained. Not taking into consideration the outer surface of the vessel, the maximum strains emerge in the vessel's feet (Figure 9.7 - point 1), where the critical fracture strain of 0.06% is approached but not reached. After one minute, the strains are de-

creased (orange and red colours). Except from this outermost surface layer, however, the strains do not exceed the critical strain. The highest strains within the vessel are reached after approximately half a minute. When looking at the development of strain at different points in the vessel over time (Figure 9.7), it is observed that not only the magnitude of the maximum strains that are reached in different

⁴⁸ In reality, the vessel contents would slowly heat up and not stay constant at 30°C. This reduces the temperature difference between the vessel's inside and the lower part of the vessel which is in contact with the heat source, so that it is expected that the resulting strains are further reduced. An estimation based on heat flux and assuming that the vessel contains water, revealed that the content's temperature remains virtually constant within the first minute (increase <1°C), the time interval in which significant strains occur (see Figure 9.7).

creasing in all parts of the vessel. After six minutes steady-state conditions start being approached and the strains within the vessel have nearly disappeared, only at the connection with the feet remain some subcritical strains.

As discussed with the structural analyses, since the critical strain values are obtained from strength tests, they allow for an estimation of the threshold for crack initiation only. Also for thermal stresses, it is not only the magnitude of these stresses arising in a vessel, but also the constituting materials' capability to resist to them, which define a vessel's response. Although for the tripod cooking pot critical strains are apparently reached under conditions of thermal shock in a thin outer surface layer which is in contact with the heat source, we can assume that the substantial toughness of the material, impaired by high amounts of coarse temper material, enables the cooking pots to absorb the strains arising from thermal gradients. Consequently, placing a vessel on a heat source was in all probability not endangering its structural integrity.

Summing up, the thermal analyses showed that the thermal strains which arose in Late Bronze Age cooking ware from Akrotiri appear to have been negligible during cooking activities, but probably were considerable when the vessels were exposed to sudden major changes in ambient temperature. It seems that if critical stresses occurred in a cooking pot, they did so shortly after placing it on a heat source: it is within the first minute only that considerable strains arise in the material. Taking into account that the cooking ware examined is manufactured of a coarse, highly tempered fabric, with presumably high toughness levels, it can be assumed that even when thermal stresses led to crack initiation that vessels did not necessarily fail.

Furthermore, in a highly tempered material with interconnected pores and microcracks (Kilikoglou *et al.* 1995), we would expect these to be saturated with water when a filled cooking vessel is placed on a fire, resulting in a considerable reduction of the temperature gradients and accordingly thermal strains within the ceramics matrix, especially in the critical initial phase. This effect, however, might be counteracted to a certain extent by the deposition of organic residues, which results in partially sealed off pores. However, although the thermal conductivity of organic residues is lower than that of water, it is still one order of magnitude greater than that of

air⁴⁹, so that also the presence of organic deposits can be argued to be beneficial, at least as long as it does not result in a complete sealing off of the remaining pores that subsequently cannot be filled either with water or organic residues.

One important point that has not been included in the present analysis is thermal fatigue. Thermal fatigue refers to the cumulative degree of structural damage caused by repeated exposure to subcritical thermal stresses (Lawrence and West 1982, 225-226). Significant strains do appear in the material under conditions of thermal shock, shortly after placing it on a heat source, so that it is expected that thermal fatigue will play a role for the long-term survival prospects of a vessel. This parameter is, however, difficult to calculate and is therefore usually determined experimentally, by thermal cycling. If one would want to include this parameter in an assessment, therefore, vessel replicates should be manufactured which are then repeatedly exposed to thermal stresses under controlled conditions.

9.4 Summary

Finite element analyses have been employed to assess the response of cooking vessels to mechanical and thermal stresses. Although the high amounts of coarse temper material attested in the cooking ware fabrics at Akrotiri result in increased strains under static loading, the vessels are still expected to have withstood the mechanical stresses that occurred during their handling. More relevant than resistance to mechanical stresses, so it could be argued, is the reaction of cooking vessels to heat. The thermal stresses caused by steady temperature differences during cooking activities appear negligible altogether. Stresses appear to become more critical, however, when sudden changes in ambient temperature occur, e.g. when placing a cold vessel on a heat source. Nevertheless, the cooking vessels are thought to have been able to accommodate the ensuing thermal strains, not least due to the high levels of toughness which are imparted by high amounts of tempering. The results highlight that cooking in the examined vessels resulted in stresses that were far below critical, and that also

⁴⁹ For water, a thermal conductivity is usually tabulated as *c.* $0.6 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$, while for air values around $0.025 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$ are reported (Stöcker 1994). Based on the values for organic oils ($0.17 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$) and paraffin ($0.26 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$), it can be assumed that the thermal conductivity of organic deposits lies probably somewhere around $0.2 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$.

the (to a certain extent avoidable) exposure to sudden, large temperature differences would not have resulted in them failing.

Thermal simulations by FEM have a great potential to elucidate conditions of and response to thermal stress and thermal shock in ancient ceramics, problems which to date remain to be resolved satisfactorily. Future computational analyses should, therefore, be extended to three-dimensional models. Also, since the thermal expansion coefficient directs the magnitude of thermal strains, this material parameter ideally should be determined experimentally, as should the heat capacity. Knowledge of individual values of those material parameters for ceramic model materials, rather than global estimates, will allow a refinement of the simulations. Additionally, as has been outlined above, the role of thermal fatigue needs to be investigated. Further thermal analyses by will therefore require the determination of additional material parameters as well as more complex modelling, but should ideally also include experimentation with replica vessels.

Chapter 10

Discussion and conclusions

The present chapter is divided into four main parts. After a brief summary of the influence of manufacturing parameters on mechanical and thermal properties of clay ceramics, the results of the investigation on experimental briquettes are transferred to the archaeological case study, and changes and variations in ceramic fabrics of the cooking ware at Akrotiri are discussed. Thereafter the methodology employed is assessed, and the main points of interest for future research that have been identified in the course of this study are briefly recapitulated.

10.1 Performance properties: summary of experimental results

Performance criteria are of importance for technological studies, since we assume that what was recognised by, and potentially relevant to, the consumer of cooking ware in antiquity, and what was therefore potentially influencing their choices, is *how the vessels performed* and not what kind of temper was used in their production or whether clays were mixed or not.⁵⁰ In this context, the study of manufacturing practices is not an objective in itself, but is a requirement to understand the performance of the vessels, since this is critically dependent on several manufacturing parameters. The influence of different such technological choices - clay, temper, and firing temperature were the parameters investigated - on the mechanical and thermal properties of ceramic materials are summarised below. The measurements on experimental briquettes and their outcome have been discussed in-depth in the relevant chapters. The following brief summary emphasises how the various performance properties are dependent on the parameters that were investigated, in order to prepare the ground for the subsequent discussion pertaining to the Akrotiri case study. Ther-

⁵⁰ Similarly, and as discussed below, the exact temperature a vessel was fired to in antiquity is of very little relevance. It is the resulting *microstructure* of the material that is important, since this is what influences the performance of the vessel.

mal shock resistance is not included in the itemised account below but treated separately at the end.

10.1.1 The influence of firing temperatures and clay type

Key to understanding the influence of firing temperature on performance properties is the development of the microstructure in a ceramic, mainly the degree of vitrification, and this depends on firing temperature as well as clay type. Since it is not the firing temperature or the clay type *per se* but the combination of the two that effects the mechanical and thermal properties examined, these two parameters are discussed together.

A ceramic's microstructure develops differently for calcareous and non-calcareous ceramics. Within those two broad groups further variation is expected, since the emergence of different stages also depends on clay minerals and fluxes in a ceramic paste. Knowledge of the exact firing temperatures which were achieved in the manufacture of the ceramics by themselves is therefore of only very limited assistance - and accordingly relevance - when assessing technological choices in ancient ceramics. Rather, it is the microstructure, the result of the (often not reconstructable) *combination* of raw materials and firing regime which provides us with a means to gauge the performance properties of the particular ceramics.

