The influence of microstructure and texture on the mechanical properties of rock tempered archaeological ceramics

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Abstract

The influence of tempering and firing practices on the fracture strength and fracture energy of traditional pottery is presented, focusing on the mechanical behaviour of low-calcareous ceramics and how it compares to that of comparable calcareous ceramics. Material tests on experimental briquettes show that the measured increase in fracture strength upon firing is linked to the degree of vitrification in the ceramic matrix and to the development of porosity. The addition of aplastic inclusions reduces fracture strength, with platy temper affecting strength levels to a lesser degree. In earthenware, high fracture energy can normally be obtained by adding high amounts of aplastic inclusions as temper. While the fracture energy of granite-tempered ceramics remains approximately constant at high firing temperatures, for phyllite-tempered materials maximum values are found at intermediate temperatures. Regarding archaeological ceramics, the data presented here are anticipated to contribute to our understanding of technological choices in their manufacture.
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Keywords: Mechanical properties; Strength; Fracture energy; Inclusions; Archaeological ceramics

1. Introduction

The study of the mechanical properties of traditional ceramics has received increasing attention in recent years. The influence of manufacturing parameters such as firing temperature or tempering practices on the mechanical properties of earthenware has been studied with the objective, on the one hand, of improving contemporary ceramic materials, mainly in the brick and tile industry[1–3] and on the other, to assess technological choices in archaeological ceramics.[4] As far as archaeological ceramics are concerned, the need to place such assessments into context and to take into account the multitude of other factors that influence technological choice has been emphasised in various reports (e.g. [5]; epilogue of Ref. [6]). An understanding of mechanical performance, while not per se explaining technological variation in the past, provides nevertheless a valuable baseline for the consideration of the overall reasons for technological choices observed in archaeological ceramics.

Pottery is exposed to various mechanical stresses during manufacture and use-life and is normally expected to remain usable without structural damage or loss of functionality. The nature and the magnitude of these external stresses depend to a large extent on the actual use of the vessel. Regarding archaeological ceramics, vessels which are expected to withstand mechanical stresses include amphorae, which need to be able to bear the load of overlying vessel layers when stacked during transportation, while all vessels used as a container should withstand the pressure exerted by their contents without fracture. For such sustained stresses it is the fracture strength as well as fracture energy of the material which determine the vessel's survival.

Fracture strength and fracture energy of traditional as well as archaeological ceramics are known to be dependent on variables such as the amount and type of temper and firing temperature as has been clearly demonstrated in the review of Tite et al.[4] A series of studies (e.g. [6–9]) have contributed to our knowledge of the effect of technological choices on the performance of archaeological ceramics, especially regarding the influence

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of the volume fraction and grain size of temper on mechanical properties. In addition, the influence of temper type and shape have been demonstrated to be of importance in the performance of clay based ceramics.[8,10–12] The overall picture is, however, complicated since the microstructure of the ceramic matrix itself also contributes to overall mechanical performance. Calcium-rich clays are known to undergo a different microstructural development during firing than calcium deficient clays[13,14] and different mechanical behaviour is therefore expected in these two cases. Both calcareous and low-calcareous clays have been used in the past. In many instances calcareous and low-calcareous clays were used for manufacturing vessel types that differed in intended function. Differentiation in the use of clays according to their calcium content is also documented ethnographically: so, for example, calcareous clays are used widely in the production of water jars, while cooking vessels are often preferentially made of low-calcareous clays.[15] Beyond synchronic variation, there are also diachronic shifts in clay preferences, such as the widespread change to calcareous clays at the start of the Middle Bronze Age in the Aegean, which largely replaced earlier low-calcareous materials.

It is clear, therefore, that a comprehensive assessment of the mechanical performance of tempered clay-based ceramics which takes into account the influence of *clay-type* – i.e. low-calcareous vs. calcareous base clays – has much to contribute to discussions of material affordance and suitability for archaeological and traditional ceramics. It is with this in mind that a range of briquettes was manufactured from both a low-calcareous and a calcareous base clay to be tested for their mechanical properties. Granite and phyllite, which are encountered frequently in Aegean Bronze Age ceramics, were chosen as temper materials. Discussion in the present article, while focusing on the mechanical behaviour of the low-calcareous clay, also elucidates how it compares to comparative calcareous ceramics, which have been presented elsewhere.[6,12] The influence of manufacturing parameters on fracture strength and fracture energy of traditional ceramics is discussed based on the microstructural and textural changes they induce in the ceramic material. Besides furthering our understanding of the mechanical behaviour of traditional clay-based ceramics, it is anticipated that this work, along with the existing literature, will provide a baseline for the discussion of the relationships connecting manufacture, function and affordances of archaeological ceramics.

2. Experimental procedure

In order to investigate the influence of tempering on the mechanical properties of clay-based ceramics, a series of experimental briquettes was manufactured, assessing the influence of amount and type of temper on their mechanical properties over a range of firing temperatures.

2.1. Materials and processing

Test specimens were fabricated with a low-calcareous (<0.5% CaO) clay from Kalami (Crete, Greece). This clay has been used in a previous study of thermal properties and its chemical and
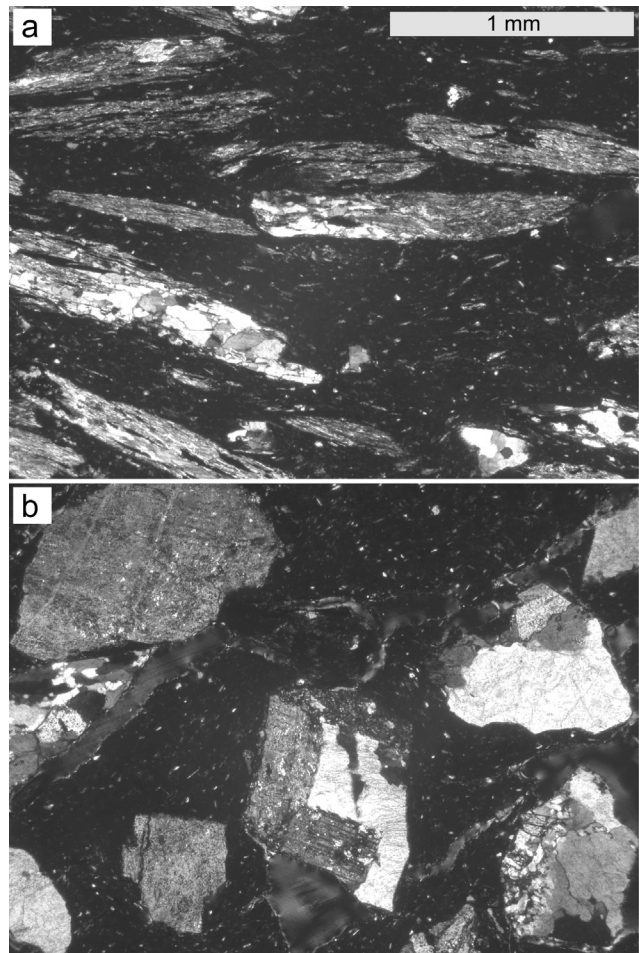

Fig. 1. Thin section micrographs of (a) phyllite and (b) granite temper. Crossed polars, 50×.

mineralogical composition is described elsewhere.[16] The calcareous clay used in the comparative experiments was obtained from Pikermi (Attica, Greece) and contains c. 14% CaO.[12] A fraction with a particle size of <30 μm was separated from the raw clay and mixed with angular granite grains from the island of Naxos (Greece) and platy phyllite from the Northeast Peloponnese (Greece), respectively. Both materials were crushed and sieved to pass through a 1 mm mesh size, discarding the fraction which would pass through a 0.5 mm mesh size (in the case of the platy phyllite, the aspect ratio of the temper particles was approximately 1:5–1:10).