The increase in *fracture strength* which was observed with higher firing temperatures is linked to the degree of vitrification and to the porosity in the clay matrix. Accordingly, although strength levels increased earlier in the case of calcareous ceramics, they then remained stable over a substantial temperature range, corresponding to the stability range of the open cellular structure which develops in calcareous clays soon after the onset of vitrification. In non-calcareous clays, on the other hand, fracture strength continued to increase after the onset of vitrification, reflecting the steady increase in vitrification and decrease in porosity observed for those clays. The dependence on firing temperatures or increasing vitrification was not as clear-cut for *toughness*. Intermediate firing temperatures did invariably result in high toughness levels. Upon a further increase in firing temperatures, however, the different temper

types resulted in different behaviour. With coarse granitic temper, high firing temperatures could be reached without losing toughness. In phyllite tempered ceramics, on the other hand, toughness has been observed to decrease with increasing vitrification. Finally, firing to sufficiently high temperatures resulted in a considerable increase in *thermal conductivity* due to the emergence of an extensive glassy phase. As with strength, also variation in toughness and thermal conductivity between calcareous and non-calcareous clays are related to the differing development of microstructure.

10.1.2 The influence of the addition of temper material

This section first points out how the presence of coarse inclusions affected the performance characteristics of clay ceramics, before the influence of type and shape of aplastic rock fragments are discussed. The *fracture strength* decreases with increasing amounts of aplastic inclusions. *Toughness*, on the other hand, was observed to increase with increasing amounts of temper added. Concerning *thermal conductivity* general statements are not possible, as the influence of inclusions on this material property was dependent on the type of temper and firing temperature.

10.1.3 The influence of the type of temper material

The notion of 'type' of temper encompasses two variables, shape and material. These two parameters will be treated together, since this study compared platy phyllitic with angular granitic temper material, so that the influence of shape and material of temper on the performance properties studied are entangled. The considerable influence of the orientation of anisotropic temper particles must be emphasised here: mechanical and thermal properties are expected to be distinctively different when measured parallel than perpendicular to the alignment axis of those particles. Manufacture was carried out in such a way as to align the phyllite fragments since in ceramic vessels in general and in those of the archaeological case study in particular, platy particles are commonly aligned parallel to a vessel wall. All performance properties have been determined perpendicular to the alignment axis.

The reduction in *fracture strength* which accompanies the tempering of a ceramic paste was less pronounced with platy phyllitic particles than with more equant granitic ones, an observation which is attributed mainly to particle shape. Comparing the impact of the two temper types on *toughness*, differences became discernible only at high firing temperatures, where platy phyllitic temper resulted in lower values than angular granitic one. When looking at the influence of temper type on *thermal conductivity*, phyllite temper has a clearly negative effect on this property (for heat flow perpendicular to the alignment of the particles), while granite tempering, at least in modest amounts, was observed to increase thermal conductivity. For higher amounts of temper, the beneficial effect of the temper material was outweighed in the higher fired samples by the high amount of orientated porosity that is induced into the ceramic, resulting in a net loss of thermal conductivity.

10.1.4 Thermal shock resistance

Thermal shock resistance has not been included in the above account, mainly because this is not an inherent material property but crucially dependent not only on the *conditions* of thermal shock, but also on the *thermal history*⁵¹ of the material. This makes thermal shock resistance more difficult to assess than the other performance properties. One could perhaps parallel thermal shock resistance to a vessels resistance to impact, in that both describe a material response to a sudden emergence of stresses, and both are dependent not only on the threshold for fracture initiation but also on the capability of a material to dissipate energy efficiently. It could be argued that coarse clay ceramics appear well suited to resist crack propagation through thermal shocking, especially when taking into account that the temperature differences commonly expected for cooking activities are substantially lower than those encountered in metallurgical activities. Accordingly, thermal shock resistance may play a far less important role in coarse cooking ware ceramics than has sometimes been assumed. Further weight is added to this hypothesis by computer simulations

⁵¹ The experiments on laboratory specimens revealed that sub-critical thermal shocking can result in toughening of a material. This shift towards more stable fracture renders subsequent subjection of a material to thermal shock less detrimental.

that have been carried out using FEM. Calculations indicated that even the thermal stresses which are expected to occur when a coarse ceramic paste is fired to high temperatures are not sufficient to cause failure of a vessel.

10.1.5 Relative importance of the investigated performance properties for cooking ware

Before plunging into the case study, it might be sensible to briefly rehearse some considerations on the relative importance of the performance properties for the materials used in the manufacture of cooking vessels. As outlined above, when we keep in mind the relatively low temperature differences and the fact that in the present case study all cooking ware fabrics are invariably coarse, it can be argued that *thermal shock resistance* is sufficient for all fabrics examined. Accordingly, it appears ill-advised to employ this performance property to assess the relative suitability of the different coarse clay ceramics to be used in the production of cooking ware. *Toughness* is probably more important than *strength* for ceramic cooking vessels, taking into account that it is the structural integrity of a vessel which relates to the energy required for fracture initiation and potential propagation that is of interest rather than the energy needed for crack initiation alone.⁵² Finally, although *thermal conductivity* can be linked to fuel efficiency, differences in this property do not only provide a means of judging a vessel's suitability for cooking as such; they might also hint at the aptness of a material to be used for different cooking methods. Generally, it could be argued that higher thermal conductivities seem beneficial especially for boiling, while somewhat lower thermal conductivities might be of advantage when simmering foodstuffs.

⁵² Strength, which indicates only the energy necessary for the initiation of fracture (regardless whether a material fails thereafter or not), appears of somehow restricted use when comparing ceramic materials, which can show stable as well as unstable fracture. Although strength indicates the material limits for material failure in the case of brittle ceramics, in tougher ceramics, it provides merely an indication as to when cracks start propagating. Although strength has been linked with the ability of a ceramic to retain fluid contents, it should be kept in mind that for coarse cooking ware ceramics this ability seems to be of only limited relevance. Coarse tempering induces microcracks and open porosity into the fabric, so that such materials would not retain fluids very well to start with. Cooking vessels can be slipped or sealed, in order to prevent the loss of water, but also cooking activities themselves gradually seal off open pores due to the deposition of organic residues. Similarly, microcracks which develop during the use-life of a cooking pot can be sealed off by organic residues.

10.2 Case study: the Akrotiri cooking ware assemblage

Having summarised the influence of particular manufacturing parameters on performance properties thought to be relevant for cooking ware, and thus laid out the necessary background, we can now set out to have a closer look at the archaeological case study. The following sections will examine the differences and variations in the various ceramic cooking ware fabrics found at Akrotiri, and discuss the resultant potential differences in performance or function, by employing the knowledge gained through the material tests on the experimental briquettes.

The petrographic analyses of the archaeological material revealed that the local manufacturing technology underwent two major changes in the period covered by this study. A first change in the ceramic recipe that was used for cooking ware took place around the transition of the Early to the Middle Cycladic period, the second occurred with the transition to Phase C of the Middle Cycladic. These changes divide the sequence in three broad phases. The following discussion will discuss the changes *between* these three phases as well as the variations observed *within* them (Table 10.1), and follows a chronological order.





Period	Main local fabric	Variation within period
Final Neolithic and Early Cycladic Phases	non-calcareous, volcanic rock inclusions (pumice and lava)	Imports vs. local ware
	 <i>change in base clay, more pumice</i> 	
Middle Cycladic, Phases A and B	calcareous, volcanic rock inclusions (pumice and lava, pumice increased)	N/A
	 <i>addition of phyllite temper</i> 	
Middle Cycladic Phase C and Late Cycladic IA	calcareous, volcanic rock inclusions (pumice and lava) and phyllite	a) Imports vs. local ware b) Firing temperatures within local ware

Table 10.1 Main changes and variation in cooking ware fabrics at Bronze Age Akrotiri.

All ceramic pastes that were used in the manufacture of cooking ware found at Akrotiri are coarse and contain substantial amounts of aplastic inclusions. As discussed

earlier, it can be argued that the respective cooking vessels therefore had an increased capability to resist crack propagation and would withstand the thermal shocking likely to occur during cooking activities. Since thermal shock resistance can be argued to be sufficient for all fabrics examined, this property - albeit referred to frequently in the archaeological literature when dealing with cooking ware - cannot be used to gauge the relative suitability of the different ceramic fabrics found at Akrotiri, and will therefore not feature prominently in the subsequent discussion. A similar argumentation, by and large, can be made also for the mechanical properties strength and toughness. Much of the following discussion focuses therefore on the impact of the changes and variations which are observed in the ceramic fabrics - and ultimately of the potters' technological choices - on the thermal conductivity of the ceramics.

10.2.1 Final Neolithic and Early Cycladic periods

The local cooking ware fabric throughout the earliest periods covered by this study is non-calcareous and contains coarse inclusions of volcanic rocks. In addition to the local vessels, a substantial amount of cooking ware is found to be of off-island provenance. The main imported fabric group, characterised by granitic to granodioritic inclusions in a non-calcareous groundmass, is believed to originate from Naxos. These imports appear as early as the Final Neolithic, and are found in all phases of the Early Bronze Age attested at Akrotiri, with the exception of ECII late. Other clearly imported vessels include Talc Ware pottery which appears uniquely in the ECII late Kastri Group phase, as well as vessels made of two other fabrics - both characterised by metamorphic rock inclusions - in ECII early, the phase to which an 'international spirit' has been attributed (Renfrew 1972, 451)⁵³. One of those imported fabrics, only found in baking plates, is thought to derive from neighbouring Ios, the other probably originates from Naxos (Figure 10.1).

The amount of non-local cooking vessels recovered from contexts dated to the earlier periods is quite striking: many of the sampled bowl and jar type vessels belong to the

⁵³ As discussed in Chapter 3, evidence for considerable trade within the Aegean goes back to the ECI late and subsequently increases throughout the ECII.

granitic⁵⁴, presumably Naxian fabric group. Local versions of these types were sampled but they are clearly outnumbered by the imports. Even if allowing for some sampling bias, the displayed pattern appears to reflect an actual trend in the assemblage, indicating the importation of substantial amounts of cooking ware from an off-island source throughout much of the Early Bronze Age at Akrotiri. While imported ware seems to predominate with jar and bowl types, a different picture emerges when looking at the other categories that were sampled, the hearths and baking plates/pans. These types occur mainly in the early local fabric group and appear much less frequently as imports. Exceptions are two hearths of Naxian origin in ECI late, and several non-local baking plates that have been found in contexts attributed to ECII.

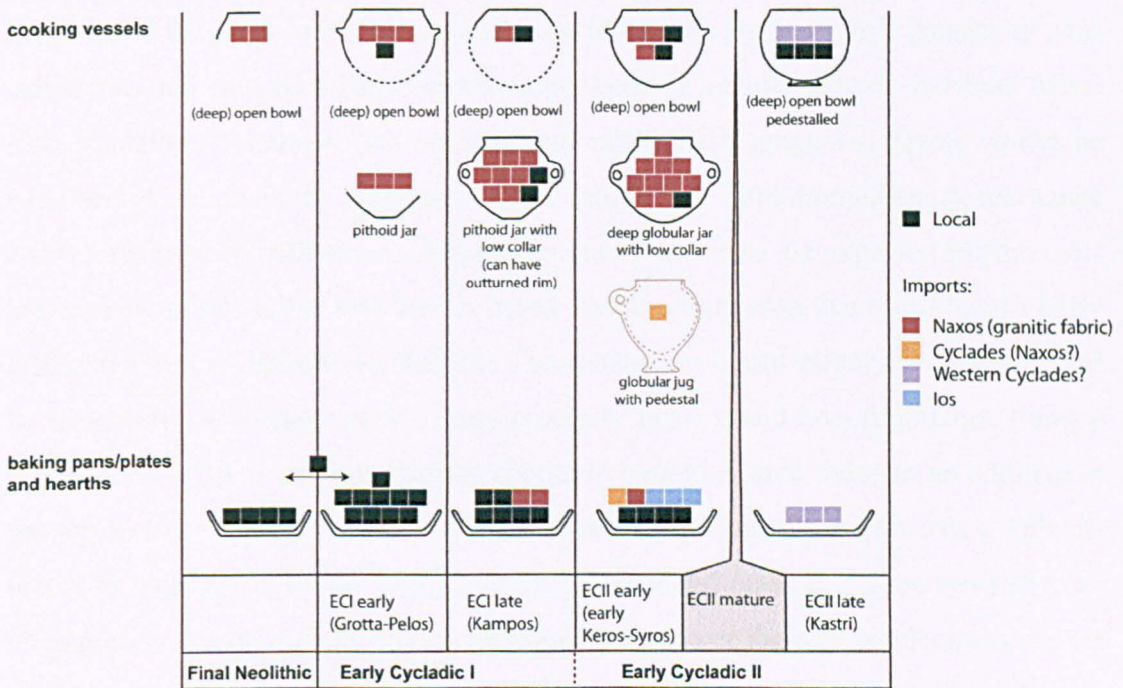


Figure 10.1 Cooking ware from the Late Neolithic and the Early Bronze Age at Akrotiri. The different types are indicated. Each coloured square corresponds to one sample, the colour indicates the provenance assigned to the sample. Please note that the pattern corresponds to the allocation of the *sampled vessels* to the different fabrics and not of the assemblage as a whole.

⁵⁴ Although the fabric (group 5 - Chapter 4) contains rock inclusions derived from plutonic rocks of granitic towards granodioritic compositions, and strictly speaking should be called 'granitic/granodioritic' it will be referred to as 'granitic' throughout the text for convenience.

There are other imported fabrics which are more restricted chronologically in distribution; all of them date to ECII, a period of generally increased movement within the Aegean. Some appear exclusively in ECII early (Figure 10.1), while in ECII late, Talc Ware which characterises Cycladic assemblages at the time (Vaughan and Wilson 1993), appears at Akrotiri in significant amounts. When attempting to examine the importation of off-island cooking ware and their distribution within the assemblage within a functional framework that accounts for performance characteristics, it therefore appears most rewarding to concentrate in a first instance on comparing and contrasting the local volcanic to the main imported granitic fabric, which is present throughout the Early Bronze Age.

As a first step, those performance properties which are potentially different for the Naxian and the early local fabric need to be identified. Both ceramic pastes are non-calcareous and contain substantial amounts of coarse angular temper. For both materials, therefore, relatively low strength but rather high toughness levels would be expected. Also, given the coarseness of the fabric, sufficient thermal shock resistance can be assumed in both cases. Differences could, however, be expected for the thermal conductivities of the two fabrics based on the observation that they contain fairly different types of aplastic inclusions. The locally produced pottery is characterised by inclusions of volcanic rocks, more precisely pumice and lava fragments. Pumice is a material with a very low thermal conductivity and is used today as an additive in the production of light-weight concrete, enhancing its insulating properties. This effect is brought about by the high porosity of the added pumice: concrete which contains porous volcanic rocks has up to seven times lower thermal conductivity values than comparable quartz sand concrete (Hossain 2004). A similar effect can certainly be expected for ceramic pastes: the presence of porous pumice fragments in a fabric most probably lowers its overall thermal conductivity. In contrast, the addition of a temper material with a higher thermal conductivity than the groundmass, such as granite, can impart an increased overall conductivity to ceramic pastes (Chapter 8, Hein *et al.* 2008b).

Also firing temperature plays an important role in determining the thermal conductivity of clay based ceramics: directly, by increasing the conductivity of the groundmass with increasing vitrification, as well as indirectly (and in the opposite direc-

tion), by increasing the amount of manufactured porosity in highly tempered specimens with increasing firing temperature. When looking at the archaeological samples, the local cooking ware does not appear to have been fired to exceedingly high temperatures. Also the vast majority of the imported granitic samples were fired to low or even very low temperatures (Appendix IV)⁵⁵. The replication experiments revealed that high amounts of granite temper can induce significant levels of manufactured porosity in a ceramic paste. Since porosity is detrimental to a material's conductivity, this counteracts the beneficial effect of the temper type on the overall thermal conductivity. Only when the shrinkage of the clay matrix is very low and the manufactured porosity accordingly small, as was the case in the low-fired non-calcareous Kalami clay, did the addition of high amounts of granite tempering further improve a paste's overall thermal conductivity (*cf.* Chapter 8).

When looking at the archaeological material, some - probably shrinkage induced⁵⁶ - porosity is indeed observed for the Naxian samples, much less pronounced, however, than what is detected in the highly tempered and well fired replica briquettes. The presence of a substantial amount of granitic inclusions in conjunction with the predominantly very low firing temperatures is, therefore, expected to lead to an increase in overall thermal conductivity.