Phyllites are fine-grained metamorphic rocks derived from argillaceous sedimentary rocks. They have well developed cleavage surfaces, due to the parallel alignment of platy minerals, usually micas. X-ray diffraction measurements using a Siemens D500 diffractometer with Cu-K$_\alpha$ source confirmed quartz, muscovite, chlorite and traces of hematite in the sample taken and used as temper material. The phyllitic temper grains are dominated by layered micas, with some more quartz rich grains present as well (Fig. 1a).

Granite is a coarser grained, igneous rock composed principally of quartz and feldspars. Weathered granitic rock fragments were collected at an exposed igneous granodiorite–granite

intrusion in the west of Naxos, inhomogeneous on an out-crop scale and associated with secondary chloritisation.[17] X-ray diffraction analysis confirmed the presence of quartz, feldspars (albite and orthoclase) and chlorite in the sample used for tempering. The granitic temper particles consist predominantly of granite clasts, feldspar grains (sometimes heavily altered), quartz grains and quartzites (Fig. 1b), but also contain minor amounts of biotite, sphene and epidote group minerals as identified in thin section.

Clay, water and tempering material were mixed to form ceramic briquettes with two different amounts of temper material, in addition to untempered reference briquettes. Temper was added as 10% and 40% by dry weight. The briquettes were formed using a mould (c. 120 mm × 70 mm × 10 mm) under uniaxial pressure (c. 0.02 MPa). For the preparation of the phyllite-tempered briquettes, the paste mixture was repeatedly folded and flattened, in order to obtain a preferred orientation of the platy phyllite particles parallel to the largest surface of the briquettes, imitating common archaeological materials. The determination of the mechanical properties of the phyllite-tempered materials was performed perpendicular to the alignment axis of the inclusions. The briquettes were dried for over ten days at ambient temperature and humidity, covered by plates made of plaster of Paris to ensure homogenous drying and avoid warping.

Briquettes of each composition were fired at 550 °C, 850 °C and 1050 °C, temperatures which correspond to different microstructures of the ceramic matrix material ('vitrification'). Firing took place with a heating rate of 200 °C/h and a soaking time of 1 h in air.

After firing, the large surfaces of the fired briquettes were ground parallel and cut into test bars of varying size about 10 mm × 10 mm × 70 mm for transverse rupture tests.

2.2. Porosity

Total, open and closed porosity were estimated for all experimental materials by water immersion according to standard methods[18] on pieces of approximately 25 mm × 10 mm × 10 mm. True density, required for the determination of total porosity, was approximated for the raw materials as the sum of the values of the constituent mineral phases multiplied by their estimated volume fractions, calculated from the weight fractions as assessed by XRD, and amounted to 2.77 ± 0.05 g/ml for the Kalami clay and 2.68 ± 0.05 g/ml for the Pikermi clay as reported elsewhere.[16]

2.3. Mechanical properties

2.3.1. Fracture strength

The transverse rupture strength (TRS) was determined by standard methods[19] from three-point bending tests on bars of approximate size 10 mm × 10 mm × 70 mm. Measurements were carried out on an INSTRON 1195 universal testing machine, at a constant crosshead speed of 109 μm/min. The load as a function of displacement was recorded for every specimen. For every kind of material (corresponding to one set of

manufacturing parameters) TRS was determined by taking the mean of five measurements. Since ceramics always contain a multitude of microstructural imperfections that can act as crack initiators (e.g. inclusions, pores, weak interfaces, microcracks), their strength is not an intrinsic material property but is strongly dependent on those pre-existent flaws, on their distribution and concentration. After final fracture, the fracture area was examined visually with the aid of a stereo microscope. TRS data from bars with clearly identifiable macroscopic flaws in the fracture surface were not included in the determination of the mean strength.

2.3.2. Fracture energy

Fracture energy was determined from four-point bending tests on pre-notched bars of approximate size 10 mm × 10 mm × 70 mm, with a notch depth of 1 ± 0.1 mm. The notch was machined using a 0.15 mm thick diamond wafering blade. The crosshead speed was 54 μm/min. For every kind of material three bars were tested. As with strength tests, load–displacement curves were recorded for every specimen. The results from the few test bars where breakage did not originate from the notch but from pre-existing macroscopic flaws were not included in the determination of the mean values.

For truly brittle materials with unstable crack propagation, fracture energy is determined by the toughness or intrinsic fracture energy G_{Ic}, which can be obtained from K_{Ic} and Young's modulus.[7(Eqs.(4),(5))] The effective fracture toughness K_{Iceff} was calculated at the point of fracture (maximum load) using the analysis of Stawley,[20] correcting for finite notch width,[7(Eqs.(1),(2))] and used to estimate the effective intrinsic fracture energy G_{Iceff} as described in the literature. The expressions employed assume that the size of any plastic zone near the tip of the crack is sufficiently small to be negligible, a condition which is usually fulfilled for these materials.[21(p44)]

In cases where specimens exhibited stable crack propagation during fracture, the effective energy dissipation G_{teff} was also estimated so as to be able to compare the effect of the different kinds and amounts of temper on crack propagation. G_{teff} was obtained by integrating the area under the stable part of the curve.[7] Only the portion of the curve after initial fracture was considered, in order to include only the contributions of the post-fracture mechanisms.

2.3.3. Young's modulus

The Young's modulus (E) of each material, required for the calculation of G_{Ic}, was obtained by determining $E_{bending}$[6] from the bending test curves, corrected for the compliance of the machine, and calibrated against a bar of known E, of identical dimensions to the test bars loaded in bending.