While it can be argued that the local, pumice containing material has a reduced ability to conduct heat, for the main imported fabric the opposite would be expected. It should be kept in mind, however, that the local fabric does not only contain pumice but also other, non porous, volcanic rock fragments, reducing the overall negative effect of the pumice particles somewhat.

When turning to the performance requirements placed on the different functional categories of the pottery examined, it can be argued that for hearths as well as for baking plates/pans, low thermal conductivities would be beneficial or, at least, that

⁵⁵ These low firing temperatures are reflected in the high optical activity of the groundmass of most samples. Additionally, in at least three cases, the presence of kaolinite indicates that firing temperatures did not exceed 550°C in the related vessels. Only three out of the 30 Naxian bowl/jar type samples were found to be high-fired.

⁵⁶ Similarly to what is observed in the experimental briquettes, also in the archaeological samples the pores are mostly aligned parallel to the vessel walls. It can be argued that the alignment of clay particles during manufacture and subsequent shrinkage results in such a pattern (*cf.* Chapter 7).

there appears to be no advantage in increasing the thermal conductivity for those vessels types. Indeed, imports of those functional types seem fairly rare. One could argue that hearths and baking plates are just generally less likely to be imported, when looking at the ECII early (Figure 10.1), however, it is apparent that imports of such types are not generally uncommon.

For cooking vessels, on the other hand, which are presumably employed to heat up their contents, there are advantages in having a higher thermal conductivity; an increase in thermal conductivity translates to a reduction in the time which is needed to heat up a vessel's contents. Acknowledging that the non-local bowls and jars most probably did perform differently - and in all likelihood better - than the local ones, allows for the possibility that they might have been selected and imported for enhanced performance properties. The appearance of large amounts of non-local cooking jars and bowls during the Early Bronze Age at Akrotiri - as well as the production of some local versions of an apparently successful type - might therefore be related to a superior performance of these vessels. Accordingly, the importation⁵⁷ of granitic cooking ware from Naxos, attested for the first time as early as the Final Neolithic, would reflect a consumption preference expressed by the inhabitants of Akrotiri.

Finally, unlike transport jars where the contents rather than the vessel are the merchandise, cooking pots are assumedly traded in their own right. Apart from testifying to a lively trade between the Cycladic islands from as early as the Final Neolithic period, therefore, the finding of clearly non-local cooking ware also implies some level of specialisation in the pottery production of the early Cyclades, as the established consumption pattern appears inconsistent with a self-sufficient household production.

⁵⁷ Alternatively to being imported, the presence of cooking ware in a clearly foreign fabric could be read as traces of itinerant people, carrying their own cooking vessels and frequently making station at the site. This scenario is, however, highly unlikely to explain the situation at Akrotiri, where abundant amounts of Naxian vessels are found throughout the Early Bronze Age sequence at Akrotiri. It must be assumed therefore, that the vessels, which had properties which could not be achieved with the locally available raw materials, were indeed imported from an off-island source to be consumed by the local populace.

10.2.2 From the Early to the Middle Cycladic period

The transition from the Early to the Middle Bronze Age at Akrotiri is marked by a change in the ceramic fabric of the local cooking ware. With the beginning of the Middle Cycladic period, all cooking ware is manufactured following a novel ceramic recipe, which, as its predecessor, is characterised by the presence of volcanic rock fragments. Unlike the earlier local fabric, though, the volcanic rock fraction is now dominated by inclusions derived from pyroclastic deposits, and the relative amount of lava fragments is in most cases greatly reduced. Furthermore, the ceramics' groundmass is more calcareous and sometimes contains abundant microfossils. Finally, higher firing temperatures are observed in some cases. This, however, does not happen consistently and, rather than indicating a general pattern, appears merely to hint at a higher variation in firing regimes in the early Middle Cycladic period, compared to the Early Bronze Age.

When examining whether the change in local ceramic recipe is related to technological progress - in the sense that it would allow the production of better performing cooking vessels - it soon becomes clear that it does not seem to influence many performance properties. Strength and toughness, for example, again are not expected to change significantly, due to high amounts of coarse inclusions in both fabrics. Although for the higher fired specimens among the early Middle Cycladic samples, somewhat higher strength and lower toughness might be anticipated, differences are certainly not great, due to the large amount of inclusions. Similarly, thermal shock resistance is not expected to have changed critically. The physical property that probably did change with the introduction of the new ceramic recipe, thermal conductivity, is expected to have decreased: as has been argued above, the presence of pumice or tuff fragments in a ceramic fabric is believed to have a detrimental impact on its thermal conductivity. In the higher fired samples, one could imagine the negative effect of increased pumice content on thermal conductivity to be perhaps somehow lessened, and maybe in some cases even compensated for, by increased vitrification. The fact that high firing only appears in some cases and does not seem to be a common practice adopted together with the introduction of the recipe, however, precludes any argumentation for an overall increased thermal conductivity of the new fabric. On the contrary, it seems that the change in ceramic recipe brought changes to

the cooking vessels' heat transfer abilities which were for the worse rather than for the better. The adoption of a novel local fabric is therefore in all probability not related to the performance of the cooking vessels. Rather, it probably best be viewed in the broader context of a far more wide-ranging change in ceramic technology, which is neither restricted to cooking vessels nor to the site of Akrotiri: namely the increasing exploitation of calcareous clays for the production of all types of pottery which is observed throughout the Aegean at this time (P.M. Day pers. comm.).

10.2.3 Phases A and B of the Middle Cycladic period

The petrographic analysis of the cooking ware which dates to the earlier two Middle Cycladic phases revealed a very homogenous picture: there is not much variation in the fabrics of the cooking vessels that could give rise to a discussion of performance differences in the related pottery. The vast majority of cooking ware is made of the local, rather calcareous fabric containing volcanic rock fragments which has been discussed above. Strikingly, and much in contrast to the previous phases attested at the site, virtually no imported cooking vessels were found in contexts belonging to the earlier two Middle Cycladic phases. Only one sample with an off-island origin could be identified. It belongs to a rim, presumably of a pedestalled cooking jug, and its fabric is compatible with Naxian provenance. The fact that this sample was not taken from a complete, securely identifiable shape, together with the observation that it is the only representative of its fabric group⁵⁸, however, rules out a comparison of the imported with the local ware for the early Middle Cycladic periods. When turning to the local cooking vessels, it is found that their fabric remains largely unchanged during Phases A and B of the Middle Cycladic period, the only exception being the two Phase B tripod feet. These are the earliest examples of a shape that becomes very common in the subsequent phases. As they can be regarded as forerunners of the later samples in what concerns both fabric and shape, their discussion is included in the next section which examines the change in manufacturing technology of the locally produced cooking ware around the transition from Middle Cycladic Phase B to C. When looking at the firing temperatures finally, although there

⁵⁸ This sample does not belong to the earlier discussed granitic group which is also believed to derive from Naxos.

is considerable variation within the local samples, there is no clear and unambiguous pattern recognisable, either for different types or over time⁵⁹. The use of one ceramic recipe for the production of virtually all cooking vessels, together with the absence of a clear pattern of variation in firing temperatures, prevents a discussion of performance-related questions for the fabrics of this phase.

10.2.4 Transition to Phase C of the Middle Cycladic period

With the transition to Phase C of the Middle Cycladic period, another drastic change in the manufacturing technology took place at Akrotiri. From Phase C onwards, significant amounts of phyllite temper appear in the local cooking ware fabrics. Apart from the additional phyllitic material, however, the clay paste seems very much the same as the one used in the local production of cooking vessels in the earlier Middle Cycladic phases. Also, and as in the earlier periods, considerable variation in firing temperatures is observed.⁶⁰

When examining the effect of the addition of phyllite temper to an otherwise unchanged clay paste on the performance properties relevant to cooking ware, again, no great differences in strength and toughness are expected. Replacing a part of the volcanic rock inclusions with the more platy phyllite temper could be argued to increase strength and decrease toughness, especially in the high-fired samples. As argued earlier, this appears not to be beneficial for cooking ware pottery. The influence of temper shape on the mechanical properties of the vessels is, however, limited, not only because the ceramics are coarse and heavily tempered, but also since it is only a part of the angular volcanic rock inclusions that is replaced with the more platy phyllite temper⁶¹. Similarly, thermal shock resistance is not expected to differ significantly.

⁵⁹ There is a slight possibility that the open, bowl type vessels are fired to somewhat higher temperatures.

⁶⁰ Unlike in the earlier periods, though, there is a clear pattern recognisable in the firing temperature variations, this will be discussed in detail in the next section.

⁶¹ Even the highly fired local fabric is expected to be able to dissipate energy and exhibit stable fracture, although low toughness has been observed for the high-fired phyllite tempered replica (*cf.* Chapter 8). The reason that higher toughness can be expected in the archaeological samples as compared to the experimental briquettes are as follows: first, the platyness of phyllite temper is less pronounced in the archaeological samples than in the replicas, so that for breakage to occur through the temper material increased amounts of energy would be required, and second, the archaeological fabric contains not only phyllite temper but also angular volcanic rock inclusions.

Concerning heat transfer, phyllite temper - when aligned perpendicular to the heat flow - has been observed to reduce a ceramic's thermal conductivity (Chapter 8). Since phyllite temper replaces part of the volcanic rock inclusions, i.e. pumice (which could be suspected to have a lower thermal conductivity than phyllite) but also lava fragments (which could be suspected to have a higher thermal conductivity than phyllite), it is very difficult to estimate the influence of phyllite tempering on the overall thermal conductivity of the ceramic material. If not worse, however, thermal conductivity of the new fabric was most probably not perceivably better.

It appears that also the second change in the manufacturing technology of cooking ware at Akrotiri, namely the introduction of phyllite tempering, was not connected to a better performance of the resultant cooking vessels. If anything, the addition of phyllite seems to have led to a reduced suitability of the ceramic paste to be used in the production of cooking ware. The causes for the shift in manufacturing technology seem therefore to lie outside a functional realm. It can be argued that there must have been some sort of incentive for the introduction of phyllite tempering: Thera's geology is predominantly volcanic, and, although phyllite outcrops were probably accessible around Mt. Profitis Elias and perhaps at locations in the caldera (*cf.* Chapter 4), this rock type is not found in the immediate vicinity of the site. The change in recipe involved therefore increased efforts on the part of the potters. This results in a behaviour which seems to be contrary to reason: namely the investment of additional effort for the production of what probably was worse quality cooking ware. A hint as to what could have triggered this at first sight irrational adoption of a new tempering practice at Akrotiri, might be provided by the simultaneous appearance of the novel fabric with a new vessel shape, the tripod cooking pot. This typically Cretan shape is found to be a common feature of the Akrotiri cooking ware assemblage from Phase C of the Middle Cycladic period onwards, with the first tripod feet retrieved from Phase B contexts. Not only is the addition of phyllite temper from Phase C onwards observed in the manufacture of all local cooking ware, interestingly, the new ceramic recipe is attested for the first time in the earliest tripod feet. These have been dated to Phase B, when other local cooking vessels were still made in the previous fabric. On Crete, the homeland of the tripod cooking pot, phyllite and schist based fabrics are used widely especially for cooking vessels (see e.g. Haggis and Mook 1993). The use of those fabrics is believed to be part of pottery making traditions since the recipe is

found almost irrespective of provenance (Day *et al.* 1997). It could be suspected therefore, that it is not only a new shape which appears to derive from Crete, but also the practice of phyllite tempering. This implies the real possibility of Cretan potters at Akrotiri during the later part of the Middle Cycladic period and the Late Cycladic⁶². These Cretan potters were presumably also catering for the 'local' Cycladic population, given the observation that it is not only the tripod cooking vessels but also the 'Cycladic' cooking jugs that have been tempered with phyllite.

As has been outlined in Chapter 3, Cretan influence in the Cyclades was on the rise during the Middle Bronze Age. This phenomenon is explained either as the result of strengthening economic ties, or of the exertion of political control by Crete, and is reflected in increased amounts of imported Minoan ware and in the emergence of local 'minoanising' pottery. At Akrotiri, it is in Phase C that Minoan imports are found in greater numbers and that potters are thought to become receptive to Minoan influences. Rather than indicating the establishment of a Minoan colony, it has been proposed that Akrotiri actively chose to become more engaged in south Aegean networks, and that it was the local population's response to novel forms of material culture which led to a gradual cultural colonisation of the community (Knappett and Nikolakopoulou 2008). The observation, however, that in the production of cooking ware not only Cretan shapes but apparently also Cretan technology was adopted, suggests that a theory of mere imitation or emulation by local potters might in fact not suffice to explain the material remains satisfactorily. Rather, one could imagine off-island craftspeople to have assumed a more active role in the implementation of this change in manufacturing practice at Akrotiri. It must be taken into account that cooking ware is found to be especially resilient to technological change (e.g. Ben-Shlomo *et al.* 2008). Indeed, this type of vessel is believed to be closely related to expression of identity and ethnicity, and accordingly is used quite frequently as a cultural tracer in archaeology (e.g. Joyner 2007; Birney 2008). Changes not only in shapes but also in the ceramic recipe of the cooking vessels could therefore imply more far reaching transformations at Akrotiri during the Middle Cycladic period than have sometimes been assumed.

⁶² The presence of Cretan potters has been hypothesised for a contemporary centre in the Cyclades with minoanising traits, Aghia Irini on Kea (Davis and Lewis 1985).

Special mention deserve the *tripod legs* which come along with the new Cretan shape, since they are the part of the vessel which is in direct contact with the heat source and supposedly buried in hot coals during cooking. While the continuous evaporation of water through the walls cools the outer surface and reduce the effective temperature gradients in the main body of a vessel, no such mechanism which would diminish the severity of thermal stresses is expected for the vessels' feet. Taking into account the outcome of the finite element analyses, which indicated that the areas of maximal stress after placing such a vessel on a heat source actually do arise in the feet, one could argue that the requirements in terms of thermal shock resistance were increased for this part of the vessel. It should be borne in mind that the cooking ware in use at the site before the introduction of the tripod cooking pot included many pedestalled vessels. If the thermal shock resistance of body attachments which were placed directly on a heat source was indeed a problem, it was therefore most probably not a new one. The solution (or perhaps better the attempt to a solution), however, might be.

Above, it has been argued that adding phyllite temper to an otherwise unchanged clay paste did not influence the mechanical and thermal properties of the vessels greatly.⁶³ The observation that the addition of phyllite temper did not help the performance of the cooking ware produced at Akrotiri, however, does not negate the possibility that the addition of this type of temper improved the performance of cooking ware elsewhere. One could imagine that in Crete, where the vessels and the tempering technique are believed to originate, phyllite tempering actually did result in better suited cooking ware. Especially for vessels fired to somewhat lower firing temperature than those found at Akrotiri, where frictional pull-out of platy particles can contribute to the overall toughness, one could well expect that phyllite tempering increased the resistance of the vessels (and especially of their feet) to thermal stresses. Without examining contemporary Cretan cooking ware, however, these considerations must remain speculation.

⁶³ It should be noted that, unlike in the body sherds, the phyllite particles are not aligned in the tripod feet. This however neither invalidates nor greatly changes the argument.

10.2.5 Phase C of the Middle Cycladic period and Late Cycladic IA

All local cooking vessels of the latest periods are produced with the phyllite tempered recipe, which has been discussed in the previous section. In addition to local cooking ware, imports were attested for two shapes, the tripod cooking vessel and the cooking jug (*cf.* Figure 3.2). The imported vessels fall in two different fabric groups which are, however, both thought to originate from Naxos. One of these is the granitic fabric group which is so common in the earliest phases at the site. In the latest phases, a tripod vessel and a few cooking jugs were found to belong to this group. The other non-local fabric, characterised by mica schist inclusions, has only been detected in samples of tripod cooking pots. As has been discussed in detail above, the tripod cooking pot appears to be an originally Cretan shape. None of the non-local tripod cooking pots found at Akrotiri, however, appears to have been imported from Crete.

The presence of non-local cooking vessels in the Late Bronze Age deposits had been recognised early on, and a Naxian origin was suspected for some tripod cooking vessels, based on the similarity of their clays' appearance with Naxian pottery (Doulas 1983, 110). The present petrographic analysis confirmed this assumption and revealed that imported cooking vessels of (at least) two different recipes, both of them presumably Naxian, were in use at Akrotiri. Assessing performance properties is not so straightforward for cooking ware of the latest periods, since - apart from variation in shape - also many material parameters vary. For example, two different fabrics are imported, and the local material has been fired to a range of temperatures. The subsequent discussion of the late periods is therefore split in two parts: In a first, the different fabrics will be compared, concentrating on the tripod cooking pot, which is found in all three fabrics, and - if locally manufactured - is frequently high-fired (*cf.* Appendix IV). The second part will discuss the variations in firing temperatures which are observed within the local ware.