3. Results and discussion

3.1. Porosity and microstructure

For the phyllite and granite-tempered *calcareous* briquettes an total porosity of 32 ± 2%, with no apparent closed porosity was measured at all firing temperatures.[12] For the
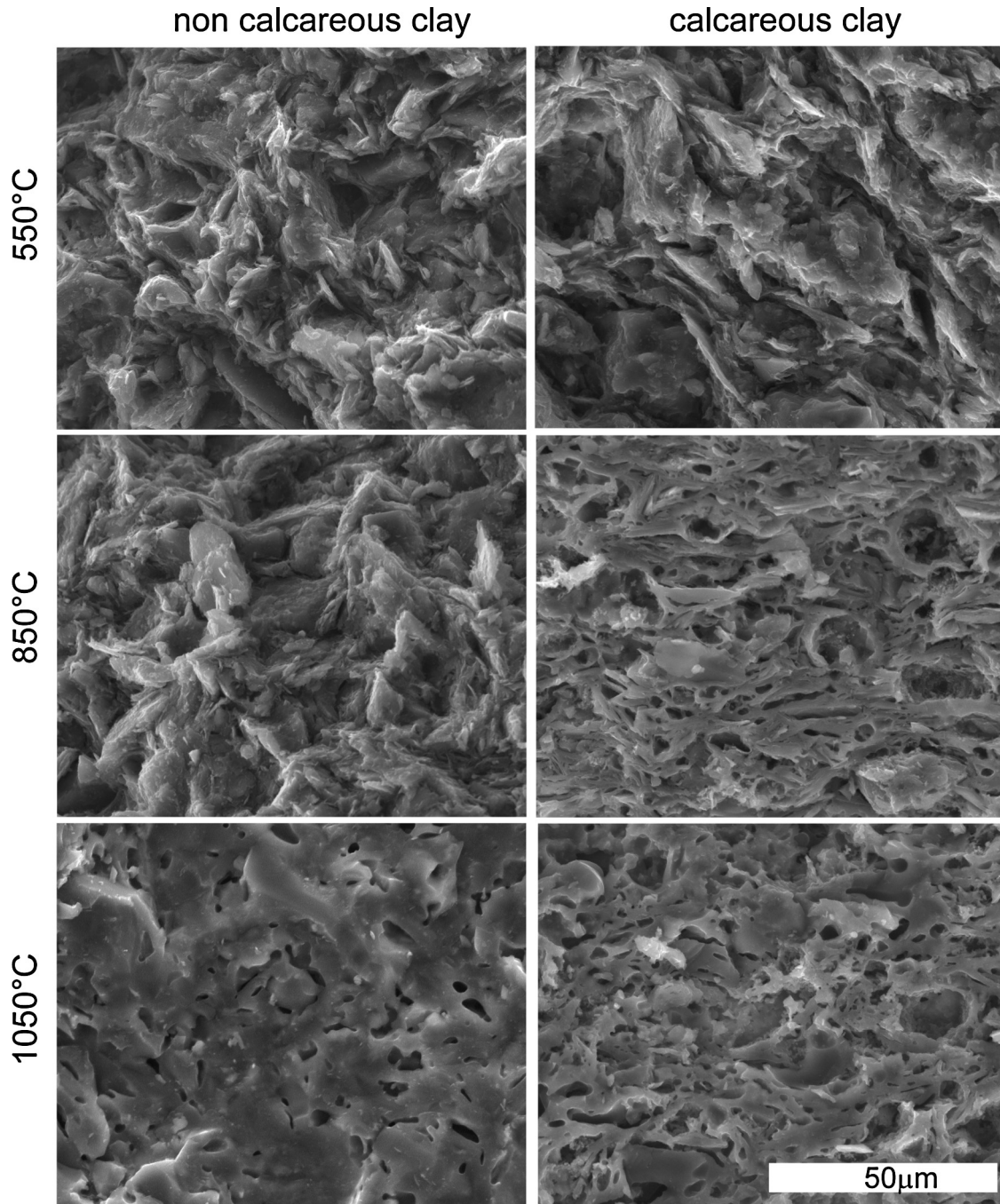
Fig. 2. SEM micrographs showing the development of matrix microstructure of low-calcareous clay from Kalami fired to different temperatures (indicated on the left). For comparison, the development of the microstructure of the calcareous clay from Pikermi is shown in the right column for the same firing temperatures. All micrographs are to the same scale.

low-calcareous ceramics fired to $550\,^\circ$C and $850\,^\circ$C total porosity is also around $32 \pm 2\%$, with no noticeable closed porosity. Upon firing at $1050\,^\circ$C, however, a considerable reduction in total porosity as well as the development of closed pores is observed in the low-calcareous ceramics. A different porosity development in calcareous and low-calcareous clays upon firing would be expected, due to the decomposition of carbonates, and has been reported elsewhere.[22] For low-calcareous clays, open porosity is usually expected to decrease from the onset of vitrification at around $850\,^\circ$C in a roughly linear manner until about

$1000\,^\circ$C where nearly no open pores are left.[23] This happens because the absence of CO_2 pressure during firing allows the clay platelets to coalesce and gradually close the open pores and channels which develop at lower temperatures. The reduction in total porosity, accompanied by the development of closed porosity, in our samples fired at $1050\,^\circ$C leads to the significant shrinkage and concomitant increase in density which is observed in these samples, accompanied by – or because of – the extensive glassy phase observed (Fig. 2). For calcareous clays, the reduction in open porosity is displaced towards higher temperatures, due to
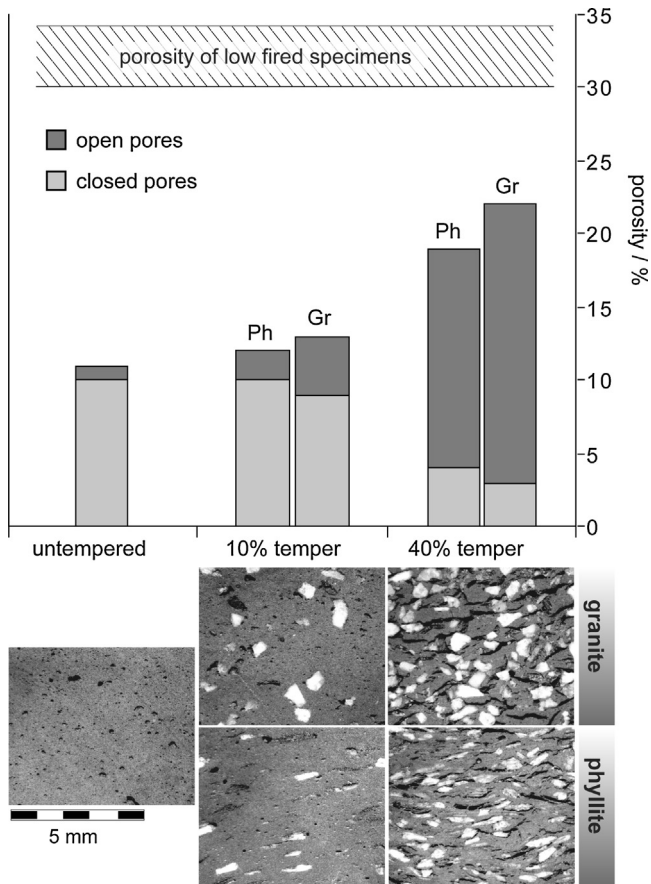
Fig. 3. Development of porosity in low-calcareous samples fired to 1050 °C, depending on amount and type of temper. Top: porosity values of high-fired (1050 °C) materials in comparison with the total porosity of lower fired (550 °C and 850 °C) samples (Ph = phyllite temper, Gr = granite temper). Bottom: texture of high-fired materials. The emergence of large elongated pores due to restricted shrinkage of the matrix is clearly observed in the highly tempered materials on the right.

the formation of an open cellular structure that is stable over a relatively wide temperature range, since the development of a liquid phase is inhibited by the formation of high-temperature phases.[24] In such materials, it has been observed that open porosity does not change significantly up to firing temperatures of 1100 °C, beyond which it rapidly decreases.[13]

The amount and type of temper material used affects the measured porosity only in the high-fired low-calcareous materials. The total porosity of the untempered ceramics is, at 11%, comparatively low. The addition of temper increases total porosity to about 22% for 40% granite temper and the difference in porosity to the lower fired samples (550–850 °C) diminishes with increasing amount of temper (Fig. 3). Tempering also causes a change in the type of porosity; whereas porosity in the untempered material is mainly closed, porosity in the highly tempered specimens is mainly open as illustrated in Fig. 2. Small differences in porosity are observed by varying temper shape: adding angular, granitic temper appears to result in a slightly more pronounced increase in porosity than adding phyllite temper and in the predominance of open over closed pores.

For all other materials, assuming that the porosity of the temper material is constant and small (up to 10%), for a value of 32% total porosity, the porosity in the clay matrix and the matrix-temper interface can be estimated at about 35% for 10% temper and 45–55% for 40% temper.