Tripod cooking pots: locally produced ware vs. imports

The two imported fabrics and the differences between them will be discussed before contrasting off-island with local manufacture. Since both Naxian fabrics contain coarse angular inclusions and are not very high-fired, the only performance property which could be argued to differ between them is thermal conductivity. In-line with the argumentation made earlier, the granitic fabric could be suspected to better conduct heat than the mica schist fabric. This is due to the nature of the aplastic inclusions: while granitic inclusions are known to have a beneficial effect on the overall thermal conductivity, mica-rich rock fragments are expected to influence this physical property negatively, especially when the mica sheets are aligned perpendicular to the heat flow. When subsequently comparing the low-fired imported fabrics with the rather high-fired local one, matters become slightly more complex. Strength could be argued to be increased in the case of the local ware, due to high firing and the replacement of some of the angular inclusions with more platy phyllite temper. Toughness, on the other hand, might perhaps be expected to be higher in the imported fabrics. However, it must be kept in mind that the intrinsic fracture energy is probably higher in the local fabric due to high firing and increased vitrification. Furthermore, because of the high amount of coarse (angular and more platy) inclusions, also the dissipation part is probably still considerable and toughness appears therefore sufficient. The argument is more or less the same for thermal shock resistance, again this is expected to be adequate for all fabrics (*cf.* also Chapter 9). Thermal conductivity, finally, is very difficult to assess, as there are two main differences between the two fabric groups which each influence this property in contrasting ways: while the nature of aplastic inclusions advantages the imported granitic fabric, the trend to higher firing temperatures in the local ware favours those vessels. At least for the moment therefore, no conclusive argument for or against a better suitability of the imported ware can be made. While sufficient thermal shock resistance was most probably ensured in all cases and differences in toughness and strength were presumably not all that relevant, for thermal conductivity, measurements on archaeological samples are required to get a clearer picture. The notion that Naxian mica fabrics were imported as they could 'better resist heat' (Doumas 1983, 110) could therefore neither be refuted nor confirmed by the present study. The available data, however, appears to

advocate against further entertaining of the possibility that off-island cooking vessels were imported due to better performance.

Differences within locally manufactured cooking vessels

In the latest period covered by this study, Late Cycladic IA, the two main types of vessels which were apparently used for cooking at Akrotiri, are the tripod cooking pot and the funnel-mouthed jar (Figure 3.2). In addition to those, cooking jugs continued to be used, but, as only one cooking jug from a secure late Cycladic context has been sampled, the following discussion is restricted to the funnel-mouthed jar and the tripod cooking pot.

Both of those vessel types are made in the same fabric, a coarse volcanic base clay tempered with phyllite, which has been discussed at length in earlier sections. The two vessel types have, however, been fired to quite different temperature ranges: a trend towards significantly higher firing temperatures is observed in the tripod cooking vessels. As the different firing strategies result in clear differences in the ceramics' microstructure, they are expected to influence the mechanical and thermal properties of the vessels. Again, for the higher fired samples, an increase in strength could be expected, while - as argued above - the simultaneous decrease in toughness in those samples was probably not too severe, and thermal shock resistance is expected to have been easily sufficient in both cases. An increase in thermal conductivity is, however, expected for the tripod cooking pot when compared to the funnel-mouthed jar.

In order to find a possible explanation for the different ranges of firing temperatures observed in the two vessel types, it appears therefore most promising to concentrate on the resulting differences in thermal conductivities. As has been noted, thermal conductivity not only influences the overall suitability of a vessel to be used for cooking food, it also directs the relative suitability of a material to be used for different *modes* of cooking. When looking at the two vessels, it is apparent that their shape is quite different, with the funnel-mouthed jar having a more constrained orifice. It has been argued for ceramic cooking ware (in a quite different regional and temporal

context though) that more closed pots with constricted openings would have been preferred for simmering food over a long time, while more open vessels were preferentially used for high temperature boiling activities (Eerkens 2005). Transferring this hypothesis to the cooking vessels at Akrotiri, different cooking modes could be imagined for the tripod cooking pot and the funnel-mouthed jar: high temperature boiling in the former and long-time simmering in the latter. According to this, a high thermal conductivity would be ideal for the tripod cooking pot, while the funnel-mouthed jar should preferably exhibit a relatively low thermal conductivity. Indeed high firing temperatures were used in the manufacture of the tripod cooking pot and resulted in a higher thermal conductivity which is beneficial for boiling activities, while the lower firing temperatures in the funnel-mouthed jars led to a lower thermal conductivity better suited for simmering food. One could therefore contemplate that the two different vessel types served - or were intended to serve - different (sub)-functions, in the sense that, even though they were both used to prepare food, they might have been designed for different ways of doing so.

As has been noted, the differences in vitrification which are observed between the two vessel types do not only influence thermal conductivity but also strength, toughness and thermal shock resistance. These properties, however, are not expected to differ decisively between the different fabrics. In any case, since they are related to the overall suitability of a vessel to be used in cooking, differences between them cannot provide criteria for selection between the two vessel types, when we assume them to be used for different modes of cooking.

10.2.6 Summary of the Akrotiri case study

When looking at the variation in the cooking ware within certain periods, on the other hand, two cases were identified where these might relate to differences in performance of the corresponding fabrics. The first is the presence of large amounts of Naxian imports during the early periods. These can be argued to have performed 'better' than cooking ware that was available locally at the time, and their importation might therefore be related to consumption preferences based on quality-related criteria. The second is the presence of differing firing regimes which are observed in two

different vessel types of the Late Bronze Age, which can be hypothesised to indicate the optimisation or adaptation of the available recipe for the respective uses to which the two vessels are believed to have been put.

The two changes that occur in the local manufacturing technology of Bronze Age cooking ware of Akrotiri over time apparently did not result in an improved performance of the resulting vessels. In both cases, it can be argued that the change in ceramic recipe resulted in cooking pots that either performed worse than their predecessors, or whose performance at best remained unchanged when compared to the previous generation. It appears therefore ill-advised to argue for increased suitability as a driving force in the technological development of Akrotiri's cooking ware pottery as the changes in manufacturing practices were apparently unrelated to improving the vessels' performance, and what the material reflects is surely not a development towards an 'ideal' cooking pot. Rather than being connected to the performance of the vessels, technological change appears to have been triggered by other incentives in both cases. The first change in paste recipe falls together with a more general adoption of more calcareous clays in the broader geographical region, which is not restricted to cooking ware. The ultimate motivations for this change remain however unclear. Explanations which have been put forward to account for use of more calcareous clays to date (e.g. Noll 1878; 1989; Aloupi and Maniatis 1990) include aesthetic reasons (provision of a pale background for painted decoration) and technological ones (easier achievement of constant quality due to the development of a stable microstructure which remains unchanged over a broad range of firing temperature). The second change in manufacturing procedures, the introduction of phyllite tempering, falls in a time of increasing Cretan influence at the site, and the adoption of a novel tempering practice alongside with a new Cretan vessel shape around the transition of Phase B to Phase C of the Middle Cycladic period, might well be connected to this phenomenon. The explanation that has tentatively been put forward here, namely that an off-island pottery tradition was introduced to Thera where it was possibly carried out by off-island craftspeople, could account for the - at a first sight - 'irrational' behaviour of the potters, namely of investing extra effort in the production of probably worse quality cooking ware.

Although for the present case study, it is only in a few cases that increased performance or suitability of the cooking vessels can be suspected to be responsible for consumption patterns which are observed in the archaeological record, this does not negate the importance of an assessment of material properties linked to performance when studying functional pottery assemblages. On the contrary, in cases where such functional ceramics do not follow the pattern laid out by the optimisation of properties related to their function, further investigations are decidedly worthwhile, as other reasons must then have triggered the change. These may be related to optimisation occurring on another stage of a vessel life-cycle, such as for example a decreased production time, or lie in a realm beyond technological (or other) improvement. At any rate, a quest into the underlying reasons which might have prompted technological change in these cases, promises to be particularly rewarding.

10.3 Methodology

The following section discusses the overall approach to assess the performance of clay ceramics that has been followed in this study. The individual techniques that have been employed to analyse the archaeological sherds and to test the experimental briquettes have been discussed and assessed in the relevant chapters. Their potential, suitability and limitations in relation to the study of ancient ceramic material will therefore not be reiterated here, rather their contribution to the overall methodology is assessed.

The present study was in the first instance concerned with an assessment of the ceramic fabrics, i.e. the ceramic material, on the performance properties. Shape has been considered at a later stage using computer modelling, while surface treatments were not included in the present study⁶⁴. The following is directed primarily at assessing the influence of ceramic *material* on the performance of clay pottery and is

⁶⁴ This is mainly due to the fact that surface treatments are not expected to influence mechanical and thermal material properties which were assessed in the present study greatly. They have, however, a significant impact on the permeability of a vessel. Accordingly, they have been observed to influence what was coined the *heating effectiveness* of a vessel (Schiffer 1990). As heating effectiveness is not only related to the permeability of a vessel but also to the thermal conductivity of the ceramic material, however, more systematic studies which correlate variations in microstructure and surface treatment with differences in heating effectiveness are required to assess the relative importance of the two parameters for a cooking vessels performance.

not applicable directly to the assessment of other parameters, such as surface treatments.

When looking at the suitability of ceramic materials to be used in the manufacture of vessels with specific functions, previous studies have determined performance characteristics either on replicates or on archaeological sherds. Due to the impact of use, discard and burial as well as for reasons of standardisation, the mechanical and thermal properties were assessed on experimental briquettes. This resulted in an experimental programme that can be divided into three tasks. These are: first, the characterisation of the archaeological material, followed by the manufacture of experimental briquettes and the determination of the performance properties on these briquettes, and finally the interpretation of the data, i.e. the transfer of the outcome of material tests on the laboratory specimens to the archaeological material. The following brief assessment of the methodology will roughly follow this sequence.

10.3.1 From archaeology to experiments: characterisation of the archaeological material and design of experimental briquettes

Questions which relate to performance properties and the suitability of functional ceramics to be used for their assumed purpose usually arise from changes and variations that are observed in manufacturing technology. If such patterns pertaining to provenance, raw material selection and manufacturing techniques have been recognised in the fabrics of an assemblage, or are suspected after a macroscopic examination of the material, as a first step, they need to be confirmed. The method of choice to characterise the archaeological material and to classify the pottery into compositional groups which relate to different production technologies and provenance in coarse ceramics is *thin section petrography*. The identification of particularly the nature of coarse inclusions allows in many cases not only distinction of local and imported pottery but also the recognition of changes in pottery traditions over time. Furthermore, by uncovering orientation of inclusions and pores, it reveals characteristics which might not be immediately relevant for tackling questions of provenance or raw material selection, but are of paramount importance in view of the ultimate aim of such a study, the assessment of the ceramic's performance. Additionally, the

technique can provide rough estimates for ancient firing temperatures and a ceramic's vitrification state. The data obtained by thin section petrography can be refined further by applying additional analytical methods, such as XRD, SEM or FT-IR to selected samples, as these potentially provide further information on raw materials and, importantly, assist in the determination of firing temperature ranges. It should be carefully considered, however, whether the potential supplementary information on the archaeological samples that these provide justifies additional efforts and material. For the subsequent assessment of performance properties, it is not the exact firing temperatures that are important, but the microstructure of a ceramic's groundmass and its degree of vitrification. This usually can be assessed to an adequate extent, by examining the groundmass's optical activity in thin section. The identification of clay minerals and high temperature phases, besides their use for firing temperature estimations, appears, at least for cooking ware, not to contribute much to an assessment of performance properties. There are exceptions to this, however. High temperature phases have been postulated to be the underlying reason for technological choices in the manufacture of metallurgical ceramics (Martinón-Torres *et al.* 2006). At least in the case of archaeological cooking ware it would appear that study by thin section petrography will, in the first instance, deliver results which are sufficient for a subsequent assessment of the fabrics' performance. This is because the main factors which influence the performance properties of cooking ware ceramics, i.e. the nature, shape and amount of coarse temper material as well as the microstructure of the groundmass, can be determined with the method. Nevertheless, it might be advisable to apply additional analytical techniques to a few selected samples, to solve issues which cannot be addressed by thin section petrography, or to confirm petrographic results. There appears, however, that there is little to be gained by screening an entire assemblage.

Once the variations and changes in fabric are identified and characterised, the key parameters which may influence performance properties can be identified, in order subsequently to assess their impact on a ceramic's performance in relevant experimental briquettes. A general understanding of the basic principles of mechanical and thermal properties is advisable when designing an experimental programme, as it aids to single out potentially critical parameters and determine the focus of the experimental part.

10.3.2 Determination of the influence of manufacturing parameters on performance properties: tests on experimental briquettes and finite element methods

In a second step, the influence of the manufacturing parameters of interest for the relevant performance characteristics of the functional type under study can be assessed on experimental briquettes. This step is not always required, since in cases where the parameters of interest have been assessed previously on relevant model materials, the results of those studies can be used as a basis for comparison. In this regard, it is hoped that the results that have been obtained on experimental briquettes in the course of the present study, will be of assistance for future investigations related to the performance of clay ceramics. In cases where no literature is available either because manufacturing parameters have been identified that have not been studied before, or because previously unassessed material properties are deemed to be of interest, additional experiments on model materials are called for.

For the manufacture of experimental briquettes, it is necessary to work under controlled conditions. In particular the grain size of the clay fraction needs to be controlled and standardised. Once the ceramic briquettes have been manufactured, they can be subjected to material tests. In order to enable meaningful interpretation of the outcome of material tests, it is imperative to examine the microstructure of the tested briquettes. This includes the determination of structural features which are recognisable under the polarising microscope and can be determined in thin sections, such as porosity (size, amount and orientation of pores) as well as those which become apparent only under the electron microscope, mainly the vitrification of the ceramic groundmass.

The material properties to be determined on experimental briquettes depend critically on the demands placed on the archaeological material investigated, which, in turn, depend on its (assumed) function. So properties relevant to transport jars and cooking vessels will be different, or the same properties have a different weight, as in the case of metallurgical ceramics and cooking ware.

When examining coarse cooking ware pottery, based on the results of the present study, it appears that the property which is of main interest is thermal conductivity.

This might be surprising as much of the previous literature on clay cooking ware focused on thermal shock resistance. It would appear though, that this performance property is perhaps less relevant than has sometime been assumed. At least for the variations observed in the invariable coarse and heavily tempered cooking ware fabrics of the present case study, and for the temperature range cooking ware is expected to be exposed to, all archaeological fabrics are thought to be clearly adequate for exposure to thermal stresses in cooking.

Once the material properties are defined, computer modelling can be used to assess, for example, the influence of shape on the mechanical and thermal performance of a vessel. Previous material tests are indispensable for computational analyses as they not only deliver the required material input, but also provide the parameters required to assess the impact of the calculated stresses on the objects studied. Computer modelling using finite element analyses can therefore not be regarded as a stand-alone technique. Rather, it is a logical addition to the suite of techniques employed to investigate the performance of archaeological pottery, as it provides further insights, especially related to shape parameters which cannot be obtained by material tests alone.

10.3.3 Data interpretation and evaluation

The outcome of the material tests on the experimental briquettes, together with literature sources and potential computer modelling, provide the baseline against which the variability and the changes in fabrics observed in an archaeological assemblage can be discussed. Based on the petrographic description, the suitability of the ceramic recipe(s) examined can be assessed. When doing so, it seems advisable to exercise caution for various reasons. It should be considered, for example, whether differences that have been assessed in material properties could potentially have been perceived by consumers. It is also important to be aware that - as highlighted in the present study - the various mechanical and thermal performance characteristics cannot be considered independent properties. Since they all are dependent on the microstructure of a material, the improvement of one property usually occurs at the expense of another. The addition of temper to a clay paste for example, which increases

the ability of a material to dissipate energy and results in an increase in toughness, simultaneously causes a decrease in strength, as the temper particles introduce flaws in the material. Thermal shock resistance, since it is dependent on a material's ability to withstand crack initiation and propagation, is linked tightly to strength and toughness. Because the performance characteristics examined in this study are not independent variables which could be freely manipulated, changes that are observed in manufacturing procedures must always be viewed considering this complex interplay, i.e. by carefully evaluating the effects of technological choices on an array of potentially significant material properties, rather than basing a discussion on an isolated variable. Furthermore the performance of a ceramic material *during* manufacture (e.g. shrinkage or workability) is of importance and can be a decisive factor for the selection of particular materials or practices. Also the contexts of ceramic production must be taken into account, in order to be able to make valid suggestions on the underlying reasons and mechanisms when interpreting differences in manufacturing techniques observed in an archaeological case study.