The increase in open porosity which is observed in the high-fired samples upon addition of temper, may be explained by the formation of decohered interfaces around the temper grains, the so-called damaged zones. During drying and firing, shrinkage of the clay matrix gives rise to tensile stresses in the matrix around the particles and on the matrix-particle interfaces which leads to decohesion and microcracking.[7] With an increasing amount of temper, the chance that these overlap and form an interconnecting network of open pores increases. For high sphericity particles the damaged area can be described as a sphere enclosing the whole particle, while the damaged zone around the edges of a flake has been argued to have a toroidal shape.[12] Therefore the overall volume fraction susceptible to the development of microcracks is much smaller in the case of phyllite-tempered materials. The porosity differences observed in this work between materials with phyllitic and granitic temper could therefore be explained by differences in the extent of the damaged zones caused by different temper shapes. It should be noted that the presence of quartz, which undergoes a reversible volume expansion around 573 °C, might contribute to increased decohesion and microcracking. The alpha–beta phase transition of quartz possibly contributes to the differences observed in materials with different temper. However, as has been detailed in a previous publication,[12] the differences in quartz content between the granite and phyllite temper employed appear relatively small so that putative differences in quartz content alone cannot be responsible for the observed differences in the behaviour of temper-bearing ceramics. In addition, at 40% temper another effect comes into play in the high-fired samples. The visual examination of cross sections under an optical microscope indicates that while the pores in the untempered and low tempered materials are predominantly below 1 mm in size and of rather spherical shape, the materials with 40% temper contain large elongated pores that are aligned parallel to the briquette's largest surfaces. This is illustrated in Fig. 3 for the low-calcareous high-fired ceramic. As has been observed for corresponding calcareous briquettes, the apparent length and amount of these voids appears more pronounced in the granitic than in the corresponding phyllitic materials, an effect which is probably due to the alignment of clay particles during manufacture in combination with more pronounced shrinkage perpendicular to the clay particles. In the lower fired materials these large elongated pores are significantly less prominent even in the highly tempered granitic materials and not observed at all in the materials containing 40% phyllite. It appears that granitic temper introduces more open porosity in the high-fired low-calcareous materials than the same amount of phyllite temper due to temper shape: the platy shape of the phyllite temper both induces less extensive damaged zones than granite temper and enables the phyllite tempered briquettes to better accommodate shrinkage perpendicular to the temper plates.
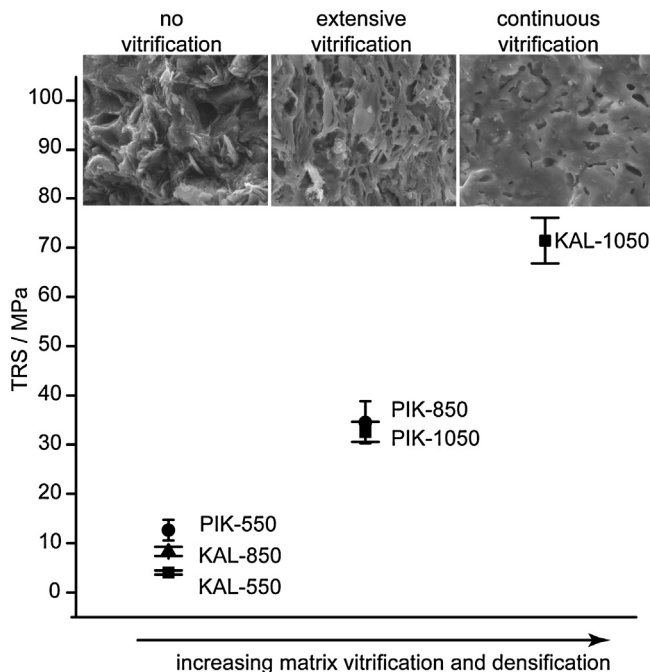
Fig. 4. Influence of ceramic microstructure on fracture strength. PIK: calcareous clay, KAL = low-calcareous clay, 550, 850, 1050: firing temperatures in °C. Micrographs: field of view: 50 μm.

Fig. 5. Transverse rupture strength of low-calcareous ceramics containing various amounts of rock temper.

Finally, for low-fired pottery containing quartz-rich temper particles it has been argued[25] that the reversible alpha–beta phase transition in ceramics which are fired in excess of 573 °C, but at a temperature low enough so that no shrinkage occurs in the clay matrix (in the present case, e.g. the low-calcareous ceramics fired to 850 °C), introduces additional porosity. In the present study, however, no significant differences in overall porosity between low-calcareous, tempered ceramics fired to 550 °C (below the temperature of quartz inversion) and 850 °C (above quartz inversion) have been ascertained, indicating that for the materials examined, the contribution of the effect – if present – is masked by the overall high porosity of the material.

3.2. Fracture strength

Generally, higher TRS was measured for briquettes fired at higher temperatures. Changes in microstructure, i.e. the degree of vitrification, are reflected directly in the measured strength values of untempered samples as illustrated in Fig. 4. Based on differences in vitrification patterns of the calcareous and low-calcareous clay (Fig. 2),[13,24] the strength of untempered ceramics fired to 550 °C and 850 °C is relatively low for the low-calcareous clay employed here and only firing to 1050 °C results in a significant increase in strength. Firing to 1050 °C results in a stronger bonding within the matrix, reflected in an extensively vitrified microstructure, while at lower temperatures clay particles are only loosely connected. For calcareous clays, an increase in strength has been reported already at 850 °C, with strength levels remaining stable upon further firing.[6,12] The strength of the low-calcareous clay fired at 1050 °C was about 70 MPa which is roughly double the 34 MPa reported for
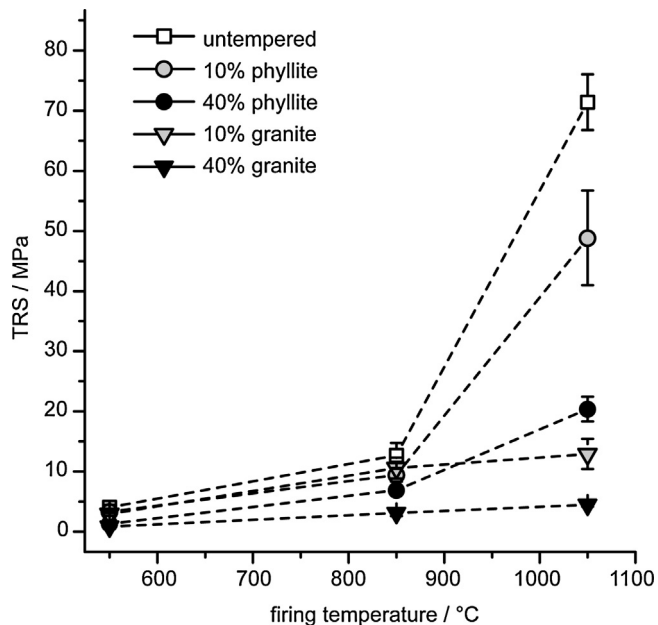
calcareous clay fired to the same temperature.[12] In another study, Carratero et al.[26] compared the fracture strength of a calcareous and a low-calcareous clay. However, the raw clays used in their study were not refined, therefore introducing an undefined tempering parameter to the experiments. Tempering has a crucial influence on fracture strength as will be discussed below, and the surprisingly low fracture strength found by Carratero et al.[26] for their high-fired low-calcareous clay may be due to the high amount of relatively large aplastic particles it contained. Accordingly, Khaloufi et al.[23] found significantly higher fracture strength for a low-calcareous clay fired to the same temperature.

The addition of temper material leads to a decrease in TRS, as illustrated in Fig. 5. For materials containing either type of temper, the higher the volume fraction the greater the decrease in strength. For the low-calcareous ceramics, the TRS values of high fired vitrified briquettes fall from around 70 MPa in the untempered briquettes to only c. 5 MPa in briquettes with 40% granite temper. As mentioned, a decrease in strength with increasing amounts of temper particles has been reported previously both for archaeological specimens[9] and in experimental briquettes.[7,12] This phenomenon is to be expected since temper particles introduce imperfections in the ceramic matrix and the different thermal expansion coefficients of temper and matrix result in the formation of microcracks around the rigid particles upon firing.[6] In addition, pronounced shrinkage in the high fired ceramics results in the emergence of large elongated pores for highly tempered specimens. The decrease in fracture strength upon tempering, therefore, is a result of the consequential increase in overall flaw population.

When comparing the influence of the two different temper types, it is apparent that the addition of phyllite has a less detrimental impact on TRS than the addition of the same volume fraction of granitic temper. This effect becomes especially pronounced at high firing temperatures, as shown in Fig. 5, when
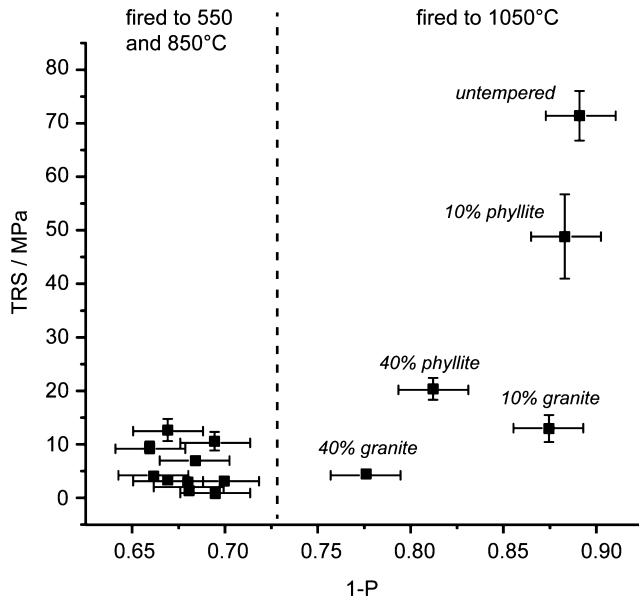
Fig. 6. Transverse rupture strength of low-calcareous ceramics containing various amounts of rock temper vs. porosity, expressed as 1-P. The experimental error of porosity determinations is estimated to ±2%.

the temper particles are embedded in a vitrified ceramic matrix. The reason for the different behaviour of the two temper types seems to lie in the relative amount of flaws introduced by the respective temper particles. As has been argued elsewhere, differences appear to be mainly due to temper shape, which influences both the extent of the damaged zone around temper particles as well as the extent and amount of large elongated pores which emerge in the highly tempered materials.[12] Since the latter occur only at high amounts of tempering, they cannot be employed to explain the differences in the behaviour of the two types of temper which are observed at lower levels of tempering. Differences in flaw population related to the extent of damaged zone, which are due to the differing impact of the two temper shapes on the integrity of the surrounding clay matrix, on the other hand, are expected for all amounts of tempering and expected to influence TRS. Fig. 6 shows the correlation between porosity, expressed as 1-P and TRS. The low and intermediate fired ceramics with a total porosity around 32% form a relatively tight cluster, while the samples fired to 1050 °C with lower total porosity generally show higher strength levels. It is observed that within similar porosity ranges, the granite tempered high-fired ceramics exhibit lower strength than phyllite tempered ceramics. This might be ascribed to the differences in extent of damaged zones around temper particles. A further factor contributing to the higher strength of phyllite-tempered over granite-tempered high fired ceramics might be the increased matrix-inclusion bonding observed in specimens fired to 1050 °C (Section 3.3). The results are in agreement with earlier measurements of Feathers[10] on low fired ceramics (firing temperature: 600 °C) who found that tempering with shell resulted in stronger materials than using sand temper, an effect that is presumably linked to temper shape. It should be noted, however, that the two temper materials in the particular study differ not only in shape but also in composition. Shell is made of

CaCO$_3$ which is expected to decompose at temperatures above 600 °C. It cannot be excluded that localised reactions which may enhance bonding of the temper particles with the surrounding clay matrix occur already at 600 °C, effectively contributing to an increased strength of these materials. This is not expected for the sand temper employed in Feathers study, which consisted predominately of quartz, especially since quartz' α → β conversion at 573 °C is expected to lead to debonding around the sand temper particles in the fired ceramics.[7]

3.3. Fracture energy

The effective stress intensity factor K_{Iceff} of the highest fired low-calcareous untempered specimens, which show brittle fracture, was found to be about 1.2 MPa m$^{-1/2}$ comparable to that of electrical porcelain and significantly higher than that measured for a comparable calcareous clay, i.e. the untempered Pikermi clay fired at 1050 °C, for which a K_{Iceff} value of 0.5 MPa m$^{-1/2}$ (G_{Iceff} = 10 J m^{-2}) was determined. The intrinsic fracture energy is linked to the stress intensity factor, K_{Ic} via $K_{Ic} = \sqrt{(EG_{Ic})}$. For the low-calcareous specimens, the effective intrinsic fracture energy G_{Iceff} was observed to increase with higher firing temperatures (Fig. 7a and b). These values were calculated using the experimentally determined Young's modulus values for the different paste recipes and firing temperatures, included in Table 1.

Although the standard deviation of G_{Iceff} in the highest fired materials is very high, there is a clear trend towards higher strength levels in higher fired ceramics, which is also observed for the tempered low-calcareous ceramics. Different apparent morphologies of the glassy phase which develops in the ceramic matrix (Fig. 2) possibly contribute to this: while the calcareous ceramic still shows typical cellular structure, in the low-calcareous samples fired at 1050 °C, a denser microstructure is observed under the scanning electron microscope, reflecting continuous matrix vitrification[13,24] and resulting in greater matrix strength for the untempered Kalami clay as compared to the Pikermi clay. Furthermore, mullite, which might contribute to the high intrinsic fracture energies observed in the high-fired samples, is formed when the Kalami clay is fired to 1050 °C as determined by XRD measurements. Martinón-Torres et al.[27] have argued for an increased ability of high-fired ceramics, which were used in metallurgical processes and contain this high temperature phase, to withstand mechanical (and other) stresses, conferred by interlocking acicular mullite crystals.

G_{Iceff} appears to be largely dependent on the type of clay and firing temperatures, and appears only minimally influenced by different amount or types of temper materials (Fig. 7a–d). An exception to this is materials with 40% phyllite temper in a vitrified matrix (Kalami samples fired to 1050 °C, as well as the comparative Pikermi samples fired to 850 and 1050 °C), for which an increase in G_{Iceff} is observed. This may be connected to increased bonding between clay matrix and phyllite particles in these materials, as discussed below. In contrast the highly vitrified low-calcareous ceramic fired to 1050 °C with 40% granitic temper presents a reduced G_{Iceff}, due to the