10.4 Outlook for further research

The final part of this chapter discusses main points which have been identified to be of further interest. Suggestions range from possible future supplementary work on the present case study to issues related to the advancement of research on performance properties of ancient ceramic materials more generally. This section is structured so as to proceed from more specific matters pertaining to the Akrotiri cooking ware assemblage to issues of more general interest for functional clay ceramics, although there is overlap between these.

First, given their ubiquity in the local cooking ware pottery, the influence of pumice inclusions on thermal (and mechanical) properties should be studied more systematically. Of main interest here is their effect on the thermal conductivity of the ceramics. Although such an undertaking requires the manufacture of additional replica briquettes, the results of material tests on those briquettes can easily be integrated into the existent dataset. So can, for example, the same reference measurements be used for such complementary samples. An assessment of the impact of pumice inclusions

on performance characteristics is therefore not so much a novel task, but rather an extension of the study which has been presented here.

Furthermore, thermal conductivity measurements on various relevant archaeological samples of the Akrotiri cooking ware assemblage are desirable, not so much to confirm the suspected differences as to determine their magnitude. This will provide the parameters required to quantify the effect of the various ceramic recipes on cooking processes, e.g. by calculating the theoretical time which is required to heat up contents in vessels made of those materials (*cf.* Appendix VI). Suitable sherds will need to be selected, as the specimens need to fulfil particular geometrical requirements for the set-up in use for the determination of thermal conductivities. Ideally they will be obtained from bases or flat hearths. Should it not be possible to find samples from which large enough disks can be cut, the current set-up will need to be slightly modified. This should be restricted, however, to the fabrication and calibration of a smaller brass disk to be used as a heat conductor.

Also, given the function of the vessels, organic residue analyses should be carried out on the samples, in order to provide more information on what was actually cooked in them. Such a programme has now been commenced (Roumpou *et al.* 2007). It will be interesting to correlate possible patterns with the difference in the performance of the vessels as revealed in the present study. Of particular interest here is the outcome of organic residue analyses on the Late Bronze Age vessels for which different cooking methods have been suggested.

Concerning the assessment of the manufacturing parameters, a priority seems to be the investigation of *calcite tempering* on the performance of cooking vessels. If calcite temper is observed in archaeological cooking ware, it is frequently explained by the thermal shock resistance it is supposed to impart on the vessels. As the available literature offers much speculation with only little supporting experimentation, this issue seems in dire need of clarification. Such a study requires the manufacture of additional briquettes, but could be carried out with reasonable effort, as it can build up on the results obtained in the present study.

Apart from the assessment of calcite tempering, there appears little sense in a general screening of the effects of all possible combinations of firing and tempering parameters detached from the enquiries of a particular study, since considerable time and effort is involved in the manufacture of experimental briquettes. Future testing is therefore likely to be designed so as to address specific issues that arise with the examination of a particular assemblage.

Turning from the assessment of the parameters which influence performance to the physical properties, it appears that for a better understanding of the reaction of ancient pottery to exposure to heat, additional material parameters need to be investigated. Important here are *heat capacity* and *thermal expansion coefficients*, both of which remain to be studied in a systematical manner for archaeological ceramics. Since these parameters can be determined on the briquettes which have been manufactured for the present study (and for which compositional and microstructural data are available), an assessment of the influence of various parameters on these additional thermal properties could be carried out with little additional effort.

A better understanding of thermal expansion coefficients and heat conductivity will also allow the refinement of future *computer modelling*; especially the thermal expansion coefficient influences greatly the magnitude of thermal strains. Thermal simulations by FEM have been shown to have a great potential to elucidate conditions of and response to thermal stress and thermal shock in ancient ceramics, problems which to date remain to be resolved satisfactorily. Due to methodological problems with thermal shock resistance measurements on archaeological ceramics, which are mainly connected to the fact that thermal shock resistance is not a material property, but a complex function of material properties and shock conditions, the determination of thermal shock resistance whether on model materials or on archaeological samples appears to be only of very limited use (*cf.* Chapter 8). It is proposed here, that a more promising route towards an assessment of the performance of ceramic materials and objects that were routinely exposed to heat might lie in modelling the magnitude and distribution of thermal stresses which develop in an object due to exposure to heat. Future computational analyses using FEM should be extended to three-dimensional models and ideally should employ experimentally determined values for heat capacity and thermal expansion factors rather than global estimates. Also

the modeling of heat effectiveness by the finite difference approach seems a promising avenue and is planned to be expanded to two and three-dimensional models.

Furthermore, the role of *thermal fatigue* is not well understood and needs further investigation, also on replica vessels. Prior to such replication experiments, however, computational analyses should be carried out. In this way different conditions can be simulated and we can identify and investigate those which give rise to stresses which are considerable but still subcritical for the vessel type. The cumulative effect of such subcritical stresses can then be examined on replica vessels, by repeated exposure to the conditions previously identified through computer modelling.

The present study has suggested that future performance assessments of cooking ware assemblages should take into account *thermal conductivity*, a material property which so far has largely been neglected in functional studies of cooking ware. Also, while the testing of strength and toughness on archaeological sherds is problematic, thermal conductivity measurements on archaeological material can be justified. This is because many of the alterations which are likely to occur during use, discard and burial of clay ceramics are less likely to influence their thermal conductivity than mechanical properties. Microcracking, for example, is detrimental for a material's strength, but does not seem greatly to influence thermal conductivity. Due to demands on material and efforts involved in sample preparation, however, measurements need to be restricted to selected archaeological samples, and should only be considered after an assemblage has been investigated and probable patterns and tendencies have been identified, in order to address specific issues that have been raised.

Finally, it appears worthwhile to apply the methodology presented here to another case study. Of interest would for example be to investigate a late Roman cooking ware assemblage, pottery which is - unlike the cooking vessels of the present case study - commonly rather high-fired and of a finer fabric (Ikaheimo 2005).

10.5 Summary

The present study makes a significant contribution to our understanding of how and why potters' choices influence the physical properties of ceramic materials. By allowing statements regarding performance and suitability of clay ceramics, this provides a baseline against which technological choices in archaeological ceramics can be discussed.

A methodology for assessing the performance characteristics of archaeological ceramics has been developed and the influence of various parameters on a ceramic's performance has been assessed. Beyond their relevance to the archaeological case study, the results obtained on experimental briquettes are applicable to clay ceramics more generally. The investigations revealed for example that tempering with platy phyllite results in a less pronounced reduction of fracture strength than adding more angular granite temper to a ceramic paste. On the other hand, phyllite temper was found to lead to reduced thermal conductivity and toughness when compared to granite temper. Considering thermal shock resistance, the complexity of the parameter has been emphasised and it was concluded that the best approach to warrant high thermal shock resistance for coarse ceramics lies in the minimisation of crack propagation, achievable by increasing the toughness of a material. A way to map the distribution and the development of thermal stresses using computer modelling, of particular importance when considering thermal shock resistance, has been presented.

Turning to the case study, it has been suggested that some of the variation which is observed in the Akrotiri cooking ware assemblage was possibly related to the performance of the vessels. The early trade of cooking vessel from Naxos can be seen in the light of improved performance of those granitic tempered vessels over the locally produced cooking ware. In the latest period covered by the study, differing firing strategies, which are observed in two different vessel shapes, might be related to different cooking methods carried out in those vessels. The introduction of phyllite temper in the Middle Cycladic Phase C, on the other hand, cannot be related to an increased performance and should probably be viewed in the context of an introduction of a 'foreign' pottery tradition. This shift in manufacturing strategies strongly suggests the presence of Cretan potters at Akrotiri during these periods, and indicates a more

close connection of the site with Crete during this time as has sometimes been assumed.

It is hoped that the present study, apart from offering insights into the particular case study, will contribute also more broadly to the study of archaeological ceramics by providing a greater understanding of some of the factors underlying pottery performance and ancient ceramic design, and will stimulate further research in the field.