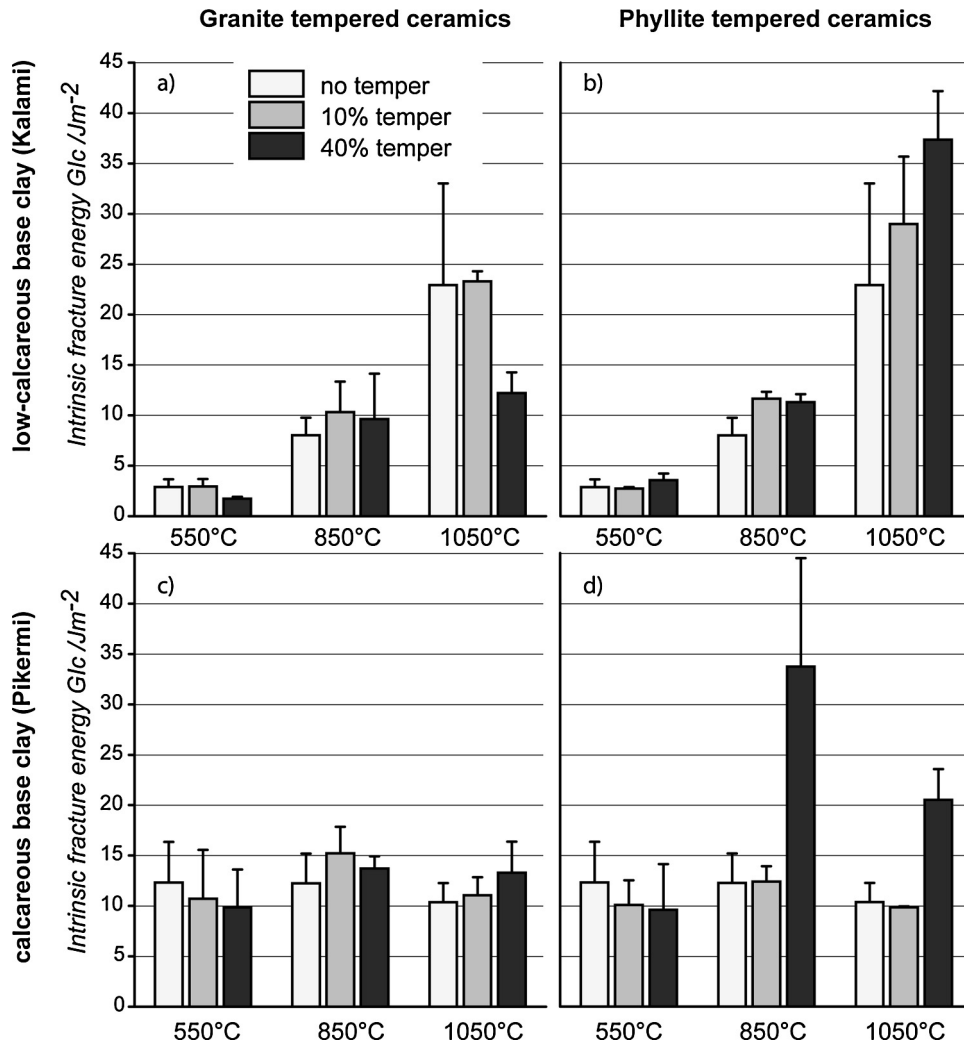**Granite tempered ceramics**   **Phyllite tempered ceramics**

Fig. 7. (a and b) Effective intrinsic fracture toughness G_{Iceff} of granite- and phyllite-tempered, low-calcareous ceramics. For comparison, previous results of comparative measurements on a calcareous base clay[12] are also given (c and d).

emergence of large elongated pores in these specimens, as discussed above.

The addition of temper increases the effective energy dissipation component G_{teff} of a material (Fig. 8a–d), with the increase depending on the volume fraction of inclusions. This behaviour has been observed in the past for calcareous ceramics,[7] and was attributed to the rigid inclusions which provide the ceramics with additional means of energy dissipation through crack deflection,

bifurcation and arrest. With platy particles, pull-out and crack-wandering processes are also expected. It should be noted that the actual strength of the platy particles themselves also plays a role in the total amount of energy dissipated since weak temper particles (such as phyllite after high temperature firing) may fracture before they have a chance to dissipate fracture energy. Furthermore, it is known that the strength of interfaces between temper inclusions and clay matrix is inversely related

Table 1

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, compliance-corrected load-displacement curves; standard deviations are given in brackets.

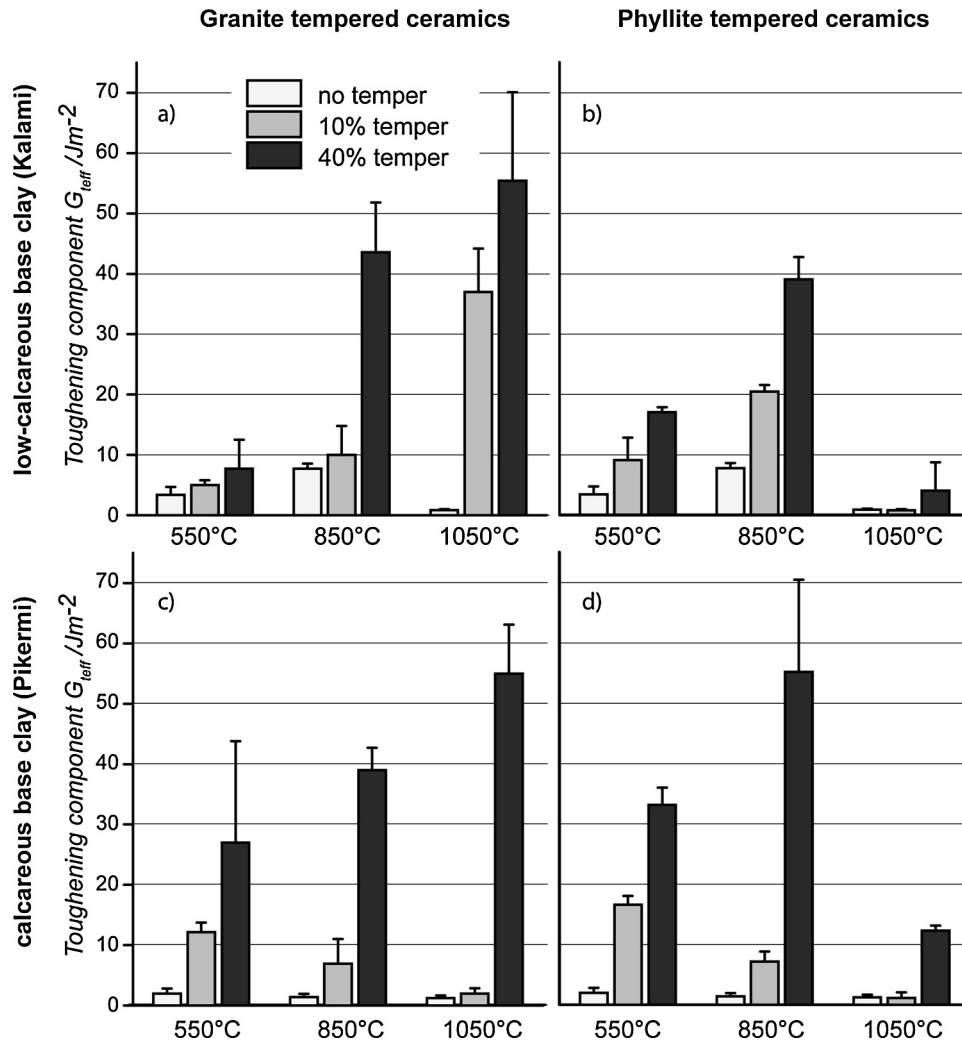| Firing temperature (°C)	Untempered	10% granite	40% granite	10% phyllite	40% phyllite
Kalami clay					
550	2.3 (±0.3)	2.6 (±0.5)	0.28 (±0.02)	2.1 (±0.2)	0.7 (±0.1)
850	5.5 (±0.8)	6.2 (±1.0)	1.1 (±0.2)	5.0 (±0.6)	2.7 (±0.5)
1050	68.4 (±7.5)	13.4 (±1.4)	2.3 (±0.2)	47.1 (±9.4)	12.0 (±1.6)
Pikermi clay					
550	3.8 (±0.4)	4.2 (±0.4)	0.7 (±0.1)	4.4 (±0.4)	1.9 (±0.4)
850	21.4 (±2.0)	12.1 (±2.0)	3.1 (±0.7)	18.4 (±2.6)	4.8 (±0.3)
1050	24.2 (±3.2)	18.6 (±2.6)	1.3 (±0.2)	25.5 (±3.4)	8.7 (±0.6)

Granite tempered ceramics   **Phyllite tempered ceramics**

Fig. 8. (a and b) Effective energy dissipation G_{teff} of granite- and phyllite-tempered, low-calcareous ceramics. For comparison, previous results of comparative measurements on a calcareous base clay[12] are also given (c and d).

to the amount of energy that can be dissipated during fracture by the above micro mechanisms. It is further noteworthy that for the *high-fired phyllite-tempered specimens*, lower effective energy dissipation values are recorded than for granite tempered samples fired to the same temperatures, but also compared to lower fired phyllite tempered specimens (Fig. 8). When fired to 850 °C, both phyllite- and granite-tempered ceramics exhibit a comparable G_{teff}, reflecting similar degree of energy dissipation after crack initiation. Upon firing the briquettes tempered with 40% phyllite to 1050 °C, G_{teff} decreases significantly. This observed decrease is connected with a change in fracture mode towards more brittle fracture.

Microscopic examination of the fracture surfaces shows that in the samples fired to 1050 °C of both calcareous and low-calcareous clays, the crack often propagates through the phyllite particles, breaking the thin plates in half and eliminating any contribution they may have had on the toughening. Such fracture of temper plates was also evident, but to a much smaller extent in samples fired to 850 °C. The granitic inclusions on the other hand still act as barriers to unstable crack propagation even in materials fired to 1050 °C (Fig. 9). In the case of 40% granitic

temper, even in high-fired specimens a significant amount of energy is needed to propagate the crack through the ceramic and stable fracture is observed.

Examination of fracture surfaces under the scanning electron microscope reveals that the phyllite inclusions undergo significant structural changes at high firing temperatures, as well as enhanced bonding with the clay matrix. Fig. 10 compares the fracture surfaces of phyllite-tempered ceramics fired to 850 °C and 1050 °C. These micrographs clearly show the different morphology and breakage of phyllite particles in a clay matrix fired to 850 °C and 1050 °C. While in the case of the low-calcareous clay the surrounding microstructure differs clearly between the medium and high-fired samples, the calcareous ceramic matrices exhibit very similar microstructures at these firing temperatures. This is reflected in the similar strength levels measured for the untempered calcareous clay fired to 850 and 1050 °C.[12] The different fracture behaviour of phyllite particles in calcareous matrices with very similar microstructure and strength, but fired to different temperatures, indicates that the observed differences in G_{teff} between medium and high fired phyllite tempered ceramics are largely due to differences in temper morphology and
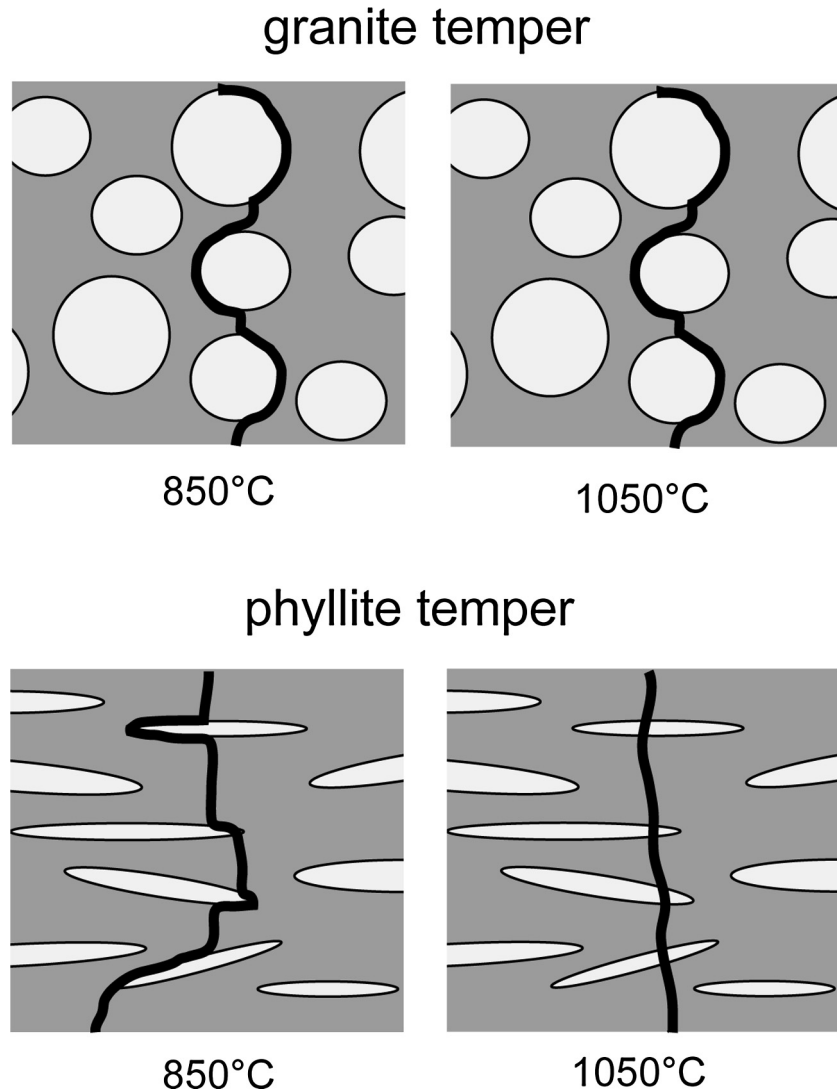
granite temper

phyllite temper

Fig. 9. Schematic crack paths for phyllite and granite-tempered materials fired to 850 °C and 1050 °C respectively. Sketch based on systematic microscopic observations.

properties, and increased temper-matrix bonding. The phyllite particles are mica rich and fine-grained (see also Fig. 1). Due to the high potassium content and the large contact area between the grains, melting proceeds rapidly at a relatively low temperature, and, when fired to 1050 °C, results in the fusion of the particles with the surrounding clay matrix as well as in the observed changes in morphology of the phyllite particles: while at 850 °C, the single mica sheets are still clearly visible in SEM, after firing to 1050 °C, phyllitic inclusions have molten into a glassy phase with isolated round pores (Fig. 10). The fact that, unlike granite inclusions, phyllite particles effectively become part of the matrix in the high fired specimens may also account for the observation that the effective intrinsic fracture energies G_{Iceff} of the high fired phyllite tempered material appear to increase slightly with increasing amount of temper (Fig. 7). For the granite-tempered ceramics fired to 1050 °C, it cannot be excluded that some feldspar might have reacted with the clay matrix. Since granite temper is inhomogeneous on a particle scale, however, with some clasts not containing any feldspar at

all, this would not affect all temper grains, so that – on the whole – granite tempering still introduces a distinct phase, only weakly bound to the ceramic matrix. Indeed with high fired granite tempered ceramics no change or, in the case of the highly tempered low-calcareous material, a decrease in effective intrinsic fracture energies is observed compared to lower fired materials (Fig. 7).

At very low firing temperatures of 550 °C, the phyllite-tempered materials show slightly higher G_{teff} values than the granite-tempered ones. This is probably due to the activation of more energy dissipation mechanisms during crack propagation (Fig. 8), for example platy phyllite temper pull-outs. This is in agreement with Feathers and Scott[11] who, for low-fired clay ceramics (firing temperature: 600 °C), found that the intrinsic fracture energy and, even more so, the energy required to propagate a crack through a tempered clay is higher for platy temper material than more equivalent inclusions.

That finding is also observed in this work. In the low-calcareous clay fired to 850 °C, which also has a non-vitrified
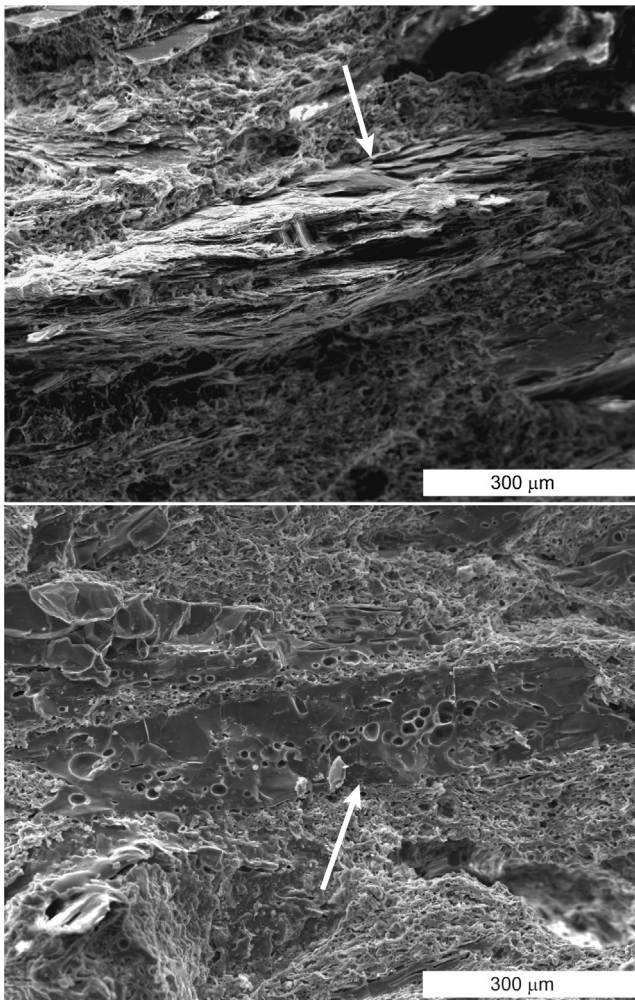
Fig. 10. Scanning electron micrographs of fresh fractures for calcareous base clay materials. The arrows indicate phyllite inclusions after firing at 850 °C (top) and at 1050 °C (bottom).

clay matrix, greater G_{teff} values are observed for phyllite-tempered briquettes containing 10% temper. This is not the case at 40% of temper, however, where G_{teff} is comparable for phyllite and granite-tempered ceramics. When fired to 850 °C, there was evidence for the emergence of a number of elongated pores in the granitic tempered materials, an effect which is not observed with 10% temper and not until higher firing temperatures with phyllite temper. These pores appear to provide further means for crack deflection and arrest and may contribute to the observed differences in G_{teff} values in this case.

The *high-fired low-calcareous sample with 10% granite temper* stands out for its high G_{teff} value, when compared to the corresponding calcareous sample. In quartz-tempered calcareous ceramics a change in fracture mode from brittle to stable fracture has been observed to occur at around 20% of temper material.[7] The granite-tempered ceramics manufactured from a calcareous base clay appear to follow this pattern, as do low and intermediate fired low-calcareous ceramics. In the high fired low-calcareous granite tempered specimens, however, the transition to stable fracture takes place at lower volume fractions of inclusions and already the samples containing 10% temper show

a substantial effective energy dissipation G_{teff}. This is probably due to the higher shrinkage observed in the low-calcareous Kalami clay upon firing to 1050 °C. This results in higher stress of the contracting matrix on the rigid inclusions, and 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 expected to be larger in the low-calcareous material. Microcracks and residual stress fields are both candidates for increasing the fracture energy of a material.[28,29]

Finally, as has been noted previously for calcareous samples, an indentation mechanism is observed with the materials containing 40% granite temper.[12] This enables the bars to support significant bending stresses without losing apparent structural integrity.

3.4. Implications for archaeological ceramics

The findings reported here have important implications when assessing technological choices in archaeological ceramics. It is clear that the selection of low-calcareous vs. calcareous clays requires adaptation of firing strategies if changes in mechanical properties are to be avoided. Moreover it should be noted that the use of calcareous clays – due to the stability of their microstructure between c. 850 and 1050 °C – allows the achievement of a relatively consistent quality, even with a moderate degree of control over firing conditions. This should be taken into account, when, e.g. considering the widespread change from low-calcareous to calcareous clays at the start of the Middle Bronze Age (c. 2100–1500 BCE) in the Aegean, along with other changes in technological practice in pottery production at the time, such as the introduction of the potter's wheel, higher firing temperatures and indication of an increased scale of production in several pottery centres.

In terms of temper material, thermally induced structural changes such as the one observed in vessels which are rich in phyllite need to be taken into account when assessing physical properties of fired ceramics. An example of this is the very high fired phyllite tempered cooking vessels found at the Late Bronze Age (c. 1600–1500 BCE) site of Akrotiri in Greece, where the theoretically beneficial effect of phyllite tempering on fracture energies (as well as resistance to thermal stresses) is negated by the high firing temperatures. In that particular case this could be taken to represent a trade-off with another physical property important for cooking vessels and cooking methods, namely thermal conductivity, which benefits from high firing.[30] In considering such observations, however, it is important to discriminate between variability and changes in performance on a theoretical level and those that would be perceived by the craftsperson or end-user of the ceramic product in the past.

In general, for ceramics where high strength is beneficial, such as, for example, transport vessels, higher firing temperatures and finer materials containing less temper material would be advantageous and platy temper preferable over that of bulky nature. For the mechanical properties of relatively coarse utilitarian vessels, such as cooking pots which are not

subjected to significant bending stresses, fracture energy rather than strength is important. Since pre-existing flaws, ubiquitous in these materials, are potential origins of cracks, it is important that a crack, once initiated, is stopped quickly and effectively before leading to total fracture. Here the addition of larger amounts of temper material or the selection of coarse clays seems beneficial.

Such variability, in terms of the clay type, as well as the size, shape, proportion and distribution of temper, is increasingly important in the classification and interpretation of archaeological ceramics. Understanding the effects of these parameters on the performance of the ceramics provides many benefits to integrated studies, especially when based not only on the affordances that such material present to the potter and consumer of the past, but also in terms of documented use, which can be shown by analyses of vessel use wear and organic content.

4. Conclusions

The increase in fracture strength with increasing firing temperatures has been found to be linked to the degree of vitrification in the clay matrix and to porosity development and depends on whether the base clay is calcareous or low-calcareous.

A reduction in fracture strength was observed with increasing amounts of aplastic inclusions in the clay. The strength decrease is less pronounced with platy temper material, probably due to temper shape.

Fracture energy depends both on the type of matrix and the type of temper used. It has been shown that the single most important parameter for obtaining high fracture energies is the use of larger fractions of temper material. While the fracture energy of granite-tempered ceramics remains stable at high firing temperatures, for phyllite-tempered materials maximum values were measured at intermediate temperatures, due to changes induced in the phyllitic temper material and increased temper-matrix bonding at higher firing temperature.

Generally, it appears that for clay-based ceramics, strategies which result in an increase in strength in many cases reduce the fracture energy of a material and vice versa. Normally, clay based ceramics with comparatively high fracture strength do not exhibit significant energy dissipation during crack propagation. On the other hand materials which rupture after applying relatively small forces may be able to dissipate a substantial amount of energy during crack propagation until final fracture.

The results presented here indicate that in the production of clay-based ceramics the technical choices of potters during manufacture may greatly affect the physical properties – and ultimately the performance – of the final products.

Acknowledgement

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